NUCLEOPHILIC DISPLACEMENT AT CARBON BEARING NITROGEN

by

Raymond John Swedo

A Dissertation Submitted to the Faculty of the

DEPARTMENT OF CHEMISTRY

In Partial Fulfillment of the Requirements
For the Degree of

DOCTOR OF PHILOSOPHY

In the Graduate College

THE UNIVERSITY OF ARIZONA

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THE UNIVERSITY OF ARIZONA

GRADUATE COLLEGE

I hereby recommend that this dissertation prepared under my direction by Raymond John Swedo

entitled Nucleophilic Displacement at Carbon Bearing Nitrogen

be accepted as fulfilling the dissertation requirement for the degree of Doctor of Philosophy

P Glass — 6/2/77

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Cornelius Steelink	6/2/77
John H. Enemark	June 2, 1977
M F Burke	6-3-77
J Brumbaugh	6/6/77

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TABLE OF CONTENTS

TABLE OF CONTENTS--Continued

TABLE OF CONTENTS--Continued

TABLE OF CONTENTS--Continued

TABLE OF CONTENTS--Continued

TABLE OF CONTENTS--Continued

LIST OF TABLES

LIST OF TABLES--Continued

LIST OF ILLUSTRATIONS

ABSTRACT

Alcohols can be activated to nucleophilic attack by conversion to their alkane or arenesulfonate derivatives; thus, the possible activation of aliphatic amines to nucleophilic attack by conversion to derivatives possessing electron withdrawing groups was considered. The derivatives studied were various arene and alkane sulfonamides and sulfonimides.

N-Alkyltrifluoromethanesulfonamides were prepared by reaction of the amine with trifluoromethanesulfonic acid anhydride. From these sulfonamides, N,N-di-alkyltrifluoromethanesulfonamides, N-alkyl-N-cyanotrifluoromethanesulfonamides, N-alkyl-N-aryl-trifluoromethanesulfonamides, and N-alkyl-N,N-di(trifluoromethane)sulfonamides were then prepared.

Although N-alkyltrichloromethanesulfonamides could not be prepared by reaction of the amine with either trichloromethanesulfonic acid anhydride or the corresponding sulfonyl chloride, N-alkyltrichloromethanesulfenamides were easily prepared from the amine and trichloromethanesulfenyl chloride. These sulfenamides were then oxidized to the corresponding sulfonamides using either peroxytrifluoroacetic acid or m-chloroperoxybenzoic acid. These sulfonamides were converted to N-alkyl-N-(trichloromethanesulfenyl)trichloromethanesulfonamides by reaction with trichloromethanesulfenyl chloride, but further oxidation of these derivatives to the corresponding sulfonimides was unsuccessful.

N-Alkyl-N-(benzenesulfenyl)benzenesulfonamides were easily prepared by reaction of the benzenesulfonamide with benzenesulfenyl chloride. In cases where the amine nitrogen was attached to a secondary carbon, oxidation of these derivatives with m-chloroperoxybenzoic acid led to the corresponding sulfonimide in good yield. However, when the nitrogen was attached to a tertiary carbon, no sulfonimide could be isolated.

The reactions of N,N-di-alkyltrifluoromethanesulfonamides, N-alkyl-N-cyanotrifluoromethanesulfonamides, N-alkyl-N-aryltrifluoromethanesulfonamides, and N-alkyl-N,N-di(trifluoromethane)sulfonamides with various nucleophiles were investigated. Neither the N,N-di-alkyltrifluoromethanesulfonamides nor the N-alkyl-N-cyanotrifluoromethanesulfonamides gave any displacement on carbon; and while N-phenyl-N-benzyltrifluoromethanesulfonamide gave a 41% yield of benzyl diethylmalonate when treated with diethyl sodiomalonate, no product was obtained with N-(4-fluorophenyl)-N-benzyltrifluoromethanesulfonamide. Displacement reactions with N-alkyl-N,N-di(trifluoromethane)-sulfonimides were carried out using two different methods. In the first method, the sulfonimide was added to a solution of the nucleophile in hexamethylphosphoric triamide solvent, and the reaction was allowed to proceed at room temperature for several days. In these reactions, high yields of alkyl iodides were obtained using potassium iodide, yields of alkyl cyanides were usually 0-5% using sodium cyanide, and low to moderate yields of displacement products were obtained using diethyl sodiomalonate and heteroatom nucleophiles other than iodide anion.

During the course of these displacement reactions, it was discovered that the solvent, hexamethylphosphoric triamide, reacts with the sulfonimides to produce tris(dimethylamino)alkoxyphosphonium salts, essentially quantitatively, within about eighteen hours. The further discovery that these phosphonium salts underwent displacement with nucleophiles led to the second displacement study with sulfonimides. In these reactions, the sulfonimide was first allowed to react with solvent to form the phosphonium salt; this was then allowed to react with nucleophile. Using this procedure, a 72% yield of n-hexyl cyanide and an 87% yield of n-hexyl diethylmalonate were obtained, contrasting with the less than 5% and 57% yields respectively obtained using the first procedure. Similar, though less dramatic, increases in yield were obtained with other nucleophiles which had yielded 0-5% product using the first procedure.

INTRODUCTION

The stereospecific cleavage of an aliphatic carbon-nitrogen bond accompanied by the formation of a new carbon-carbon bond is an attractive synthetic transformation. Although a great variety of methods are known which result in the cleavage of the carbon-nitrogen bond of an aliphatic amine (1), only recently have methods showing promise of concurrent carbon-carbon bond formation been developed.

Using the activation of alcohols as arenesulfonates as an analogy, Baumgarten (2) proposed a nucleophilic displacement on an activated amine to achieve carbon-nitrogen bond cleavage in a stereospecific manner. In his early work in this area, Baumgarten and De Christopher (3) studied nucleophilic attack on N-alkyl saccharin derivatives. Although these resulted in elimination rather than displacement products, the activation concept appeared viable.

Similarly, Hendrickson, Okano, and Bloom (4) studied the reactions of some o-benzenedisulfonimide derivatives, but the results were only fair. Later work conducted by Baumgarten and co-workers (5-10) and other groups (11-14) concerned nucleophilic displacements on N-alkyl-N,N-di(arene)sulfonimides (5-10, 13, 14) and N-alkyl-N,N-di(trifluoromethane)sulfonimides (7, 11, 12). Successful results were obtained with such nucleophiles as iodide (6), bromide (6, 12), methoxide (12), acetate (13), aniline (6), cyanide (11), and malonate (11). In some cases, however, elimination competed with or prevailed over nucleophilic displacement (4, 6, 8, 9, 12).

Few reports of the reactions of carbon nucleophiles with N-alkyl-N,N-disulfonimides appear in the literature (4, 6, 11). De Christopher et al. (6) and Hendrickson et al. (4) report only recovery of some starting materials using cyanide as a nucleophile with N,N-di(arene)sulfonimides and o-benzenedisulfonimides respectively. Glass (11), however, reports successful carbon-carbon bond formation by nucleophilic attack of cyanide or diethyl sodiomalonate on N-alkyl-N,N-di(trifluoromethane)sulfonimides in hexamethylphophoric triamide (HMPT) solvent.

The work undertaken in this study proposed to expand upon the work discussed above in developing a moiety which would suitably activate the nitrogen of an aliphatic amine to nucleophilic attack at the carbon bearing that nitrogen. In view of the results obtained by Glass (11), nucleophilic displacements on N-alkyl-N,N-di(trifluoromethane)sulfonimides seemed to offer the greatest potential for the formation of carbon-carbon bonds at the expense of carbon-nitrogen bonds. The reactions of these sulfonimides, therefore, were investigated, varying the N-alkyl group of the sulfonimides, and using a variety of carbon and heteroatom nucleophiles.

The activation of amine nitrogen by other groups was investigated as well. A variety of N-alkyl-N-arenetrifluoromethanesulfonamides and N-cyano-N-alkyltrifluoromethanesulfonamides were prepared, but of these only N-phenyl-N-benzyltrifluoromethanesulfonamide gave any displacement product. The syntheses of trifluoromethanesulfonyl triazines were attempted, but were unsuccessful.

In attempting to prepare N-alkyl-N,N-di(trichloromethane)-sulfonimides, a new approach to the preparation of N,N-di(arene)sulfonimides was developed. The preparation of N-alkyl-N,N-di(trifluoromethane)sulfonimides is easily carried out in a two-step process (7, 8, 11): the amine is first allowed to react with trifluoromethanesulfonic acid anhydride to form the sulfonamide; the sulfonamide anion is then allowed to react with trifluoromethanesulfonic acid anhydride to form the sulfonimide. Although analogous routes to the N-alkyltrichloromethanesulfonamides or N,N-di(trichloromethane)sulfonimides are not known, a method was developed herein for the preparation of the N-alkyltrichloromethanesulfonamides involving the peracid oxidation of the corresponding trichloromethanesulfenamides. These sulfonamides were successfully converted to the N-alkyl-N(trichloromethanesulfenyl) trichloromethanesulfonamide derivatives, but further oxidation to the N,N-di(trichloromethane)sulfonimides could not be accomplished.

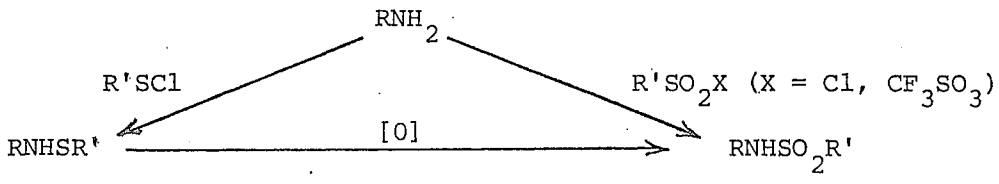
Application of this technique to the preparation of N,N-di(arene)sulfonimides was more successful. N-Alkyl-benzenesulfonamides were prepared by the oxidation of the corresponding sulfenamides. In cases in which the nitrogen was attached to a secondary carbon, the intermediate N-alkyl-N-(benzenesulfenyl)benzenesulfonamide derivatives were smoothly oxidized to the N,N-di(benzene)sulfonimides; but when the nitrogen was attached to tertiary carbon, the N,N-di(benzene)sulfonimide could not be isolated.

RESULTS AND DISCUSSION

The sulfonamides (II) used in this work were prepared by two pathways: direct sulfonylation of the amine, and oxidation of the sulfenamide (I) intermediate (see Figure 1). As most of the sulfonamides and sulfenamides prepared herein have not been reported in the literature, their methods of preparation and yields, physical properties, spectral data, and elemental microanalyses are given in Tables 1-4 and 7 (pp. 6-11 and 18) and 8 (p. 19).

The reactions of amines with various arene sulfonyl chlorides (8, 15-25) or trifluoromethanesulfonic acid anhydride (7, 8, 11, 12) are well documented in the literature, and are commonly used methods for the synthesis of sulfonamides. The preparation of trichloromethanesulfonamides, however, presented a problem. Direct sulfonylation of amines with trichloromethanesulfonyl chloride was not attempted, since literature reports indicate that these result only in mixtures of the trichloromethanesulfinate salt of the amine, and the N-chloroamine (26). Although sulfonylation via the sulfonic acid anhydride was the next reasonable approach, trichloromethanesulfonic acid anhydride is not mentioned in the literature.

The reaction of trichloromethanesulfonyl chloride with aqueous barium hydroxide solution to produce the trichloromethanesulfonate salt has been reported (27). It was found that the corresponding potassium salt could be prepared in the same manner. Reaction of the barium salt with concentrated sulfuric acid resulted in a product containing



I

a) R = s-C_4H_9 R' = CCl_3
b) R = C_6H_{13} R' = CCl_3

II

a) R = i-C_4H_9 R' = CF_3
b) R = s-C_4H_9 R' = CF_3
c) R = s-C_4H_9 R' = CCl_3
d) R = t-C_4H_9 R' = Ph
e) R = $CH_3OCH_2CH_2$ R' = CF_3
f) R = EtO_2CCH_2 R' = CF_3
g) R = C_6H_{13} R' = CF_3
h) R = C_6H_{13} R' = CCl_3
i) R = c-C_6H_{11} R' = Ph
j) R = adamantyl R' = Ph
k) R = c-dodecyl R' = Ph
l) R = Ph R' = CF_3
m) R = p-FC_6H_4 R' = CF_3
n) R = $PhCH_2$ R' = CF_3
o) R = $PhCH_2CH_2$ R' = CF_3

Figure 1. Preparation of Sulfonamides Directly from Amines and via the Sulfenamides

Table 1. Yields, Melting Points, and Ir Data of Sulfonamides

Compound	Method[a]	Yield, %	Mp, °C (Bp, °C/mm)	Ir[b], cm^{-1} NH	Ir[b], cm^{-1} SO_2 Frequencies Symmetric	Ir[b], cm^{-1} SO_2 Frequencies Asymmetric
$(i\text{-}C_3H_7)_2NTf$[c]	B	65	subl. 25	--	1365	1175
$(i\text{-}C_3H_7)_2NTc$[d]	I	68	101-103	--	1380	1265
$i\text{-}C_4H_9NHTf$	B	79	(47/0.45)	3850,3680	1375	1195
$(i\text{-}C_4H_9)_2NTf$	D	15	(68/0.35)[e]	--	1395	1195
$s\text{-}C_4H_9NHTf$	B	26	(45/0.3)	3070,3010	1380	1195
$s\text{-}C_4H_9NHTc$	I	80	91-91.5	3300,3100	1370	1190
$t\text{-}C_4H_9NHBs$[f]	G[g]	36	88-88.5	3380,3260	1330	1150
	H[g]	81				
$CH_3OCH_2CH_2NHTf$	B	31	(55-56/0.32)	3975	1365	1180
$(CH_3OCH_2CH_2)_2NTf$	D	52	(92/0.35)[e]	--	1390	1185
EtO_2CCH_2NHTf	--[h]	--	93-94	3950	1195	1140
$(EtO_2CCH_2)_2NTf$	C	38	(120/0.35)[e]	--	1390	1155
$C_6H_{13}NHTf$	A	62	(83/0.1)	3350,3190	1385	1205
	B	79				
$(C_6H_{13})_2NTf$	A	23	(109/0.1)	--	1390	1180
$C_6H_{13}NHTc$	I	94	36.5-38	3790,3520	1380	1195
	J	66				
$C_6H_{13}N(CN)Tf$	F	85	(69-70/2)	--	1425	1200
$c\text{-}C_6H_{11}NHBs$	G[i]	78	89.5-90	3640	1325	1175
adamantylNHBs[j]	H[k]	67	144-144.5	3750	1320	--
c-dodecylNHBs[l]	H[m]	51	162-162.5	3600	1320	1150
PhNHTf	A[k]	62	65.5-66.5	3390,3290	1365	1185
PhN(CN)Tf	F	54	(87/0.35)[e]	--	1430	1140
$p\text{-}FC_6H_4NHTf$[l]	B	43	57-58	3630	1355	1195
$p\text{-}FC_6H_4N(CH_2Ph)Tf$	E	33	(130/0.3)[e]	--	1405	1210
$PhCH_2NHTf$	A[k]	71	41.5-42.5	3400,3305	1375	1185
	B[k]	44				

Table 1.--Continued Yields, Melting Points, and Ir Data of Sulfonamides

Compound	Method[a]	Yield, %	Mp, °C (Bp, °C/mm)	Ir[b], cm^{-1} NH	Ir[b], cm^{-1} SO_2 Frequencies Symmetric	Ir[b], cm^{-1} SO_2 Frequencies Asymmetric
$(PhCH_2)_2NTf$[n]	B	94	(140/0.35)[e]	--	1375	1175
$PhCH_2N(CN)Tf$[j]	F	83	(107/0.35)[e]	--	1430	1220
$PhCH_2N(Ph)Tf$	B[k]	97	77-78	--	1395	1180
$PhCH_2CH_2NHTf$	B	82	(95-96/0.25)	3200	1375	1195
$(PhCH_2CH_2)_2NTf$	C	31	63.5-64.5	--	1390	1185

[a]Details of methods A-J given in Experimental section.

[b]Unless otherwise noted, spectra were recorded as CCl_4 solutions, and calibrated with polystyrene.

[c]Tf = trifluoromethanesulfonyl.

[d]Tc = trichloromethanesulfonyl.

[e]Temperature is that of the air bath in bulb to bulb distillation.

[f]Bs = benzenesulfonyl.

[g]Recrystallized from ligroin.

[h]Sample provided by Dr. R. Glass.

[i]Recrystallized from 50% aqueous ethanol.

[j]Ir spectrum recorded as $CHCl_3$ solution.

[k]Recrystallized from hexane.

[l]Ir spectrum recorded as KBr pellet,

[m]Recrystallized from ethyl acetate.

[n]Ir spectrum recorded as thin film.

Table 2. NMR Data of Sulfonamides[a]

Compound	Aliphatic	>N-CH_2-	-NH-	Aromatic
$(i\text{-}C_3H_7)_2NTf$[b]	1.34(d,6H,J=7)	3.85(m,1H,J=7)[c]	--	--
$(i\text{-}C_3H_7)_2NTc$[d]	1.40(d,6H,J=7)	4.05(m,1H,J=7)[c]	--	--
$i\text{-}C_4H_9NHTf$	0.96(d,6H,J=7)	3.08(d,2H,J=7)	5.58(s,1H)	--
	1.80(m,1H)			
$(i\text{-}C_4H_9)_2NTf$	0.97(d,6H,J=6)	3.10(d,2H,J=7)	--	--
	1,90(m,1H)			
$s\text{-}C_4H_9NHTf$	0.88-2.82(m,8H)	3.52(m,1H)[c]	5.33(s,1H)	--
$s\text{-}C_4H_9NHTc$	0.82-2.80(m,8H)	3.66(m,1H)[c]	5.55(d,1H,J=9)	--
$t\text{-}C_4H_9NHBs$[e]	1.18(s,9H)	f	5.95(s,1H)	7.34-7.96(m,5H)
$CH_3OCH_2CH_2NHTf$	3.40(m,7H)	g	6.00(s,1H)	--
$(CH_3OCH_2CH_2)_2NTf$	3.32(s,3H)	4.03(t,2H,J=5)	--	--
	3.58(t,2H,J=5)			
EtO_2CCH_2NHTf	1.30(t,3H,J=7)	3.96(d,2H,J=6)	5.60(s,1H)	
	4.25(m,2H,J=7)			
$(EtO_2CCH_2)_2NTf$	1,30(t,3H,J=7)	4.22(s,2H)	--	--
	4.20(m,2H,J=7)			
$C_6H_{13}NHTf$	0,80-1,75(m,11H)	3.26(m,2H)	5.17(s,1H)	--
$(C_6H_{13})_2NTf$	0.80-1.80(m,11H)	3.30(t,2H,J=7)	--	--
$C_6H_{13}NHTc$	0.62-1.90(m,11H)	3.39(m,2H)	5.62(t,1H,J=6)	--
$C_6H_{13}N(CN)Tf$	0.66-2.08(m,11H)	3.62(t,2H,J=7)	--	--
$c\text{-}C_6H_{11}NHBs$	0.60-1,96(m,10H)	3.11(m,1H)[c]	5.03(d,1H,J=7)	7.11-8.02(m,5H)
adamantylNHBs	1.42-2,12(m,15H)	g	5.09(s,1H)	7,11-8.00(m,5H)
c-dodecylNHBs	1.29(s,22H)	3.30(m,1H)[c]	4,58(d,1H,J=8)	7.30-8.02(m,5H)
PhNHTf	--	--	h	7.03(s)
PhN(CN)Tf	--	--	--	7.40(s)
$p\text{-}FC_6H_4NHTf$[i]	--	--	h	6.82-7.42(m)
$p\text{-}FC_6H_4N(CH_2Ph)Tf$	--	4.76(s,2H)	--	6.69-7.30(m,9H)
$PhCH_2NHTf$	--	4.35(d,2H,J=6)	5.11(s,1H)	7.18(s,5H)
$(PhCH_2)_2NTf$	--	4.31(s,2H)	--	7.18(s,5H)
$PhCH_2N(CN)Tf$[i]	--	4.70(s,2H)	--	7.37(s,5H)
$PhCH_2N(Ph)Tf$	--	4.90(s,2H)	--	7.00-7.46(m,10H)

Table 2.--Continued NMR Data of Sulfonamides[a]

Compound	Aliphatic	$>N-CH_2-$	-NH-	Aromatic
$PhCH_2CH_2NHTf$	2.75(t,2H,J=7)	3.39(m,2H)	5.20(t,1H,J=5)	7.12(s,5H)
$(PhCH_2CH_2)_2NTf$	2.82(t,2H,J=7)	3.46(t,2H,J=7)	--	7.19(s,5H)

[a]Unless otherwise indicated, all spectra were recorded as CCl_4 solutions. Chemical shifts are in δ(ppm) from internal tetramethylsilane. Coupling constants are reported in hertz.

[b]Tf = trifluoromethanesulfonyl.

[c]Signal is that of methinyl rather than methylene proton.

[d]Tc = trichloromethanesulfonyl.

[e]Bs = benzenesulfonyl.

[f]Nitrogen attached to quaternary carbon.

[g]Signal hidden under other aliphatic absorptions.

[h]Signal hidden under aromatic absorptions.

[i]Spectrum recorded as $CDCl_3$ solution.

Table 3. Yields, Boiling Points, and Ir Data of Sulfenamides and N-Sulfenyl-N-Sulfonamides

Compound	Method[a]	Yield, %	Bp, °C/mm (Mp, °C)	Ir[b], cm^{-1}		
				NH	SO_2 Frequencies	
					Symmetric	Asymmetric
$(i\text{-}C_3H_7)_2NSCCl_3$	(A)[c]	72	67/0.1	--	--	--
$s\text{-}C_4H_9NHSCCl_3$	(A)[c]	89	59/0.80	3140	--	--
$s\text{-}C_4H_9N(SCCl_3)Tf$[d]	C	60	75°/0.35[g]	--	1415	1205
$t\text{-}C_4H_9N(SPh)Bs$[e]	A	88	oil	--	1315	1150
$C_6H_{13}NHSCCl_3$	(A)[c]	88	88/0.5	3170	--	--
$C_6H_{13}N(SCCl_3)Tc$[f]	D	75	98/0.35[g]	--	1400	1195
	C	86				
$C_6H_{13}N(SCCl_3)Tf$	B	81	89/0.35[g]	--	1420	1205
	C	73				
$c\text{-}C_6H_{11}N(SPh)Bs$	A	82	(118.5-119)	--	1355	1165
adamantylN(SPh)Bs[h]	A	72	(150-151)	--	1340	1150
c-dodecylN(SPh)Bs[h]	A	34	(166.5-167)	--	1330	1130

[a] Details of methods A-D given in preparation of N-sulfenyl-N-sulfonamides in Experimental section, unless otherwise noted.

[b] Unless otherwise noted, spectra were recorded as CCl_4 solutions, and calibrated with polystyrene.

[c] Details of this method given in preparation of sulfenamides in Experimental section.

[d] Tf = trifluoromethanesulfonyl.

[e] Bs = benzenesulfonyl.

[f] Tc = trichloromethanesulfonyl.

[g] Temperature is that of air bath in bulb to bulb distillation.

[h] Ir spectrum recorded as $CHCl_3$ solution.

Table 4. NMR Data of Sulfenamides and N-Sulfenyl-N-Sulfonamides[a]

Compound	Aliphatic	$>N-CH_2-$	-NH-	Aromatic
$(i\text{-}C_3H_7)_2NSCCl_3$	1.29(d,6H,J=7)	3.64(m,1H,J=7)[b]	--	--
$s\text{-}C_4H_9NHSCCl_3$	0.76-2.04(m,8H)	3.47(m,1H)[b]	3.78(s,1H)	--
$s\text{-}C_4H_9N(SCCl_3)Tf$[c]	0.60-2.12(m,8H)	4.02(m,1H)[b]	--	--
$t\text{-}C_4H_9N(SPh)Bs$[d]	1.49(s,9H)	e	--	6.96-8.06(m,10H)
$C_6H_{13}NHSCCl_3$	0.69-1.88(m,11H)	3.33(m,2H)	3.79(s,1H)	--
$C_6H_{13}N(SCCl_3)Tc$[f]	0.62-2.36(m,11H)	4.04(t,2H,J=7)	--	--
$C_6H_{13}N(SCCl_3)Tf$	0.67-2.23(m,11H)	3.91(t,2H,J=7)	--	--
$c\text{-}C_6H_{11}N(SPh)Bs$	0.78-1.87(m,10H)	4.06(m,1H)[b]	--	7.00-8.03(m,10H)
adamantylN(SPh)Bs[g]	1.56(s,6H) 2.18(s,9H)	e	--	7.03-8.09(m,10H)
c-dodecylN(SPh)Bs[g]	1.28(s,22H)	4.27(s,1H)[b]	--	7.12-8.02(m,10H)

[a] Unless otherwise indicated, all spectra were recorded as CCl_4 solutions. Chemical shifts are in δ(ppm) from internal tetramethylsilane. Coupling constants are reported in hertz.

[b] Signal is that of methinyl rather than methylene proton.

[c] Tf = trifluoromethanesulfonyl.

[d] Bs = benzenesulfonyl.

[e] Nitrogen attached to quaternary carbon.

[f] Tc = trichloromethanesulfonyl.

[g] Spectrum recorded as $CDCl_3$ solution.

less than 10% by weight of trichloromethanesulfonic acid. Reaction of the potassium salt with perchloric acid gave equally poor results, but passing an aqueous solution of the potassium salt through an ion exchange column gave a product containing 86% by weight of the sulfonic acid. Treatment of this trichloromethanesulfonic acid with phosphorus pentoxide in carbon tetrachloride, acetonitrile, or 1,2-dimethoxyethane gave products whose ir spectra suggest the sulfonic acid anhydride. Attempts to prepare the trichloromethanesulfonamides of benzyl and n-hexylamines, however, were not successful. No reaction took place.

N-Trifluoromethanesulfonyl imidazole has been shown to be superior, in some cases, to trifluoromethanesulfonic acid anhydride for the preparation of trifluoromethanesulfonates (28), as no strong acid is produced. It was hoped that a trichloromethanesulfonate ester or mixed anhydride might have similar properties. Attempts to prepare phenyl-trichloromethanesulfonate from the sulfonyl chloride, however, resulted only in chlorophenols. Likewise, an attempt to prepare a mixed anhydride from silver trifluoromethanesulfonate (29) and trichloromethanesulfonyl chloride proved unsuccessful.

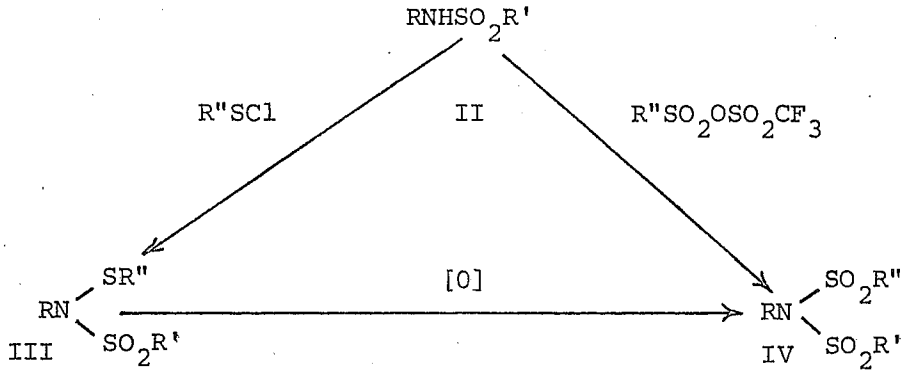
Sulfenamides are smoothly prepared by the reaction of amines with sulfenyl chlorides (30-42), including trichloromethanesulfenyl chloride (43-48). The oxidation of these intermediates to sulfonamides is known for aryl and alkyl derivatives (33-35, 49-53), but not for the trichloromethanesulfenamides. Reported attempted oxidations of trichloromethanesulfenates with peroxyacetic acid, hydrogen peroxide, alkaline or neutral potassium permanganate, or ozone resulted only in cleavage products (54). Braverman and Duar (55), however, were

successful in preparing benzyl trichloromethanesulfinates from the corresponding sulfenates by reaction with m-chloroperoxybenzoic acid in methylene chloride at 0°. Further oxidation to the sulfonates could not be accomplished, even with excess m-chloroperoxybenzoic acid at reflux.

Following these results, N,N-di-iso-propyltrichloromethanesulfenamide was prepared, and treated with ozone in methylene chloride at -78°. Only unreacted starting material was recovered. Reaction with slightly more than two equivalents of m-chloroperoxybenzoic acid in refluxing hexane, however, gave the sulfonamide in 68% yield. In the same manner, sec-butyl and n-hexyltrichloromethanesulfenamides were converted to the corresponding sulfonamides in 80 and 82% yields respectively. Having established one successful route to the preparation of trichloromethanesulfonamides, other oxidizing agents were investigated.

Glander and Golloch (56) used active manganese dioxide (57) to convert pentafluorobenzenesulfenamide selectively to the sulfonimide or to the sulfonamide, but the reagent gave no reaction with n-hexyltrichloromethanesulfenamide. The use of anhydrous peroxytrifluoroacetic acid (58) in refluxing methylene chloride, however afforded a 66% yield of the sulfonamide.

The required sulfonimides (IV) were prepared by methods analogous to the preparation of the sulfonamides: by direct sulfonylation of the sulfonamides, and by oxidation of the N-sulfenyl-N-sulfonamide intermediates (III) (see Figure 2). As most of the sulfonimides and N-sulfenyl-N-sulfonamides prepared herein have not



a) R = s-C_4H_9 R' = CF_3 R" = CCl_3
b) R = t-C_4H_9 R' = Ph R" = Ph
c) R = C_6H_{13} R' = CCl_3 R" = CCl_3
d) R = C_6H_{13} R' = CF_3 R" = CCl_3
e) R = c-C_6H_{11} R' = Ph R" = Ph
f) R = adamantyl R' = Ph R" = Ph
g) R = c-dodecyl R" = Ph R" = Ph

a) R = i-C_4H_9 R' = R" = CF_3
b) R = C_6H_{13} R' = R" = CF_3
c) R = c-C_6H_{11} R' = R" = Ph
d) R = c-dodecyl R' = R" = Ph
e) R = EtO_2CCH_2 R' = R" = CF_3
f) R = $CH_3OCH_2CH_2$ R' = R" = CF_3
g) R = $PhCH_2$ R' = R" = CF_3
h) R = $PhCH_2CH_2$ R' = R" = CF_3

Figure 2. Preparation of Sulfonimides Directly from Sulfonamides and via the N-Sulfenyl-N-Sulfonamides

been reported in the literature, their methods of preparation and yields, physical properties, spectral data, and elemental microanalyses are given in Tables 3-8.

N-Alkyl-N,N-di(trifluoromethane)sulfonimides were prepared by reaction of N-alkyltrifluoromethanesulfonamides with trifluoromethanesulfonic acid anhydride, as reported by De Christopher et al. (8), Glass (11), and others (12). For the reasons discussed above, N-alkyl-N,N-di(trichloromethane)sulfonimides could not be prepared in an analogous manner.

The preparation of aryl sulfenimides has been reported by Zincke and Eismayer (59) and Lecher et al. (60), although the yields were low. This information, together with the successful oxidation of sulfenamides to sulfonamides, prompted the attempted synthesis of trichloromethanesulfonimides via the sulfenimides. Unfortunately, the attempted syntheses of N-n-hexyl-N,N-di(trichloromethane)sulfenimide from the amine and the sulfenyl chloride resulted only in mixtures of the sulfenimide and sulfenamide. Although these mixtures were not separable due to the instability of the sulfenimide, attempts were made to oxidize these mixtures to mixtures of the sulfonamide and sulfonimide. These compounds presumably would be more stable and therefore could be separated without decompositon. The use of chromic acid or hydrogen peroxide in acetone, potassium permanganate in aqueous acetic acid, or aqueous commercial bleach resulted only in the complete decomposition of the mixtures.

Pan and Fletcher (61) reported preparing mixed N-aryl-N-trifluoromethanesulfonimides via the arylsulfonamide thallium (I) salts.

Table 5. Yields, Boiling Points, and Ir Data of Sulfonimides

Compound	Method[a]	Yield, %	Bp, °C/mm (Mp, °C)	Ir[b], SO_2 Frequencies, cm^{-1}	
				Symmetric	Asymmetric
i-$C_4H_9N(Tf)_2$[c]	A	27	33-34/0.55	1420	1120
	B	23			
$C_6H_{13}N(Tf)_2$	B	56	50/0.15	1435	1135
c-$C_6H_{11}N(Bs)_2$[d,e]	C	65	(subl. > 150)	1360	1150
c-dodecylN$(Bs)_2$[e]	C	84	(195.5-196)	1365	--
$EtO_2CCH_2N(Tf)_2$	A	34	78/0.35[f]	1400	1110
	B	10			
$CH_3OCH_2CH_2N(Tf)_2$	B	47	43/0.45	1415	1115
$PhCH_2N(Tf)_2$[g]	B	36	--	--	--
$PhCH_2CH_2N(Tf)_2$	B	61	84-85/0.63	1415	1200

[a]Details of methods A-C given in Experimental section.

[b]Unless otherwise noted, spectra were recorded as CCl_4 solutions, and calibrated with polystyrene.

[c]Tf = trifluoromethanesulfonyl.

[d]Bs = benzenesulfonyl.

[e]Ir spectrum recorded as $CHCl_3$ solution.

[f]Temperature is that of air bath in bulb to bulb distillation.

[g]No Bp or ir spectrum was recorded as compound was unstable.

Table 6. NMR Data of Sulfonimides[a]

Compound	Aliphatic	$>N-CH_2-$	Aromatic
$\underline{i}$-$C_4H_9N(Tf)_2$[b]	1.02(d,6H,J=7) 2.08(m,1H)	3.70(d,2H,J=7)	--
$C_6H_{13}N(Tf)_2$	0.70-2.10(m,11H)	3.89(t,2H,J=7)	--
$\underline{c}$-$C_6H_{11}N(Bs)_2$[c,d]	0.60-2.60(m,10H)	3.92(m,1H)[e]	7.16-8.15(m,10H)
$\underline{c}$-dodecylN$(Bs)_2$[d]	0.71-2.02(m,22H)	3.70(m,1H)[e]	7.21-8.19(m,10H)
$EtO_2CCH_2N(Tf)_2$	1.32(t,3H,J=7) 4.31(m,2H,J=7)	4.50(s,2H)	--
$CH_3OCH_2CH_2N(Tf)_2$	3.31(s,3H) 3.59(t,2H,J=5)	4.09(t,2H,J=5)	
$PhCH_2N(Tf)_2$	--	4.36(s,2H)	7.20(m,5H)
$PhCH_2CH_2N(Tf)_2$	3.02(t,2H,J=7)	4.02(t,2H,J=7)	7.20(s,5H)

[a] Unless otherwise indicated, all spectra were recorded as CCl_4 solutions. Chemical shifts are in δ(ppm) from internal tetramethylsilane. Coupling constants are reported in hertz.

[b] Tf = trifluoromethanesulfonyl.

[c] Bs = benzenesulfonyl.

[d] Spectrum recorded as $CDCl_3$ solution.

[e] Signal is that of methinyl rather than methylene proton.

Table 7. Elemental Microanalyses of Various Sulfonamides and Sulfonimides

Compound	Calculated			Found		
	%C	%H	%S	%C	%H	%S
i-C_4H_9NHTf[a]	29.27	4.91	15.62	29.32	4.87	15.65
$(i\text{-}C_4H_9)_2NTf$	41.37	6.94	12.27	41.08	6.89	12.20
i-$C_4H_9N(Tf)_2$	21.37	2.69	19.01	21.43	2.69	19.06
$CH_3CH_2O_2CCH_2NHTf$	25.54	3.43	13.63	25.66	3.02	13.72
$CH_3CH_2O_2CCH_2N(Tf)_2$	21.50	2.11	--	21.31	2.34	--
$CH_3OCH_2CH_2NHTf$	23.19	3.89	15.48	23.14	3.86	15.52
$CH_3OCH_2CH_2N(Tf)_2$	17.70	2.08	18.90	17.80	2.11	18.81
$C_6H_{13}NHTf$	36.05	6.05	13.75	36.06	6.10	13.80
$(C_6H_{13})_2NTf$	49.19	8.25	10.11	49.29	8.26	10.15
$C_6H_{13}N(Tf)_2$	26.30	3.59	17.55	26.37	3.83	17.58
$PhCH_2NHTf$	40.17	3.37	13.40	40.13	3.33	13.43
$(PhCH_2)_2NTf$	54.71	4.29	9.74	54.90	4.01	9.75
$PhCH_2CH_2NHTf$	42.69	3.98	12.66	42.78	3.92	12.75
$PhCH_2CH_2N(Tf)_2$	31.17	2.36	16.64	31.20	2.39	16.75
$C_6H_{13}NHTc$[b]	29.75	4.99	11.34	29.79	5.00	11.38
c-$C_6H_{11}N(SPh)Bs$[c]	62.22	6.10	18.45	62.20	5.99	18.35
adamantylN(SPh)Bs	66.13	6.31	16.05	65.15	6.20	15.89
c-dodecylN(SPh)Bs	66.78	7.71	14.86	66.50	7.87	14.77
c-dodecylN$(Bs)_2$	62.17	7.17	13.83	62.90	7.53	11.91

[a] Tf = trifluoromethanesulfonyl.

[b] Tc = trichloromethanesulfonyl.

[c] Bs = benzenesulfonyl.

Table 8. Mass Spectra of Various Sulfenamides and Sulfonamides

Compound	m/e (M^+) Fragments[a]
$(i\text{-}C_3H_7)_2NSCCl_3$	117, 119, 121, 132, 214, 216, 249(P), 251, 253, 255
$(i\text{-}C_3H_7)_2NTc$[b]	117, 119, 121, 149, 164, 281(P), 283, 285, 287
$C_6H_{13}NHSCCl_3$	117, 119, 121, 130, 132, 157, 159, 161, 178, 180, 249(P), 251, 253, 255
$C_6H_{13}NHTc$	117, 119, 121, 146, 148, 150, 164, 210, 212, 214, 281(P), 283, 285, 287
$C_6H_{13}N(SCCl_3)Tf$[c]	117, 119, 121, 133, 162, 164, 166, 199, 201, 203, 233, 235, 237, 382(P), 384
$p\text{-}FC_6H_4N(CH_2Ph)Tf$	82, 84, 91, 117, 119, 121, 333(P)

[a] In most cases, fragments are in $\geq$ 20% abundance. The symbol (P) indicates the parent peak.

[b] Tc = trichloromethanesulfonyl.

[c] Tf = trifluoromethanesulfonyl.

The synthesis of N-n-hexyl-N,N-di(trichloromethane)sulfenimide from the sulfenyl chloride and the thallium (I) salt of the sulfenamide was not feasible, however, since the attempted synthesis of the thallium (I) salt only resulted in the decomposition of the sulfenamide.

The reported preparations of N-trichloromethanesulfenyl derivatives of phthalimide and N-alkylarylsulfonamides (47, 48) by reaction of the sulfenyl chloride with the corresponding sodium salts led to another approach to the preparation of N,N-di(trichloromethane)sulfonimides. N-n-Hexyl-(N-trichloromethanesulfenyl)trichloromethanesulfonamide was successfully prepared by the reaction of the sulfenyl chloride with the lithium salt of N-n-hexyltrichloromethanesulfonamide; the oxidation of this intermediate to the sulfonimide was then investigated.

Reactions of m-chloroperoxybenzoic acid in refluxing hexane gave mixtures of unreacted starting material and N-n-hexyltrichloromethanesulfonamide. The use of peroxytrifluoroacetic acid (58, 62, 63) as the oxidizing agent was much more thoroughly investigated: solvents, reactions times and temperatures, and buffering agents were all varied. In no case was the N,N-di(trichloromethane)sulfonamide obtained. With these last unsuccessful reactions, the attempted synthesis of N,N-di(trichloromethane)sulfonimides was abandoned, but some hope remained of possibly preparing N-alkyl-(N-trichloromethanesulfonyl)trifluoromethanesulfonimides.

Using methods described earlier, N-sec-butyl and N-n-hexyl-(N-trichloromethanesulfenyl)trifluoromethanesulfonamides were prepared. Reaction of these intermediates with m-chloroperoxybenzoic acid in hexane gave unreacted starting material and/or N-sulfenyl group

products. Attention was once again focused on the possibility of using trichloromethanesulfonyl chloride as a means of preparing these mixed sulfonimides. Although the reactions of amines with this sulfonyl chloride do not lead to the sulfonamides, as discussed earlier, the reactions with sulfonamides have not been reported. To this end, the reactions of various trifluoromethanesulfonamide salts with trichloromethanesulfonyl chloride were studied.

The sodium salt and Grignard derivative of N-n-hexyltrifluoromethanesulfonamide were prepared and allowed to react with trichloromethanesulfonyl chloride, but in each case only the original sulfonamide was isolated. The Pan and Fletcher thallium (I) salt method for preparing mixed sulfonimides was again attempted, but, again, it was not possible to prepare the thallium (I) salt of either N-n-hexyl or N-sec-butyltrifluoromethanesulfonamide. With these results, attempts to prepare N-alkyl-(N-trichloromethanesulfonyl)trifluoromethanesulfonamides were discontinued.

The N,N-diarylsulfonimides of a great many primary amines attached to primary or secondary carbons are known (6-8, 12-14, 17, 64-98), but none have been reported for primary amines attached to tertiary carbons. De Christopher et al. (8) report a successful synthesis of N-t-butyl-p-toluenesulfonamide, but were unsuccessful in converting it to the N,N-di(p-toluene)sulfonimide. Hutchins et al. (14) report analogous results with 1-adamantylamine and diphenylmethylamine. It was conjectured that the sulfonamides were either too sterically hindered to undergo sulfonylation, or that the sulfonimides

were formed as unstable intermediates which thermally decomposed to give alkene.

Coates and Chen (99) demonstrated the preparation of several unstable and hindered tosylates by the m-chloroperoxybenzoic acid oxidation of the corresponding p-toluenesulfinate esters. Since the synthesis of even N-sec-butyl-(N-trichloromethanesulfenyl)trifluoromethanesulfonamide proceeded smoothly, it was thought that the aryl analogues of these intermediates might provide a successful route to the N,N-diarylsulphonimides of amines attached to tertiary carbons. To test this proposal, the method was first tried with two secondary cases.

N-Cyclohexyl-(N-benzenesulfenyl)benzenesulfonamide was prepared in 82% yield by treating N-cyclohexylbenzenesulfonamide with n-butyllithium and benzenesulfenyl chloride. The use of either sodium hydride or lithium hydride in place of n-butyllithium resulted in yields of only about 10%. In a similar manner, N-cyclododecyl-(N-benzenesulfenyl)benzenesulfonamide was prepared, but only in 34% yield. Treatment of each of these intermediates with slightly more than two equivalents of m-chloroperoxybenzoic acid in refluxing hexane resulted in 65 and 84% yields, respectively, of the corresponding sulfonimides.

The tertiary cases chosen for this study were t-butyl and 1-adamantylamines. N-t-Butyl-(N-benzenesulfenyl)benzenesulfonamide and N-1-adamantyl-(N-benzenesulfenyl)benzenesulfonamide were prepared in 89 and 72% yields, respectively, from the corresponding sulfonamides as described above.

The reaction of N-t-butyl-(N-benzenesulfenyl)benzenesulfonamide with m-chloroperoxybenzoic acid in refluxing hexane gave only a small amount of N-t-butylbenzenesulfonamide, resulting from N-sulfenyl group cleavage. The bulk of the material was in some manner lost during the reaction. The reaction was repeated using chloroform as the solvent at 0°. Work up of the reaction led once again to cleavage products only; less material was lost than in the previous reaction. A third reaction was carried out using peroxytrifluoroacetic acid (58) in methylene chloride at 0°. The addition of the peroxyacid solution to the N-sulfenyl sulfonamide solution was accompanied by the vigorous evolution of gas. The nmr of an aliquot taken shortly after mixing showed two sharp upfield absorptions, presumably due to t-butyl groups. The further upfield of the two had a shift of 1.18δ, which corresponds to that of N-t-butylbenzenesulfonamide. The other absorption had a shift of 1.50δ, which is close to the 1.55δ shift reported (100) for t-butyltrifluoroacetate in deuteriochloroform solution. Although only N-t-butylbenzenesulfonamide was isolated from the reaction mixture, it could be inferred from these observations that N-t-butyl-N,N-di(benzene)sulfonimide was indeed formed in the reaction mixture, but decomposed as it formed via an elimination to give isobutylene, most of which was lost, but some of which was trapped as the trifluoroacetate derivative. These conjectures are somewhat supported by an observation made by Hendrickson et al. (12). In attempting to prepare N-t-butyl-N,N-di(trifluoromethane)sulfonimide by a bis trifluoromethanesulfonylation of t-butylamine in methylene chloride at -78°, isobutylene was quantitatively evolved from the reaction mixture. It is

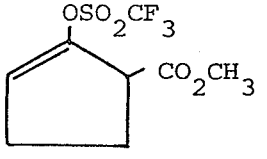
also not unreasonable to assume that isobutylene would be trapped as the trifluoroacetate under the reaction conditions, as Latrémonille and Eastham (101) have reported a preparation of t-butyltrifluoroacetate by passage of isobutylene into a cold dichloroethane solution of trifluoroacetic acid.

As the reaction of N-t-butyl-(N-benzenesulfenyl)benzenesulfonamide with peroxytrifluoroacetic acid in methylene chloride was very vigorous at 0^{o}, the analogous reaction with N-1-adamantyl-(N-benzenesulfenyl)benzenesulfonamide was carried out at an initial temperature of -78^{o}. In this case, no evolution of gas was noted. After mixing, the reaction mixture was warmed to 0^{o}, and an nmr of an aliquot was taken. The spectrum appeared to be a mixture of the starting material and N-1-adamantylbenzenesulfonamide; the mixture was allowed to remain at -10^{o} for two days before working it up, since starting material was still present. Upon work up, only a small amount of material was obtained. Tlc on silica gel showed the product to be a mixture, but no starting material was present. Although an nmr of the crude product resembled a mixture of starting material and N-1-adamantylbenzenesulfonamide, an ir clearly showed the absorption band at 1770 cm^{-1}, characteristic of trifluoroacetates. Due to the small amount of material obtained, however, no attempt was made to separate the mixture.

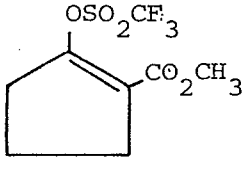
While the above work did not result in the isolation of the N,N-diarylsulfonimides of amines attached to tertiary carbons, the results strongly imply that they are indeed formed, but decompose immediately be elimination and/or solvolysis pathways.

Having prepared a variety of N-alkyl-N,N-di(trifluoromethane)-sulfonimides, the study of the reactions of these compounds with various nucleophiles was initiated, expanding on the work reported by Glass (11).

The first compound chosen for study was N-n-hexyl-N,N-di(trifluoromethane)sulfonimide, with 2-carbomethoxycyclopentanone potassium salt (102) and ethyl sodioacetoacetate as the nucleophiles, and hexamethylphosphoric triamide (HMPT) as the solvent. The reaction with 2-carbomethoxycyclopentanone potassium salt gave a mixture of 2-carbomethoxycyclopentanone n-hexyl enol ether, N-n-hexyltrifluoromethanesulfonamide, N,N-di-n-hexyltrifluoromethanesulfonamide, 3-carbomethoxy-2-cyclopentenyl-2-trifluoromethanesulfonate (V), and 2-carbomethoxy-1-cyclopentenyl-2-trifluoromethanesulfonate (VI).



V



VI

A sample of each product was obtained by preparative gas-liquid chromatography (glc), and ir and nmr spectra were taken and compared with those of independently prepared authentic samples. Glc retention times were also compared. While preparing VI by the method of Stang and Dueber (103), isomer V was also found in substantial amount. This result was not expected, and a more detailed study of the preparation of these vinyl trifluoromethanesulfonates was made. The results are reported in Appendix A.

The presence in the reaction mixture of V and VI, in addition to 2-carbomethoxycyclopentanone n-hexyl enol ether indicated that attack at the sulfonimide sulfur was competing with attack at the carbon bearing the sulfonimide group. The origin of N,N-di-n-hexyltrifluoromethanesulfonamide was not as clear, and a series of experiments was run to help clarify the reaction pathway.

The reaction was repeated, and its progress followed by analytical glc. It was found that the O-alkylated product increased from 8% after 40 hr to a maximum of 39% after 233 hr. Over the same time period, the yields of V and VI decreased from 30% to 15%, but the yields of each of the sulfonamides remained the same throughout.

The reaction of N-n-hexyltrifluoromethanesulfonamide sodium salt with VI in HMPT did not produce any of the sulfonimide, indicating that attack at the sulfonimide sulfur is not a reversible process with this nucleophile.

No reaction was observed when N,N-di-n-hexyltrifluoromethanesulfonamide was allowed to react with 2-carbomethoxycyclopentanone potassium salt in HMPT; O-alkylated product did not arise by this pathway.

Reaction fo 2-n-hexyl-2-carbomethoxycyclopentanone with 2-carbomethoxycyclopentanone potassium salt in HMPT produced none of the O-alkylated product.

Since the increase in O-alkylated product and concurrent decrease in products V and VI with time could not be accounted for by these reactions, the possibility of solvent participation was considered. N-n-Hexyl-N,N-di(trifluoromethane)sulfonimide was mixed with

HMPT, and the solution was stirred at room temperature for two days. Preparative glc of the product mixture showed a small amount of unreacted sulfonimide, N-n-hexyltrifluoromethanesulfonamide, and n-hexyltrifluoromethanesulfonate. The presence of the sulfonamide implied the surprising occurrence of solvent attack at the sulfonimide sulfur. The trifluoromethanesulfonate ester was difficult to account for until the crude reaction mixture was more closely examined. After washing with base to remove sulfonamide, an nmr of the mixture indicated the presence of an HMPT salt with the proposed structure VII. The origin of the trifluoromethanesulfonate ester was considered to be the pyrolysis of VII in the glc injection port during isolation of the products.

$$[(CH_3)_2N]_3\overset{+}{P}O(CH_2)_5CH_3\ \bar{N}(SO_2CF_3)_2 \qquad \text{(VII)}$$

The reaction of N-n-hexyl-N,N-di(trifluoromethane)sulfonimide with ethyl sodioacetoacetate in HMPT was examined to determine if this nucleophile, too, would attack at the sulfonimide sulfur. The reaction was worked up in two portions: half after one day, and the other half after ten days at room temperature. In each case, analytical glc showed a mixture of N-n-hexyltrifluoromethanesulfonamide, and O-alkylated product. Also, in each case, the proportions of each component of the mixture were the same, indicating that the reaction was over fairly quickly. Once again, the presence in the reaction mixture of both sulfonamides indicated that attack at sulfonimide sulfur had taken place.

Except to note that the sulfonimide underwent attack at the sulfonimide sulfur, as well as at the carbon bearing the sulfonimide

group, by both the nucleophile and the solvent, the full import of solvent participation was not appreciated until much later in the study. As attack at the sulfonimide sulfur was considered to be of greater importance, modifications of the leaving group were proposed to circumvent this problem.

Attack at sulfonimide sulfur might be prevented by sterically hindering the sulfonyl group. To achieve sufficient steric hindrance and still maintain a good electron withdrawing group, substitution of trichloromethanesulfonyl for trifluoromethanesulfonyl groups was attempted. However, as discussed above, the syntheses of N-alkyl-N,N-di(trichloromethane)sulfonimides and N-alkyl-N-(trichloromethanesulfonyl)trifluoromethanesulfonimides were unsuccessful.

Attention was next turned to various N-substituted trifluoromethanesulfonamides. It was hoped that some grouping could be found which would statistically reduce the number of sulfonyl sulfurs available to nucleophilic attack, without seriously compromising the reactivity of the leaving group. The substitution of an alkyl group for one of the trifluoromethanesulfonyl groups of the sulfonimide did not satisfy these conditions, as seen above in the reaction of N,N-di-n-hexyltrifluoromethanesulfonamide with 2-carbomethoxycyclopentanone potassium salt. Similarly, the reaction of N,N-di-iso-propyltrifluoromethanesulfonamide with diethyl sodiomalonate in HMPT gave back only starting materials.

N-Phenyl-N-benzyltrifluoromethanesulfonamide was prepared in nearly quantitative yield by reaction of the amine with trifluoromethanesulfonic acid anhydride. While the reaction of this sulfonamide

with sodium cyanide resulted only in decomposition products at 150° in HMPT, reaction with diethyl sodiomalonate at the same temperature resulted in a 41% yield of diethyl benzylmalonate. Encouraged by this result, the syntheses of substituted N-aryl sulfonamides was attempted.

The synthesis of N-(4-nitrophenyl)-N-benzyltrifluoromethanesulfonamide was attempted by several routes, all of them unsuccessful. N-(4-Nitrophenyl)-N-benzylamine was prepared by the method of Kehrmann and Tichwinski (104), but the reaction of this amine with trifluoromethanesulfonic acid anhydride under various conditions failed to produce any of the desired trifluoromethanesulfonamide.

As N-phenyl-N-benzyltrifluoromethanesulfonamide was readily available, the nitration of this compound was next attempted. Reaction of this sulfonamide with mixtures of nitric and sulfuric acids in either glacial acetic or trifluoroacetic acids, or with acetyl nitrate (105-108) in acetic anhydride resulted in mixtures of polynitration and decomposition products.

One final approach to this synthesis was via the benzylation of N-(4-nitrophenyl)trifluoromethanesulfonamide, but as the reaction of 4-nitroaniline with trifluoromethanesulfonic acid anhydride gave only unreacted starting amine, attempts to synthesize N-(4-nitrophenyl)-N-benzyltrifluoromethanesulfonamide were terminated.

The synthesis of N-(4-fluorophenyl)-N-benzyltrifluoromethanesulfonamide was accomplished by benzylation of 4-fluorobenezenetrifluoromethanesulfonamide, followed by column chromatography on silica gel. The overall yield from 4-fluoroaniline, however, was only 14%.

The reaction of this sulfonamide with diethyl sodiomalonate in HMPT at up to 145° gave no reaction. This result was quite unexpected.

Due to their surprising lack of reactivity and, at least in some cases, difficulty of preparation the study of N-aryl sulfonamides was discontinued.

White, Baum, and Eitel (109) have demonstrated the preparation of 1-methyl-3-p-tolyltriazine by the reaction of p-toluenediazonium chloride with methylamine in aqueous sodium carbonate solution. The utility of this compound in the esterification of carboxylic acids was also shown, and the fact that other 1-alkyl triazenes could be similarly prepared and utilized was pointed out (110, 111). Attempts to apply these methods to the preparation of 1-alkyl-1-trifluoromethanesulfonyl-3-p-tolyltriazenes, however, were unsuccessful. The reaction of benzenediazonium chloride with aqueous sodium hydroxide or sodium carbonate solutions of N-benzyltrifluoromethanesulfonamide gave only unreacted sulfonamide. The same results were obtained with N-n-hexyltrifluoromethanesulfonamide under the same conditions.

As the synthesis of the desired triazenes could not be accomplished by reaction of the sulfonamides with a diazonium salt, the modification of an existing triazene was proposed. However, the attempted trifluoromethanesulfonylation of 1-methyl-3-p-tolyltriazene with trifluoromethanesulfonic acid anhydride in ether failed to produce any of the desired 1-methyl-1-trifluoromethanesulfonyl-3-p-tolyltriazene product. With these disappointing results, this approach to the modification of the sulfonamide was also abandoned.

The extensive studies of von Braun (112-114) and others (115-118) into the reactions of primary, secondary, and tertiary amines with cyanogen bromide show that N-cyano amine derivatives are first formed, then undergo attack by the bromide ion to give displacement and/or elimination products. The possibility of using an N-cyano group to activate the trifluoromethanesulfonamides was therefore considered.

The N-cyano derivatives of N-benzyl-, N-phenyl-, and N-n-hexyltrifluoromethanesulfonamides were prepared by reaction of the respective sulfonamide sodium salt with cyanogen bromide in ether solution, followed by purification by column chromatography on silica gel. The reaction of N-cyano-N-n-hexyltrifluoromethanesulfonamide with diethyl sodiomalonate in HMPT at room temperature gave a mixture of N-n-hexyltrifluoromethanesulfonamide and N,N-di-n-hexyltrifluoromethanesulfonamide as the only products. Although unexpected, attack at the N-cyano group is evident from the products here; the presence of the N,N-di-n-hexylsulfonamide suggests attack at the carbon bearing the sulfonamide group by another sulfonamide anion. These results prompted the investigation of N-cyano-N-phenyltrifluoromethanesulfonamide as a possible cyanating agent in the preparation of aromatic cyanates.

As the cyanate of 2,6-di-t-butyl phenol has been prepared by Stroh and Gerber (119) by reaction with cyanogen bromide or chloride, and the cyanate of phenol has only been prepared by indirect methods (120), these were chosen as test cases for N-cyano-N-phenyltrifluoromethanesulfonamide. The reaction of this N-cyano sulfonamide with sodium phenoxide in HMPT at room temperature gave only decomposition

products, but reaction with sodium 2,6-di-t-butyl phenoxide in HMPT at up to 50° gave only unreacted starting materials. A test of the stability of the N-cyano sulfonamide in both HMPT and acetonitrile was made, but was inconclusive: initial tests showed decomposition, but a repeat in HMPT showed no reaction.

As the reaction of N-cyano-N-n-hexyltrifluoromethanesulfonamide with diethyl sodiomalonate did not give nucleophilic attack at the carbon bearing the sulfonamide group, the N-cyano-N-phenyltrifluoromethanesulfonamide did not show promise as a cyanating agent, at least in the preparation of cyanates, the study of these derivatives was also ended.

With the attempts to synthesize N-alkyl-N,N-di(trichloromethane)sulfonimides and N-alkyl-N-(trichloromethanesulfonyl)trifluoromethanesulfonimides proving unsuccessful, and since the results of nucleophilic displacements on N-substituted trifluoromethanesulfonamides were not promising, a more thorough investigation of N-alkyl-N,N-di(trifluoromethane)sulfonimides seemed prudent.

Using the procedures discussed above, N-i-butyl-, N-(2-methoxyethyl)-, N-(2-phenethyl)-, and N-n-hexyl-N,N-di(trifluoromethane)sulfonimides and N,N-di(trifluoromethanesulfonyl)glycine ethyl ester were prepared. With the exception of the N-n-hexyl sulfonimide, each derivative was allowed to react separately with sodium cyanide, potassium iodide, and diethyl sodiomalonate. In each case, the nucleophile and sulfonimide were present in approximately equimolar amounts, and the reactions were allowed to proceed at room temperature in HMPT solution for four days. The results of these experiments are given in

Table 9. Since the reactions of N-n-hexyl-N,N-di(trifluoromethane)-sulfonimide with these three nucleophiles have already been reported (11), they were not repeated here. However, the reactions of this sulfonimide with a variety of other nucleophiles in HMPT solution have been investigated, and these results are given in Tables 10 and 11.

Examination of Tables 9 and 10 reveals that the yields of nucleophilic displacement products resulting from attack at the carbon bearing the nitrogen group are disappointingly low. In general, potassium iodide gives the best yields, followed by salts of active methylene compounds, followed by sodium cyanide, with other hetero-atom nucleophiles and phenyl Grignard somewhere in between.

Although some of the alkyl cyanides and iodides were lost during the workup of the initial reactions due to their volatility, caution was exercised in repeat reactions to overcome this problem. As the reactions were worked up, the yields of the cyanides and iodides were determined by quantitative glc of the ether extracts before distilling off the solvent.

By far the most common side products of these displacement reactions are the N-alkyl and N,N-di-alkyltrifluoromethanesulfonamides. To account for these sulfonamide products, a reaction pathway such as that depicted in Figure 3 was initially proposed.

By this scheme, attack at sulfonimide sulfur competes with attack at carbon to produce a mixture of sulfonylated nucleophile and sulfonamide anion in the first case, and a mixture of alkylation product and sulfonimide anion in the second. The sulfonamide anion could then attack sulfonimide: attack at sulfur would lead to more

Table 9. Products of Reactions of Various N-Alkyl-N,N-di(trifluoromethane)sulfonimides with Various Nucleophiles in HMPT

$RN(SO_2CF_3)_2$	Nucleophile	% Yield[a]		
		R-X[b]	$RNHSO_2CF_3$[b]	$R_2NSO_2CF_3$[b,c]
$i\text{-}C_4H_9N(SO_2CF_3)_2$	NaCN	2[d]	25	19
$CH_3OCH_2CH_2N(SO_2CF_3)_2$	NaCN	5[e]	14	40
$PhCH_2CH_2N(SO_2CF_3)_2$	NaCN	2	8	39
$CH_3CH_2O_2CCH_2N(SO_2CF_3)_2$	NaCN	10	15	0
$i\text{-}C_4H_9N(SO_2CF_3)_2$	KI	76	16	0
$CH_3OCH_2CH_2N(SO_2CF_3)_2$	KI	39	8	0
$PhCH_2CH_2N(SO_2CF_3)_2$	KI	53	2	0
$CH_3CH_2O_2CCH_2N(SO_2CF_3)_2$	KI	28[f]	0	0
$i\text{-}C_4H_9N(SO_2CF_3)_2$	$NaCH(CO_2CH_2CH_3)_2$	12	10	31
$CH_3OCH_2CH_2N(SO_2CF_3)_2$	$NaCH(CO_2CH_2CH_3)_2$	51	0	19
$PhCH_2CH_2N(SO_2CF_3)_2$	$NaCH(CO_2CH_2CH_3)_2$	11[g]	3	25
$CH_3CH_2O_2CCH_2N(SO_2CF_3)_2$	$NaCH(CO_2CH_2CH_3)_2$	--[h]	2	0

[a]Based on quantitative glc by comparison with authentic samples.

[b]Identified by comparison of ir and nmr spectra and glc retention times of isolated products with authentic samples.

[c]Based on two moles of sulfonimide yielding one mole of sulfonamide.

[d]5% unreacted sulfonimide found.

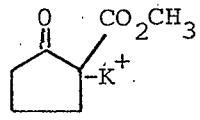
[e]10% unreacted sulfonimide found.

[f]72% yield of $CH_3CH_2OCH_2CO_2CH_2CH_3$ found.

[g]16% yield of $(CH(CO_2CH_2CH_3)_2)_2$ found, based on two moles of $CH_2(CO_2CH_2CH_3)_2$ yielding one mole of product.

[h]18% yield of $CH_3CH_2O_2CCH{=}C(CO_2CH_2CH_3)_2$ found, based on one mole of sulfonimide yielding one mole of product; identified by comparison of spectra of isolated material with authentic methyl ester.

Table 10. Products of Reactions of N-n-Hexyl-N,N-di(trifluoromethane)-sulfonimide with Various Nucleophiles in HMPT

Nucleophile	% Yield[a] R-X[b]	$RNHSO_2CF_3$[b]	$R_2NSO_2CF_3$[b,c]
	39[d,e]	30	15
$CH_3CO\underset{Na}{\overset{-}{C}}HCO_2CH_2CH_3$	--[d,f]	0	--[f]
$CH_3CO_2^-K^+$	0	--[f]	--[f]
PhS^-Na^+	15[g]	23	12
NaN_3	0	52	14
$CH_3CO\underset{Ti}{\overset{-}{C}}HCOCH_3$	46[d]	29	25
$NCCHCN^-Na^+$	0	47	18
PhMgBr[h]	0[i]	0	0
PhMgBr[j]	0[i]	0	0
PhMgBr[k]	0[l]	21[f]	0
HMPT	--[f,m]	--	0
HMPT[n]	100	0	0

[a] Based on quantitative glc by comparison with authentic samples.

[b] Identified by comparison of ir and nmr spectra and glc retention times of isolated products with authentic samples.

[c] Based on two moles of sulfonimide yielding one mole of sulfonamide.

[d] O-alkylated product.

[e] Maximum yield. 15% combined yield of compounds V and VI also found.

[f] Yield not determined.

[g] 50% yield of $(PhS)_2$ found.

[h] Reaction done in refluxing benzene solvent.

[i] Quantitative yield of unreacted sulfonimide.

[j] Reaction done in toluene solvent at 90°.

[k] Reaction done in refluxing p-dioxane solvent.

[l] 15% yield of unreacted sulfonimide, and 14% yield of Ph-Ph found.

[m] Product is the phosphonium salt VII.

[n] Reaction followed by nmr.

Table 11. Products of Reactions of N-n-Hexyl-N,N-di(trifluoromethane)sulfonimide with Water in HMPT

moles Water / moles Imide	Temperature (°C)	Time (days)	% Yield[a]		
			$CH_3(CH_2)_5OH$[b]	$CH_3(CH_2)_5OSO_2CF_3$[b]	Salt VII[c]
1	20	6	0[d]	94	3
10	45	5	84[e]	0	5
10	75	5	49	--[f]	0
20	45	6	44	--[f]	14
20	75	2	25	--[f]	--[f]
20	75	4	34	7	--[f]
5	45	5	<1	0	53
10[g]	75	6	35	5	28

[a]Based on quantitative glc by comparison with authentic samples.

[b]Identified by comparison of ir and nmr spectra and glc retention times of isolated products with authentic samples.

[c]Identified by ir spectra.

[d]Traces of unreacted sulfonimide and both sulfonamides found.

[e]8% yield of $CH_3(CH_2)_5NHSO_2CF_3$, and 4% yield of unreacted sulfonimide found.

[f]Yield not determined.

[g]One mole of calcium carbonate per mole of sulfonimide added.

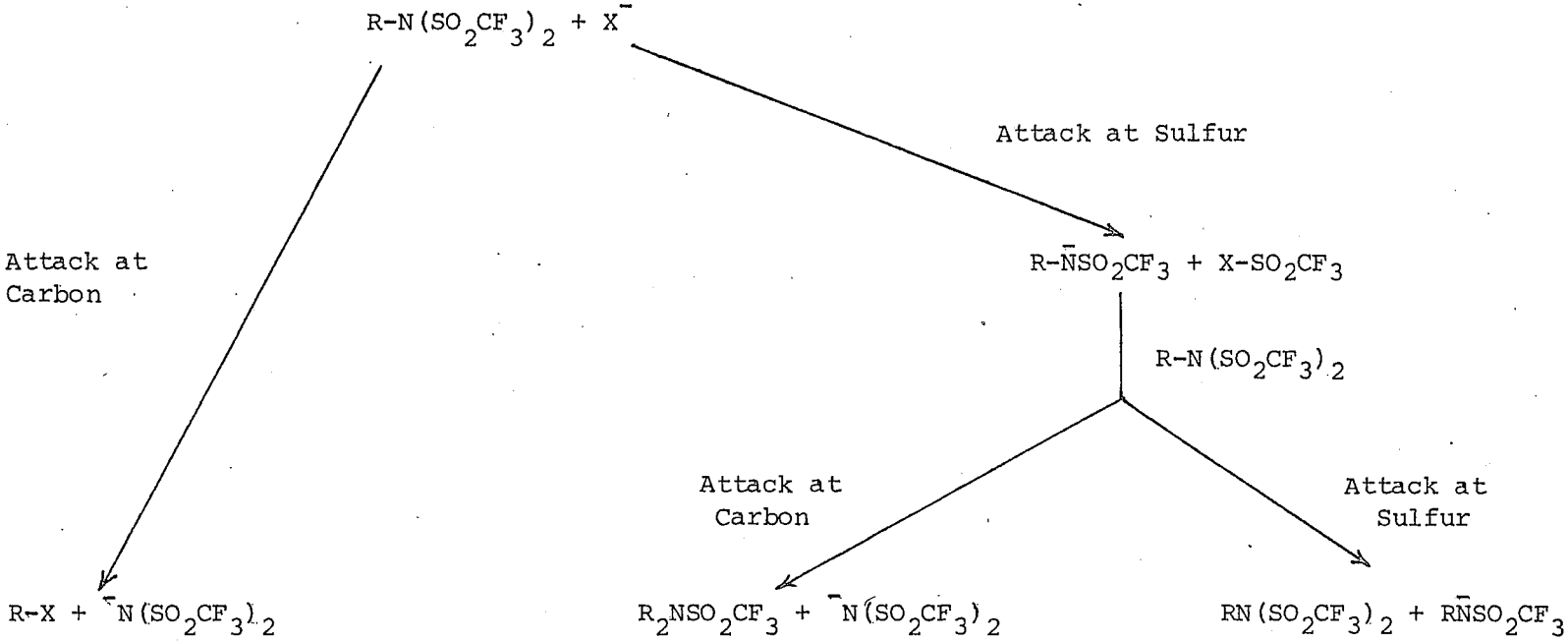


Figure 3. Initially Proposed Displacement Reaction Mechanism

sulfonimide and sulfonamide anion, and would produce no new products; but attack at carbon would produce N,N-di-alkyltrifluoromethane-sulfonamide and sulfonimide anion. During aqueous work up, any sulfonamide anion would presumably be protonated and isolated as sulfonamide, but sulfonimide anion would be lost to the aqueous phase. The sulfonylated nucleophile might either be hydrolyzed or isolated, depending upon its reactivity.

Although attractive for its simplicity, this scheme fell short in explaining all the product data. In most of the reactions, one-third to one-half of the alkyl groups could not be accounted for, based on the starting sulfonimide. One obvious source of alkyl group loss was the failure to protonate the sulfonamide anion, thus losing it to the aqueous phase. A control experiment did, in fact, indicate that sulfonamide ion was lost to the aqueous phase during the work up procedure employed, but not in great enough amount to account for the entire loss.

Another possible source of loss considered was through the formation of alkene via a β-elimination reaction. In at least two cases, however--the reaction of N-i-butyl-N,N-di(trifluoromethane)-sulfonimide with potassium iodide and the reaction of N-(2-phenethyl)-N,N-di(trifluoromethane)sulfonimide with sodium cyanide--the reaction vessels were equipped with traps containing carbon tetrachloride solutions of bromine. Work up and analysis of these solutions, however, showed no brominated alkenes were present, and in no reaction was any significant pressure build up noted. Also, alkenes were never found during the glc product analyses.

Authentic samples of N,N-di-alkyltrifluoromethanesulfonamides were prepared by reaction of the N-alkyltrifluoromethanesulfonamide sodium salts with the appropriate alkyl chloride or iodide in HMPT. It was found that even with reaction times of nine days, the yields of N,N-di-alkyltrifluoromethanesulfonamides were low, and unreacted halide and N-alkyltrifluoromethanesulfonamide were recovered. These results would seem to question whether the sulfonamide anion was a sufficiently reactive nucleophile to behave as indicated in Figure 3.

The hydrolysis of N-n-hexyl-N,N-di(trifluoromethane)sulfonimide in HMPT was studied, varying the amount of water used and the reaction temperature and duration (see Table 11). The amount of n-hexanol produced varied from 0 to 84%, with the average being about 40%. n-Hexyltrifluoromethanesulfonate was commonly found in the reaction mixture, although the yield was usually less than 10%. But the most surprising product found in these reactions was the phosphonium salt, VII. The amounts actually isolated varied, but were often quite substantial. The identity of VII was established by its ir and nmr spectra. These results, together with the fact that VII was detected among the products of the reaction of the sulfonimide with HMPT itself, indicated that the pathway followed in these displacement reactions was not quite as simple as that depicted in Figure 3.

To determine to what extent N-n-hexyl-N,N-di(trifluoromethane)-sulfonimide reacts with HMPT to produce the phosphonium salt, VII, a solution of the sulfonimide in HMPT was studied by nmr from the time of mixing. Just after mixing, the nmr showed a triplet at 4.20δ, due to the methylene group adjacent to the sulfonimide group. After six hours,

the signal had shifted to about 4.3δ, and was no longer a clearly resolved triplet; eighteen hours after mixing, the signal appeared as a quartet at 4.35δ. No indication of the original sulfonimide was evident. It would seem then that either the reaction did not involve an equilibrium, or, if it did, that it lay on the side of the phosphonium salt.

Although ir and nmr spectra of the phosphonium salt supported the proposed structure, VII, additional structural proof was sought. Anselme et al. (121) and Schmidpeter and Brecht (122) have shown that the reaction of HMPT with dimethyl sulfate produces the tris(dimethylamino)methoxyphosphonium salt, VIII, which was subsequently isolated as the tetraphenylboron salt. Downie, Lee, and Matough (123) isolated the phosphonium salt IX as an intermediate in the reaction of n-pentanol

$[(CH_3)_2N]_3\overset{+}{P}OCH_3\ \bar{B}(Ph)_4$ VIII

$[(CH_3)_2N]_3\overset{+}{P}O(CH_2)_4CH_3\ \bar{P}F_6$ IX

with phosphorus trisdimethyl amide and carbon tetrachloride to produce the alkyl chloride. Since the N,N-di(trifluoromethane)sulfonimide salt of VII was an oil and VIII and IX were isolated as the crystalline tetraphenylboron and hexafluorophosphate salts respectively, attempts were made to isolate VII as one of these salts.

Solutions of VII in HMPT were prepared by mixing N-n-hexyl-N,N-di(trifluoromethane)sulfonimide with HMPT, and stirring the solutions at room temperature overnight to allow the phosphonium salt to form. These solutions were then mixed with aqueous solutions of potassium hexafluorophosphate or sodium tetraphenylboron. The

hexafluorophosphate salt of VII was an oil, but the tetraphenylboron salt was obtained as a crystalline white solid after recrystallization from methanol. The ir and nmr spectra of each salt supported the proposed structure of VII. Spin decoupling experiments were also performed on the tetraphenylboron salt: irradiation in the 1.63δ region caused the quartet at 4.23δ to collapse to a doublet with J = 6; irradiation at 4.23δ resulted in a simplification of the multiplet at 1.63δ. These results indicate a methylene coupled both to an adjacent methylene and through oxygen to phosphorus (124, 125). Finally, the results of the elemental microanalysis of the tetraphenylboron salt of VII were in good agreement with the calculated values.

To learn something of the scope of the hydrolysis of N-alkyl-N,N-di(trifluoromethane)sulfonimides, the hydrolysis of N-(2-phenethyl)-N,N-di(trifluoromethane)sulfonimide was carried out. A ten-fold excess of water was used, and the reaction was heated at 45° for five days. Work up of the reaction mixture gave a 31% yield of 2-phenethyl alcohol, and a product whose ir and nmr spectra suggested the tris-(dimethylamino)-2-phenethyloxyphosphonium salt, X. An authentic sample

$$[(CH_3)_2N]_3\overset{+}{P}O(CH_2)_2Ph\ \bar{N}(SO_2CF_3)_2$$

X

of X as the tetraphenylboron salt was prepared in a manner analogous to the preparation of VII as the tetraphenylboron salt.

The results of the hydrolysis and solvolysis experiments, then, seem to indicate that in the previous displacement reactions, HMPT solvent competes with nucleophile in attacking the sulfonimide. Since

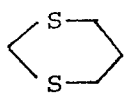
phosphonium salts of the type VII have been isolated from the hydrolysis and solvolysis reactions, it was proposed that the displacement reactions be repeated, adding nucleophile after first allowing the phosphonium salt to form.

The reaction of sodium cyanide with N-n-hexyl-N,N-di(trifluoromethane)sulfonimide was chosen as a test case. Glass (11) has reported that none of the alkyl cyanide was produced when this nucleophile and sulfonimide were mixed with HMPT at approximately the same time. As was observed above in the nmr study of N-n-hexyl-N,N-di(trifluoromethane)sulfonimide with HMPT, approximately eighteen hours were required for the conversion of the sulfonimide to the phosphonium salt, VII. In this modification, then, the sodium cyanide was not added to the sulfonimide-HMPT mixture until sufficient time had been allowed for the phosphonium salt to form. After the sodium cyanide had been added, the reaction was followed by nmr. No change was noted until nearly five hours after mixing, when the multiplet at 4.35δ due to the phosphonium salt was seen to diminish. No further change was noted until seventy-seven hours after mixing, when the signal had nearly disappeared. At this point, another equivalent of sodium cyanide was added. Twenty-eight hours after the second equivalent was added, a new signal appeared at 4.08δ as a broad singlet. Twenty-four hours after it appeared, the new signal increased in intensity, then remained unchanged. The reaction was worked up one week after the first equivalent of sodium cyanide was added. Analysis by glc, and ir and nmr spectra of isolated products, showed a 36% yield of n-hexyl cyanide; a 16% yield of N,N-di-n-hexyltrifluoromethanesulfonamide and a 6% yield of of VII

were also found. The reaction was repeated, mixing the sulfonimide with HMPT and allowing the phosphonium salt to form, then adding one equivalent of sodium cyanide and allowing the mixture to stir at room temperature for four days before working it up. In this reaction, the yield of n-hexyl cyanide was 58%. The yields of N,N-di-n-hexyltrifluoromethanesulfonamide and VII were 10% and 17%, respectively. To demonstrate the synthetic utility of the method, the reaction was again repeated, using approximately twice the scale used previously. Work up gave an 11% yield of VII, and glc yields of 72% for n-hexyl cyanide and 20% for N,N-di-n-hexyltrifluoromethanesulfonamide. Distillation of the reaction mixture using a Kugelrohr apparatus resulted in a 60% yield of n-hexyl cyanide.

Since these reactions clearly demonstrate a great improvement over the results obtained using the former procedures (11), other displacement reactions with N-n-hexyl-N,N-di(trifluoromethane)sulfonimide were carried out using this phosphonium salt procedure. The results of these reactions are given in Tables 12 and 13. Comparison of Table 13 with Table 11 indicates that the phosphonium salt procedure is only marginally better than the previous method for the sulfonimide hydrolysis. This result might be expected if attack by water on the sulfonimide was much slower than attack by HMPT solvent; in either case, then, the key step would be attack by water on the phosphonium salt. But comparison of Table 12 with both Table 10 and the results reported by Glass (11) shows a dramatic difference. Previous reactions gave 0% yields of alkylation products with sodium cyanide, malononitrile sodium salt, and sodium azide. Displacement reactions via the phosphonium

Table 12. Products of the Reactions of N-n-Hexyl-N,N-di(trifluoromethane)sulfonimide with Various Nucleophiles via the Phosphonium Salt in HMPT

Nucleophile	% Yield[a]		
	R-X[b]	$R_2NSO_2CF_3$[b,c]	Salt VII[d]
NaCN	72[e]	18	10
$NaCH(CO_2CH_2CH_3)_2$	87[f]	12	1
$NaCH(CN)_2$	15[f]	9	57
NaN_3	14	0[g]	26
$Li^+ -$ 	0[h]	7	46
PhCuLiBr	0[i]	0	0

[a]Based on quantitative glc by comparison with authentic samples.

[b]Identified by comparison of ir and nmr spectra and glc retention times of isolated products with authentic samples.

[c]Based on two moles of sulfonimide yielding one mole of sulfonamide.

[d]Identified by ir spectra.

[e]60% isolated yield.

[f]19% yield of di-n-hexylmalononitrile found, based on two moles of sulfonimide yielding one mole of product.

[g]2% yield of N-n-hexyltrifluoromethanesulfonamide found.

[h]11% yield of 2,2-di-n-hexyl-1,3-dithiane found, based on two moles of sulfonimide yielding one mole of product.

[i]Only identifiable product was benzoic acid.

Table 13. Products of the Reactions of N-n-Hexyl-N,N-di(trifluoromethane)sulfonimide with Water via the Phosphonium Salt in HMPT

moles Water / moles Imide	Temperature (°C)	Time (days)	% Yield[a]		
			$CH_3(CH_2)_5OH$[b]	$CH_3(CH_2)_5OSO_2CF_3$[b]	Salt VII[c]
5	20	4	9	5	75
5	20	18	13	--[d]	--[d]
5	45	5	43	--[d]	--[d]
10	45	7	47	0	--[d]

[a] Based on quantitative glc by comparison with authentic samples.

[b] Identified by comparison of ir and nmr spectra and glc retention times of isolated products with authentic samples.

[c] Identified by ir spectra.

[d] Yield not determined.

salt resulted in 60% (average), 34% (total products), and 14% yields, respectively. Similarly, using this procedure, the yield of alkylation product with diethyl sodiomalonate was increased from 57% to 87%; and although the reaction with phenyl copper (126) gave no alkylation products, the results of the reaction with 1,3-dithiane lithium salt were not entirely discouraging.

The improvement in the yields of carbon alkylation products using this phosphonium salt modification was probably the result of two factors. First, since the production of salt VII appears to be greatly favored over salt XI, nucleophilic attack at sulfur is nearly eliminated as a competing reaction. Second, although the N,N-di(trifluoromethane)sulfonimide leaving group is no longer present, alkoxyphosphonium salts have been shown to have utility as alkylating agents (127-133), and in some cases HMPT was generated as the leaving group (123, 134). Reactions carried out by the earlier procedure resulted in nucleophile competing with HMPT solvent for attack at the carbon and at the sulfur of the sulfonimide.

The presence of N-n-hexyltrifluoromethanesulfonamide or N,N-di-n-hexyltrifluoromethanesulfonamide in the product mixtures of the reactions reported in Tables 11 and 12 indicated attack at the sulfonimide sulfur. The fact that this occurred when only solvent was present indicates that HMPT itself attacks sulfonimide at both carbon and sulfur, but whether these processes are in equilibrium remained uncertain. Following the reaction of N-n-hexyl-N,N-di(trifluoromethane)sulfonimide with HMPT by nmr failed to show any of the sulfonamide, but this did not completely discount the possibility of an

equilibrium reaction. It was still quite possible that the products resulting from attack at sulfonimide sulfur were present in too small amounts to be observed under the experimental conditions.

In view of these results, the proposed reaction pathways resulting from equilibrium and non-equilibrium reactions of HMPT with sulfonimide are shown in Figures 4 and 5, respectively. It can readily be seen that the pathways are essentially the same, differing only in the mode of production of salts VII and XI. Each pathway explains the formation of all the observed products: N-alkyl sulfonamides result either from hydrolysis of unreacted salt XI, or from hydrolysis of the free sulfonamide anion; N,N-di-alkyl sulfonamides result either from attack of the free sulfonamide anium of salt VII, or, probably less likely, from the interaction of salts XI and VII; and normal carbon alkylation product results from attack by nucleophile on salt VII. In the case of the hydrolysis reactions, the trifluoromethanesulfonate ester would probably arise from attack of the alcohol on salt XI.

In an attempt to elucidate the reaction pathway followed in the phosphonium salt displacements, two types of experiments were carried out. If the reaction of sulfonimide with HMPT involved an equilibrium, then formation of salt VII should be prevented by effective trapping of the N-alkyl sulfonamide produced as salt XI. The first experiment, then, was an attempt to trap the sulfonamide anion using either methyl iodide or methyl trifluoromethanesulfonate as alkylating agents. In each case, the sulfonimide, alkylating agent, and HMPT were mixed together at one time, and the mixture stirred at room temperature for five days. Work up of the methyl iodide trapping experiment showed a

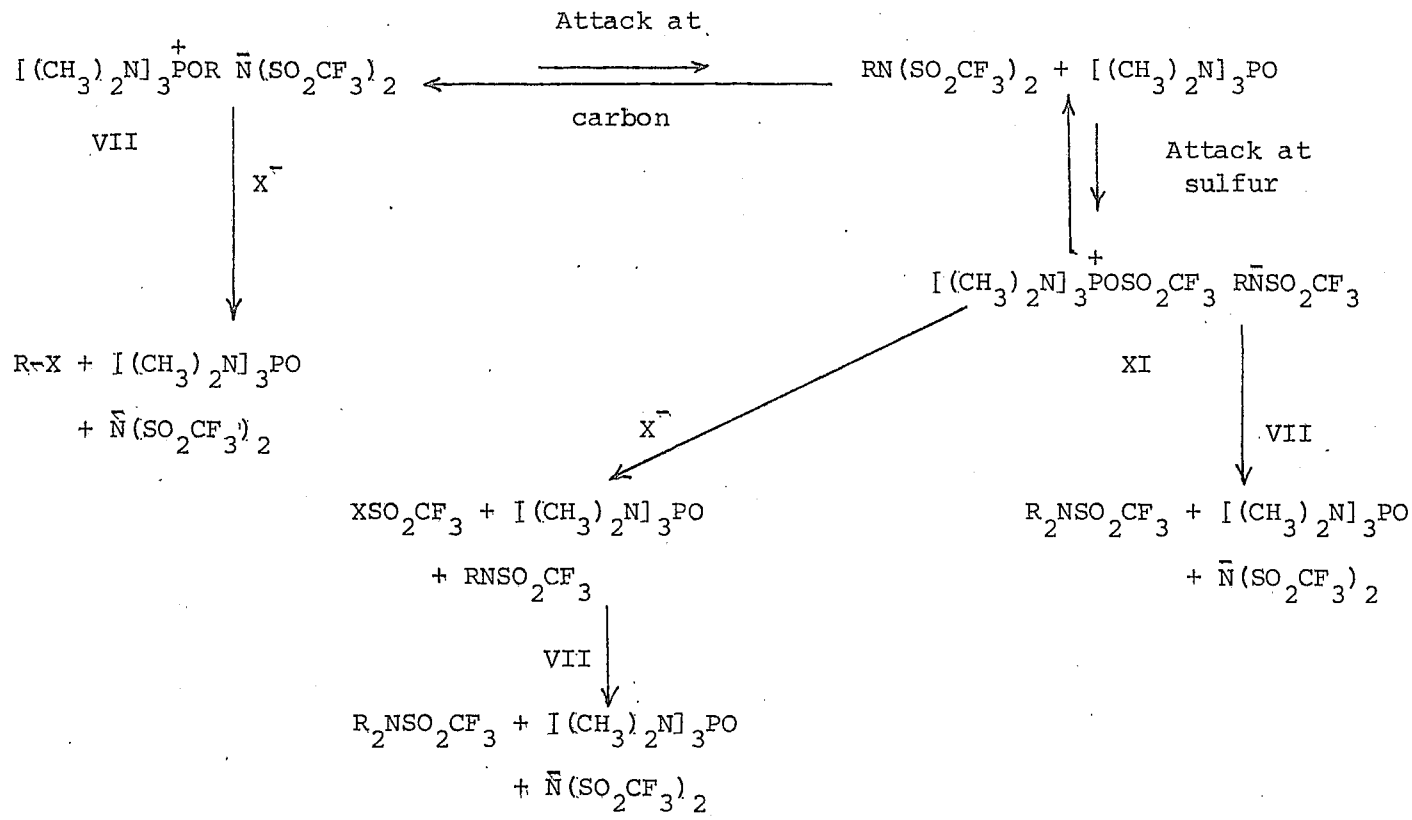


Figure 4. Displacement Reaction Mechanism via Phosphonium Salt VII: Equilibrium Between Solvent Attack at Sulfur and Carbon

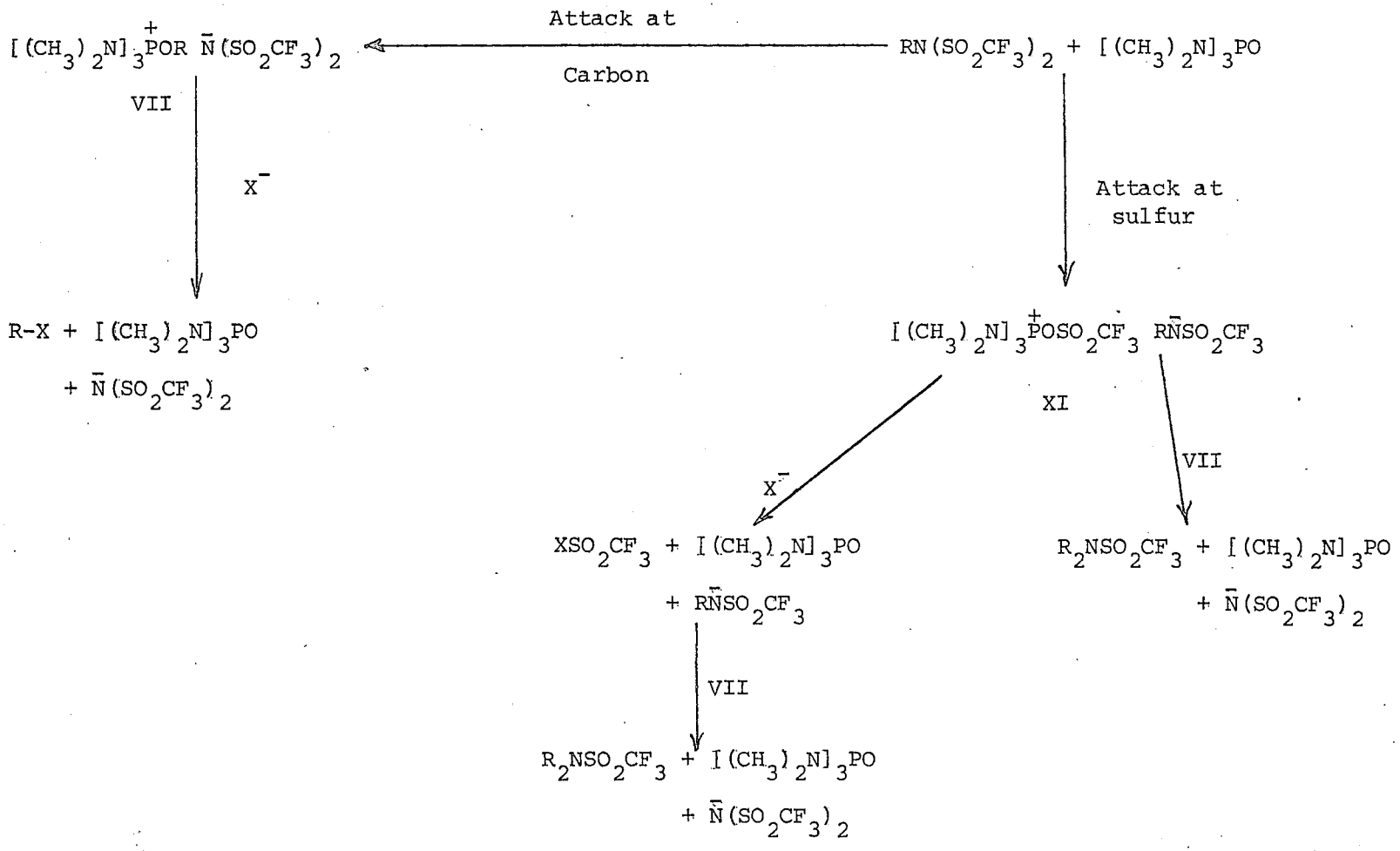


Figure 5. Displacement Reaction Mechanism via Phosphonium Salt VII: No Equilibrium Between Solvent Attack at Sulfur and Carbon

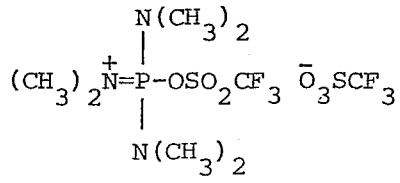
10% yield of n-hexyltrifluoromethanesulfonamide, a 10% yield of n-hexyltrifluoromethanesulfonate, a 33% yield of 1-iodohexane, and an 18% yield of phosphonium salt VII. The methyl trifluoromethanesulfonate reaction gave a gelatinous white precipitate, which ir showed to be tris(dimethylamino)methoxyphosphoniumtrifluoromethanesulfonate, resulting from reaction of HMPT with alkylating agent. Also found were a 20% yield of phosphonium salt VII, a 10% yield of n-hexyltrifluoromethanesulfonate, a 22% yield of N-n-hexyltrifluoromethanesulfonamide, and a 9% yield of unreacted sulfonimide.

The second experiment was an attempt to determine the reversibility of attack at sulfonimide sulfur. Due to the unavailability of salt XI, it was proposed to carry out the reaction using N-n-hexyltrifluoromethanesulfonamide sodium salt with the phosphonium salt XII.

$$[(CH_3)_2N]_3\overset{+}{P}OSO_2CF_3\ \bar{O}_3SCF_3$$

XII

The synthesis of salt XII was attempted by reaction of HMPT with trifluoromethanesulfonic acid anhydride under varying conditions. In each case, a white solid was obtained whose ir spectrum suggested the desired product, but whose nmr showed three signals rather than the expected two: 2.90, 3.08, and 3.17δ. The first and third signals appeared to constitute a doublet with J = 12 Hz, but the signal at 3.17δ appeared as a broad singlet. This nmr evidence would at first seem to question whether salt XII was formed. However, it may simply indicate the resonance form of salt XII, or salt XIII. In this case, the coupling of the methyl ammonium groups to phosphorus may be



XIII

broadened by interaction with the nitrogen quadrupole (135, 136), resulting in a broad singlet. This type of interaction with a bis(dimethylamino)alkoxyphosphonium salt has been reported (137).

Whatever the nature of the product obtained by reaction of HMPT with trifluoromethanesulfonic acid anhydride, this material was used in the reaction with N-n-hexyltrifluoromethanesulfonamide sodium salt in HMPT. Attempts were made to follow the course of the reaction by nmr, but, as the mixture was heterogeneous, signals were too broadened to make this possible. Six and one-half hours after mixing the reactants, one-fourth of the mixture was quenched by mixing with water. Work up showed only 78% of the original sulfonamide was present, but no sulfonimide was found. Twenty-one hours after mixing, another one-fourth of the reaction mixture was poured into an aqueous sodium tetraphenylboron solution. A precipitate immediately formed which was shown to be salt VII as the tetraphenylboron salt. Finally, forty-seven hours after mixing, the remainder of the reaction mixture was worked up. Half of this remaining portion was poured into water and analyzed for sulfonamide: an amount corresponding to only 63% of the initial amount was found. The other half of the mixture was poured into aqueous sodium tetraphenylboron solution: a precipitate which was shown to be salt VII as the tetraphenylboron salt was again obtained.

The results of these experiments fell short of fully differentiating between the pathways depicted in Figures 4 and 5. The results of the trapping experiments were inconclusive. Whether they represent poor nucleophilicity on the part of the free sulfonamide anion, or an inability of the alkylating agents used to alkylate the anion as complexed in salt XI remains open to question. Earlier observations that sulfonamide anions are alkylated with difficulty, together with the observed alkylation of HMPT by methyl trifluoromethanesulfonate further complicate these results.

The reaction between the N-n-hexyltrifluoromethanesulfonamide anion and the (presumably) trifluoromethanesulfonylated HMPT gave more tantalizing results. In this case, N-n-hexyl-N,N-di(trifluoromethane)-sulfonimide was indeed produced in the reaction, formed the phosphonium salt VII by reaction with HMPT, and was isolated as the tetraphenylboron salt of VII. This result would confirm the premise that attack by HMPT at sulfonimide sulfur was reversible, were it not for the doubt as to the actual identity of the phosphonium salt used in the reaction. This reduces the significance of the result to a statement that the N-n-hexyltrifluoromethanesulfonamide anion was converted to N-n-hexyl-N,N-di(trifluoromethane)sulfonimide by some trifluoromethanesulfonylating agent.

To complicate matters still further, one final observation can be made. Examination of Tables 9 and 10 shows that heteroatom nucleophiles have a greater affinity for attack at sulfonimide sulfur than do the carbon nucleophiles (with the exception of iodide). The case of these earlier reactions run without the phosphonium salt modification

can be rationalized by assuming that the heteroatom nucleophiles react generally faster with the sulfonimide than does HMPT. Carbon nucleophiles, on the other hand, react more slowly, allowing phosphonium salt to form, and thus increasing the yield of carbon alkylation products. But the reason for the preference of attack at carbon with HMPT seems strange in this light. It may be that HMPT attack at sulfonimide sulfur is the kinetically favorable process, but is reversible, giving way to thermodynamically favored attack at carbon. This is what the reaction of sulfonamide anion with sulfonylated HMPT hinted. But, in fact, the actual pathway followed in these displacement reactions remains to be elucidated.

SUMMARY

The role of sulfonimides as useful synthetic intermediates is gaining recognition. The synthesis of N-alkyl-N,N-di(trifluoromethane)-sulfonimides,(7, 10-12), N-aklyl-N,N-di(arene)sulfonimides (73-75, 91, 92, 96-98), and N-aklyl-N-trifluoromethanesulfonyl-N-arenesulfonimides (61) have been reported in the literature. Similar methods were used herein to prepare a variety of N-alkyl-N,N-di(trifluoromethane)-sulfonimides, although the yields obtained were not optimized. The preparation of N-alkyl-N,N-di(trichloromethane)sulfonimides was attempted, but proved unsuccessful; however, N-alkyltrichloromethane-sulfonamides, N-alkyl-N-(trichloromethanesulfenyl)trichloromethane-sulfonamides, and N-alkyl-N-(trichloromethanesulfenyl)trifluoro-methanesulfonamides--all previously unreported classes of compounds--were successfully prepared. The use of these procedures also led to the successful preparation of N-alkyl-N-(benzenesulfenyl)benzene-sulfonamides. Oxidation of these intermediates constituted a facile preparation of sulfonimides in which the alkyl carbon bearing the nitrogen was secondary, but isolation of sulfonimides in which the alkyl carbon was tertiary was not possible.

Nucleophilic displacements on sulfonimides using carbon nucleophiles, and resulting in the formation of new carbon-carbon bonds, are attractive synthetically because of the ready availability of a wide variety of amines. Reports of displacements with carbon nucleophiles on N-alkyl-N,N-di(arene)sulfonimides (4, 9) and

N-alkyl-N,N-di(trifluoromethane)sulfonimides (11) gave only poor results in the former case, and moderate results in the latter.

The study of nucleophilic displacements on N-aklyl-N,N-di(trifluoromethane)sulfonimides was continued in this work, with particular interest in carbon nucleophile reactions. The results of the displacement reactions of carbon and heteroatom nucleophiles were disappointing overall (see Tables 9, 10, and 11), resulting in only low to moderate yields of carbon alkylation products. The hydrolyses of these sulfonimides to the corresponding alcohols, however, were carried out under much milder conditions than those employed by DeChristopher et al. (10), although the yields obtained here were somewhat lower.

The most interesting result of this study was the unexpected discovery that the HMPT solvent employed readily reacted with the N-alkyl-N,N-di(trifluoromethane)sulfonimides to produce phosphonium salts of the type VII. Phosphonium salts of this type are known (121-123, 125, 133, 134, 137), but this represents a novel approach to their synthesis.

Having demonstrated the presence of these phosphonium salts in the displacement reaction mixtures, their role in the reactions was further investigated. It was shown that by first allowing the HMPT solvent and the sulfonimide to react to form the phosphonium salt, and then adding the nucleophile, the yields of carbon alkylation products are greatly increased (see Table 12).

The participation of the phosphonium salts in the displacement reactions indicated that the reaction pathway proposed in Figure 3 was

incorrect. However, further investigation into the reaction failed to determine whether either of the pathways proposed in Figures 4 and 5 were correct, or whether an entirely different pathway involving the phosphonium salt was being followed.

Although the actual reaction pathway followed in these reactions was not fully determined, the utility of these phosphonium salts as intermediates in these displacement reactions suggested some interesting synthetic applications.

Conversion of an alkyl amine to an N-alkyl-N,N-di(trifluoromethane)sulfonimide sufficiently activated the nitrogen to permit displacement at the carbon bearing the nitrogen by the HMPT solvent. But the preparation of these sulfonimides involves the use of expensive reagents and a multistep route. In order to make these phosphonium salts more attractive as synthetic intermediates, a more direct route to their preparation from alkyl amines was sought.

Using n-hexyl amine as a test case, attempts were made to prepare the N-nitrosoamine using either nitrosyl hexafluorophosphate or isoamyl nitrite, and then converting this to the phosphonium salt by reaction with HMPT. Although temperatures, solvents, and methods of addition were varied, no phosphonium salt was obtained using nitrosyl hexafluorophosphate. In each case, the reagent appeared to react with HMPT rather than with the amine. No reaction was observed to take place using isoamyl nitrite.

Although these experiments were unsuccessful, the potential of this method is great enough to warrant further investigation. The use of nitrosyl chloride or dinitrogen tetroxide, for example, may meet

with greater success than nitrosyl hexafluorophosphate in preparing N-n-hexyl-N-nitrosoamine, and from it the phosphonium salt. It would also seem worthwhile to attempt to apply the methods of Moss and co-workers (138-142), for the reactions of alkyl diazotates--particularly the solvolysis (143)--to the system studied here.

The successful preparation of phosphonium salts from amines in which the nitrogen is attached to a secondary carbon would greatly extend the synthetic utility of these intermediates. Unfortunately, attempts to prepare N-alkyl-N,N-di(trifluoromethane)sulfonimides from these types of amines have been unsuccessful, eliminating these compounds as a possible origin of the phosphonium salts. Preparation of the phosphonium salts via the N-nitrosoamines or alkyl diazotates may prove successful, however. Alternatively, N-alkyl-N,N-di(arene)-sulfonimides, prepared either by the method developed in this work, or by the method of DeChristopher et al. (8), may be considered as a starting point.

EXPERIMENTAL

Proton nuclear magnetic resonance (nmr) spectra were recorded on a 60 MHz Varian Associates T-60 nmr spectrometer. Chemical shifts are given in δ(ppm) relative to tetramethylsilane ($(CH_3)_4Si$, δ=0) internal standard. Peak multiplicity is indicated as s=singlet, d=doublet, t=triplet, and m=multiplet. Coupling constants (J) are given in hertz, and relative integrated area is given in number of hydrogens. Infrared (ir) spectra were recorded on either a Perkin Elmer Model 337, or a Perkin Elmer Model 137 spectrophotometer, calibrated at the 1028 cm^{-1} and/or the 1601 cm^{-1} lines of polystyrene. Absorptions are reported in wavenumbers ($\pm$ 5 cm^{-1}). Mass spectra (ms) were recorded on a Hitachi/Perkin Elmer RMU-6E mass spectrometer. Ultraviolet (uv) spectra were recorded on a Cary 14 Vis/UV/IR spectrophotometer. Melting points were determined using either a Thomas-Hoover melting point apparatus, or a Thermolyne microstage melting point apparatus. In the former case, samples were contained in glass capillary tubes, and in the latter case, they were placed on glass cover slips.

Elemental microanalyses were performed by Spang Microanalytical Laboratory, P.O. Box 1107, Ann Arbor, Michigan 48106. Deuterium analysis using the falling drop method was performed by Josef Nemeth, 303 W. Washington Street, Urbana, Illinois 61801.

Gas-liquid chromatography (glc) was carried out on a Varian Associates Series 1700 gas chromatograph with thermal conductivity

detector, and a Varian Associates Model A-25 strip chart recorder equipped with a disc integrator. Separations were effected using one of the following liquid phases: 10% SE-30, 10% Carbowax 20M, 10% Ucon 50LB 550X, 10% TCEP, 5% SE-30, 5% QF-1, and 5% DEGS. All were supported on 80/100 mesh Chromosorb W, which was acid washed and DMCS treated, and were made into 5' x 1/4" columns.

Quantitative glc product analyses were carried out as follows: A response factor was first calculated by diluting a weighed amount of an authentic sample of the compound to a known volume. A specific volume of this solution was then injected into the chromatograph by means of a Hamilton syringe equipped with a Chaney adapter. The integration of the resulting peak was divided by the total weight of the sample used to prepare the solution, yielding a response factor expressed in grams per unit of integration. The actual identity of the compound under investigation was determined by collecting a sample by preparative glc, then comparing its ir, nmr, and glc retention time with an authentic sample of the compound.

Carbon tetrachloride (CCl_4), chloroform ($CHCl_3$), dichloromethane (CH_2Cl_2), and acetonitrile (CH_3CN) were distilled from phosphorus pentoxide; benzene, toluene, 1,4-dioxane, and diethyl ether (ether) were distilled from sodium; amines, N,N-dimethylformamide (DMF), and dimethylsulfoxide (DMSO) were distilled from calcium hydride; tetrahydrofuran (THF) was first distilled from sodium, then from lithium aluminum hydride; and hexamethylphosphoric triamide (HMPT) was distilled from sodium under vacuum.

Column chromatography was carried out on Silica gel Woelm (0.063-0.2 mm, ICN Pharmaceuticals, Inc.). Columns were prepared by first making a slurry of the silica gel in the solvent to be used for elution, then pouring the slurry into a standing column of the same solvent in the chromatography column.

Thin-layer chromatography (TLC) was carried out on Silica gel HF-254 (for TLC Acc. to Stahl, Type 60, EM Laboratories, Inc.). Plates were prepared by dipping 1" x 3" microscope slides into a slurry of the silica gel in either chloroform or dichloromethane.

Preparation of Trifluoromethanesulfonic Acid Anhydride

This compound was prepared by the method of Gramstad and Haszeldine (144).

Preparation of N-Alkyl- and N,N-Dialkyltrichloromethanesulfenamides

These compounds were all prepared using the same procedure, which is illustrated in the specific example below.

N-n-Hexylamine (1.02g, 10.0mmol) was dissolved in 50ml of cyclohexane, and the solution was cooled in ice. A solution of 0.93g (5.0mmol) of trichloromethanesulfenyl chloride in 25ml of cyclohexane was added over 3/4 hr. After 15 hr at room temperature, the mixture was filtered free of the amine salt, the salt was washed with cyclohexane, and the washings and filtrate were combined. Removal of solvent and vacuum distillation gave 1.10g of N-n-hexyltrichloromethanesulfenamide with bp 88°/0.5mm.

Preparation of Sulfonamides

Ten different methods were used in preparing the various types of sulfonamides. Each method is illustrated below with a specific example.

Procedure A

To a solution of benzylamine (7.60g, 71.0mmol) in 50ml of ether cooled in ice were added over 1 hr 10.00g (35.5mmol) of trifluoromethanesulfonic acid anhydride. After 15 hr at room temperature, the mixture was filtered free of the amine salt, and the salt was washed with ether. The filtrate and washings were washed with 20ml of water, 20ml of 3N hydrochloric acid, 20ml of water, and 20ml of brine, and were dried over anhydrous magnesium sulfate. The solvent was removed to yield 6.14g of yellow oil, which solidified. The product was recrystallized from hexane to give 5.99g of N-benzyltrifluoromethanesulfonamide (71% yield) with mp 41.5-42.5°.

Procedure B

N-Phenylbenzylamine (6.52g, 35.6mmol) was dissolved in 40ml of cyclohexane, and the solution was cooled in ice. Trifluoromethanesulfonic acid anhydride (4.99g, 17.7mmol) was added over 1 hr, and the mixture was allowed to come to room temperature. After 4 hr, the mixture was filtered free of the amine salt, the salt was washed with cyclohexane, and the washings and filtrate were combined. Removal of the solvent gave 5.91g (96% yield) of N-phenyl-N-benzyltrifluoromethanesulfonamide as a white solid with mp 77-78°. Product was used without further purification.

Procedure C

Sodium hydride (0.09g, 57% oil dispersion, 2.02mmol) was washed with ether then suspended in 1ml of HMPT. While cooling in ice, a solution of N-(2-phenethyl)trifluoromethanesulfonamide (0.50g, 1.97mmol) in 1/2ml of HMPT was added over 3/4 hr. The mixture was further stirred for 1/2 hr, then a solution of 2-phenethyl chloride (0.28g, 1.97mmol) in 1/2ml of HMPT was added over 1/2 hr. After stirring at room temperature for 9 days, the mixture was poured into 75ml of water and extracted with 3 x 10ml of ether. The combined extracts were washed with 3 x 10ml of water and 3 x 10ml of brine, and were dried over anhydrous magnesium sulfate. The solvent was removed to give 0.45g of pale yellow liquid, which was a mixture of unreacted starting sulfonamide, unreacted chloride, and product. Quantitative and preparative glc on 5% QF-1 indicated a 31% yield of N,N-di-(2-phenethyl)-trifluoromethanesulfonamide.

Procedure D

The method is the same as C above, but the alkyl iodide is used in place of the chloride. In this manner, N,N-di-iso-butyltrifluoro-methanesulfonamide was prepared in 15% yield from N-iso-butyltrifluoro-methanesulfonamide and iso-butyl iodide.

Procedure E

Sodium hydride (0.17g, 57% oil dispersion, 4.07mmol) was washed with ether, and suspended in 2ml of toluene. While cooling the suspension in ice, a solution of 0.80g (3.31mmol) of N-(4-fluorophenyl)-trifluoromethanesulfonamide in 1ml of toluene was added over 1/4 hr.

The mixture was refluxed for 2 days, then poured into 80ml of water, and extracted with 3 x 15ml of ether. The combined extracts were washed with 2 x 20ml of water and 2 x 15ml of brine, and were dried over anhydrous magnesium sulfate. Removal of solvent gave 0.58g of brown oil. The pure N-(4-fluorophenyl)-N-benzyltrifluoromethanesulfonamide was obtained in 32.7% yield by column chromatography on a 1 x 35cm silica gel column, containing 32g of silica gel, and using CCl_4-$CHCl_3$ (3.5:0.5) as eluting solvent.

Procedure F

Using a procedure similar to that of von Braun (112-114), sodium hydride (0.22g, 57% oil dispersion, 5.2mmol) was washed with ether, then suspended in 10ml of ether. While cooling the suspension in ice, a solution of 1.17g (5.0mmol) of N-n-hexyltrifluoromethanesulfonamide in 2ml of ether was added over 1 hr. After an additional 1/2 hr, a solution of 0.58g (5.5mmol) of cyanogen bromide in 2ml of ether was added over 1/2 hr. The mixture was stirred at room temperature for 15 hr, then was poured into 5ml of water. The layers were separated, and the aqueous layer was extracted with 2 x 5ml of ether. The combined extracts were washed with 3 x 5ml of water and 1 x 5ml of brine, and were dried over anhydrous magnesium sulfate. Removal of solvent gave 1.15g of colorless oil. The product was purified by dissolving it in 20ml of ether, then washing with 1 x 5ml of 10% sodium hydroxide solution, followed by 3 x 5ml of water and 1 x 10ml of brine. The ether layer was dried over anhydrous magnesium

sulfate; removal of solvent gave 0.74g of N-cyano-N-n-hexyltrifluoromethanesulfonamide as a colorless oil (57% purified yield, bp 69-70°/2mm).

Procedure G

The method of DeChristopher et al. (8) was used to prepare N-cyclohexylbenzenesulfonamide. The product was recrystallized from 50% ethanol to give a 78% yield of white crystals with mp 89.5-90.0°.

Procedure H

To 1.78g (10.05mmol) of benzenesulfonyl chloride in 30ml of benzene were added over 5 min 1.54g (21.0mmol) of t-butylamine in 10ml of benzene. The mixture was refluxed for 40 hr, then mixed with 50ml of $CHCl_3$. The mixture was extracted with 3 x 10ml of 10% hydrochloric acid, 1 x 20ml of saturated sodium bicarbonate solution, and 1 x 20ml of brine, and was dried over anhydrous magnesium sulfate. Removal of solvent gave 1.87g slightly yellow solid, which was recrystlalized from ligroin to yield 1.73g of N-t-butylbenzenesulfonamide as white crystals with mp 88.0-88.5°. Yield 81%.

Procedure I

N-n-Hexyltrichloromethanesulfenamide (3.46g, 13.5mmol) was dissolved in 100ml of hexane, and 6.10g (85%, 30mmol) of m-chloroperoxybenzoic acid were added in one portion. The mixture was refluxed for 12hr, then cooled and filtered free of m-chlorobenzoic acid. The filtrate, after rotary evaporation, yielded 4.09g of a solid-liquid mixture. Column chromatography on a 2 x 35cm column

containing 32g of silica gel and using benzene as eluting solvent gave N-n-hexyltrichloromethanesulfonamide as a white solid with mp 36.5-38.0°. Yield 82%.

Procedure J

To 0.15ml (6.0mmol) of 90% hydrogen peroxide suspended in 3ml of CH_2Cl_2 were added in one portion 1.02ml (7.0mmol) of trifluoroacetic anhydride. The mixture was stirred at room temperature for 15 min until homogeneous, then 0.48g (1.93mmol) of N-n-hexyltrichloromethanesulfenamide in 3ml of CH_2Cl_2 were added over 10 min. After refluxing for 1 hr, the mixture was poured into 25ml of saturated sodium bicarbonate solution, the layers were separated, and the aqueous layer was washed with 10ml of CH_2Cl_2. The combined organic layers were washed with 2 x 10ml of saturated sodium bicarbonate solution, 2 x 10ml of water, and 1 x 20ml of brine, and were dried over anhydrous magnesium sulfate. Removal of solvent gave 0.41g of yellow solid. Column chromatography as in Procedure I above gave N-n-hexyltrichloromethanesulfonamide as a white solid with mp 35-37°. Yield was 66%.

Preparation of N-Sulfenyl-N-sulfonamides

These types of compounds were prepared by four different methods, each of which is illustrated below with a specific example.

Procedure A

N-Cyclohexylbenzenesulfonamide (0.24g, 1.02mmol) was dissolved in 5ml of THF, and the solution was cooled to -78° in a dry ice-acetone bath. N-Butyl lithium (0.63ml, 1.6M, 1.0mmol) in hexane was added over

1/2 hr, and the solution was allowed to warm to 0°. Benzenesulfonyl chloride (0.15g, 1.05mmol) in 1ml of THF was added over 3/4 hr. After 15 hr at room temperature, the mixture was poured into 100ml of water, and extracted with 3 x 20ml of ether. The extracts were washed with 2 x 15ml of water and 2 x 15ml of brine, and were dried over anhydrous magnesium sulfate. Removal of solvent gave 0.39g of yellow oil. Column chromatography on a 1 x 35cm column containing 32g of silica gel with $CHCl_3$ as eluting solvent gave 0.29g of N-cyclohexyl-N-(benzenesulfenyl)benzenesulfonamide as white crystals with mp 118.5-119.0°. Yield was 82%.

Procedure B

Sodium hydride (0.06g, 57% oil dispersion, 1.30mmol) was washed with ether, then suspended in 5ml of ether. While cooling in ice, 0.23g (0.98mmol) of N-n-hexyltrifluoromethanesulfonamide in 2ml of ether were added over 3/4 hr. After stirring for an additional 1/4 hr, a solution of 0.21g (0.98mmol) of trichloromethanesulfenyl chloride in 2ml of ether was added over 1/2 hr. After 15 hr at room temperature, the mixture was poured into 10ml of water, and the layers were separated. The aqueous layer was extracted with 10ml of ether, and the extracts were combined with the organic layer. The ether solution was washed with 2 x 5ml of water and 1 x 5ml of brine, and was dried over anhydrous magnesium sulfate. Removal of solvent gave 0.30g of yellow oil, which showed one spot on TLC with benzene solvent. Yield of N-n-hexyl-N-(trichloromethanesulfenyl)trifluoromethanesulfonamide was 81%.

Procedure C

Lithium hydride (0.01g, 1.65mmol) was suspended in 2ml of ether, and a solution of 0.33g (1.43mmol) of N-n-hexyltrifluoromethanesulfonamide in 2ml of ether was added over 3/4 hr. The mixture was further stirred at room temperature for 1 hr, then the solution was cooled in ice, and a solution of trichloromethanesulfenyl chloride (0.26g, 1.40mmol) in 2ml of ether was added over 1 hr. After 3 hr, the mixture was poured into 25ml of water, and the layers were separated. The aqueous layer was washed once with 10ml of ether, and the organic layers were combined, washed with 2 x 5ml of water and 2 x 5ml of brine, and were dried over anhydrous magnesium sulfate. Removal of solvent gave 0.43g of N-n-hexyl-N-(trichloromethanesulfenyl)-trifluoromethanesulfonamide. Yield was 76%.

Procedure D

Lithium hydride (0.02g, 2.68mmol) was suspended in 6ml of CH_3CN, and a solution of 0.71g (2.50mmol) of N-n-hexyltrichloromethanesulfonamide in 5ml of CH_3CN was added over 1/2 hr. The mixture was further stirred at room temperature for 1 hr, then it was cooled in ice. Trichloromethanesulfenyl chloride (0.47g, 2.50mmol) in 5ml of CH_3CN was added over 3/4 hr. After 4 hr at room temperature, the mixture was poured into 200ml of water, and extracted with 3 x 20ml of ether. The combined extracts were washed with 2 x 25ml of water and 2 x 15ml of brine, and were dried over anhydrous magnesium sulfate. Removal of solvent gave 0.93g of N-n-hexyl-N-(trichloromethanesulfenyl)-trichloromethanesulfonamide as a yellow oil. Yield was 86%.

Preparation of Sulfonimides

The various types of sulfonimides were prepared by three methods. Examples of each method are illustrated below.

Procedure A

Sodium hydride (0.17g, 57% oil dispersion, 3.9mmol) was washed with ether, then suspended in 1ml of ether. The suspension was cooled in ice, and a solution of 0.80g (3.4mmol) of N-trifluoromethanesulfonylglycine ethyl ester in 3ml of ether was added over 1/2 hr. After stirring and cooling for a further 1/2 hr, trifluoromethanesulfonic acid anhydride (0.97g, 3.45mmol) in 1ml of ether was added over 1/2 hr. After 2-1/2 hr, the mixture was poured into 20ml of 3N hydrochloric acid, and was extracted with 3 x 10ml of ether. The combined extracts were washed with 2 x 10ml of water, 2 x 10ml of 5% aqueous sodium hydroxide solution, 1 x 10ml of water, and 1 x 10ml of brine, and were dried over anhydrous magnesium sulfate. Removal of solvent gave 0.53g of yellow oil, which was bulb to bulb distilled at 0.35mm at an air bath temperature of 78° to yield 0.42g (34% yield) of N,N-di(trifluoromethanesulfonyl)glycine ethyl ester.

Procedure B

Sodium hydride (0.37g, 57% oil dispersion, 8.68mmol) was washed with ether, then suspended in 10ml of CH_3CN. The suspension was cooled in ice, and a solution of 2.0g (7.90mmol) of N-(2-phenethyl)trifluoromethanesulfonamide in 2ml of CH_3CN was added over 1 hr. After stirring for an additional 1 hr, a solution of 2.2g (7.90mmol) of trifluoromethanesulfonic acid anhydride in 0.5ml of CH_3CN was added over 1 hr.

After stirring with cooling for 1 hr, the mixture was poured into 75ml of water, and was extracted with 3 x 20ml of ether. The extracts were washed with 2 x 15ml of water and 2 x 10ml of brine, and were dried over anhydrous magnesium sulfate. Removal of solvent gave 2.42g of two brown liquid phases. Column chromatography on a 1 x 35cm column containing 32g of silica gel with benzene as eluting solvent gave 1.85g of N-(2-phenethyl)-N,N-di(trifluoromethane)sulfonimide (bp 95-96°/ 0.25mm, yield 61%).

Procedure C

N-Cyclohexyl-N-(benzenesulfenyl)benzenesulfonamide (0.21g, 0.62mmol) was dissolved in 5ml of hexane, and m-chloroperoxybenzoic acid (0.28g, 1.49mmol, 85%) was added in one portion. The solution was refluxed for 5 hr, then cooled and filtered free of the solid which separated. The precipitate was washed with hexane, and the washings and filtrate were combined. Removal of solvent gave 0.08g of white crystals. Examination of this product, and also of the precipitate, on TLC with $CHCl_3$ as solvent indicated that the greater portion of the product was present in the precipitate. Column chromatography on a 1 x 35cm column containing 32g of silica gel with $CHCl_3$ as solvent gave 0.15g (65% yield) of N-cyclohexyl-N,N-di(benzene)sulfonimide as white crystals with mp sub. > 150°. Ir and nmr spectra compare peak for peak with an authentic sample provided by Baumgarten (145).

Attempted Preparation of N-n-Hexyl-N,N-di-(trichloromethane)sulfenimide

Attempts were made to prepare this compound from n-hexylamine and from N-n-hexyltrichloromethanesulfenamide. The attempts are outlined below.

From n-Hexylamine

Procedure A. In ether, one equivalent of n-hexylamine was added to two equivalents of sodium hydride (as a 57% oil dispersion). Two equivalents of trichloromethanesulfenyl chloride in ether were added, and the mixture allowed to react while cooling in ice for 1 hr. Work up of the mixture gave approximately a 1:1 mixture of N-n-hexyltrichloromethanesulfenamide and N-n-hexyl-N,N-di(trichloromethane)sulfenimide.

Procedure B. A solution of one equivalent of n-hexylamine and two equivalents of triethylamine in CH_2Cl_2 was cooled in an ice bath, and a solution of two equivalents of trichloromethanesulfenyl chloride in CH_2Cl_2 was added. After stirring at room temperature for 2 days, the mixture was worked up to yield N-n-hexyltrichloromethanesulfenamide as the only identifiable product.

From N-n-Hexyltrichloromethanesulfenamide

Procedure A. One equivalent of N-n-hexyltrichloromethanesulfenamide in ether was added to one equivalent of a 57% oil dispersion of sodium hydride in ether. To this was added a solution of one equivalent of trichloromethanesulfenyl chloride in ether. After 2 days

at room temperature, the mixture was worked up to give unreacted start starting sulfenamide as the only identifiable product.

Procedure B. Using the procedure of Pan and Fletcher (61), one equivalent of N-n-hexyltrichloromethanesulfenamide in benzene was added to one equivalent of thallous ethoxide in benzene. A yellowish precipitate formed, but the mixture was stirred at room temperature for 15 hr. The mixture was filtered with difficulty, and the solid was washed with benzene. After drying under vacuum, the solid had mp > 250°, and ir and nmr suggested thallous chloride, rather than the thallium (I) salt of the sulfenamide.

Attempted Preparation of N-n-Hexyl-N,N-di-(trichloromethane)sulfonimide

The unsuccessful syntheses of this compound were attempted from two different starting points: (a) from N-n-Hexyl-N,N-di(trichloromethane)sulfenimide, and (b) from N-n-Hexyl-N-(trichloromethanesulfenyl)trichloromethanesulfonamide. A summary of these attempts is given below.

From N-n-Hexyl-N,N-di(trichloromethane)-sulfenimide

Procedure A. N-n-Hexyl-N,N-di(trichloromethane)sulfenimide, prepared above as a mixture with the sulfenamide, was mixed with two equivalents of Jones reagent (146) in acetone. After stirring at room temperature for 20 hr, the mixture was worked up to give only a trace of material, which did not appear by ir to be the sulfonimide.

Procedure B. One equivalent of the sulfenimide mixture used above was mixed with two equivalents of potassium permanganate in 50% aqueous acetic acid solution. After stirring at room temperature for 31 hr, during which time the precipitated manganese dioxide had dissolved, the solution was worked up to give a colorless liquid which ir showed to contain a carboxylic acid group. No sulfonimide was found.

Procedure C. One equivalent of the sulfenimide mixture used above was mixed with ten equivalents of an acetone solution of 30% hydrogen peroxide. The mixture was stirred at room temperature for 15 hr. After about 1 hr, a white precipitate began to separate. The mixture was poured into water, which caused the solid to dissolve. Work up gave a white solid. Although ir suggested the possibility of starting material being present, nmr showed only a singlet at 1.46δ. No sulfonimide was noted.

Procedure D. An acetone solution of the sulfenimide mixture used above, containing about 0.1mmol of the sulfenimide, was mixed with 0.5ml of commercial bleach. After stirring at room temperature for 15hr, the mixture was worked up to give a very small amount of colorless oil, which ir indicated to be mainly starting material.

From N-n-Hexyl-N-(trichloromethanesulfenyl)-trichloromethanesulfonamide

Procedure A. One equivalent of N-n-hexyl-N-(trichloromethanesulfenyl)trichloromethanesulfonamide was mixed with 2.1

equivalents of m-chloroperoxybenzoic acid in hexane. The mixture was refluxed for 48 hr, then worked up. Column chromatography on silica gel with CCl_4-$CHCl_3$ (3.5:0.5) as eluting solvent gave a mixture of N-n-hexyl-N-(trichloromethanesulfenyl)trichloromethanesulfonamide, and N-n-hexyl-trichloromethanesulfonamide.

Procedure B. The procedure here was the same as above except that the reaction mixture was refluxed for 4 days. Work up was the same and led to the same product mixture.

Procedure C. A solution of peroxytrifluoroacetic acid in CH_2Cl_2, prepared from trifluoroacetic anhydride and 90% hydrogen peroxide by the method of Emmons (58), was mixed with one equivalent of anhydrous sodium carbonate. One-half equivalent of N-n-hexyl-N-(trichloromethanesulfenyl)trichloromethanesulfonamide in CH_2Cl_2 was added, and the solution was stirred at room temperature for 23 hr. The mixture was worked up, then column chromatography on silica gel with CCl_4-$CHCl_3$ (3.5:0.5) as eluting solvent gave unreacted starting material.

Procedure D. This procedure is the same as above except that the mixture was stirred at room temperature for 36 hr. Work up and column chromatography gave the same result.

Procedure E. This procedure is similar to above, with the modification of Emmons and Pagano (62): CH_3CN was used as the solvent, and disodium hydrogen phosphate was used as the buffer. The mixture was refluxed for 1 hr, then worked up. Ir and nmr spectra of the

product showed a mixture of N-n-hexyltrichloromethanesulfonamide and CH_3CN.

Procedure F. The procedure is the same as above except that no buffering agent was used. The mixture was stirred at room temperature for 20 hr, then worked up. Column chromatography on silica gel with benzene as eluting solvent gave a white crystalline solid with mp 70-72°. Ir (CCl_4 solution) showed absorptions at 2990, 2920, 1395, 1170-1160 (d), and 1045 cm^{-1}. Mass spectral analysis showed significant peaks at (m/e, M^+) 85 (43%), 117 (100%), 119 (96%), 121 (30%), 123 (3%), 328 (10%), 330 (10%), and 332 (4%), with no peaks > 3% of the base peak occurring between (m/e, M^+) 123 and 328. Although a complete structural assignment could not be made for this product, these data, together with the nmr, indicated a compound containing C_6H_{13}-, $-SO_2-$, and $-CCl_3$ groupings.

Procedure G. This procedure is the same as above except that the mixture was refluxed for 1 hr instead of being stirred at room temperature. Work up and column chromatography were carried out as above, and gave a product with identical mp and spectral characteristics.

Preparation of Ethyl Ethoxyacetate

This ester was prepared by the method of Henry (147).

Preparation of 3-n-Hexyl-2,4-pentanedione and 2,4-Pentanedione n-Hexyl Enol Ether

Sodium hydride (0.43g, 57% oil dispersion, 10.5mmol) was washed with ether, and suspended in 10ml of HMPT, and the slurry was cooled in ice. A solution of 2,4-pentanedione (1.01g, 10.0mmol) in 2ml of HMPT was added over 3/4 hr. After 15 min additional stirring, a solution of 1-iodohexane (2.11g, 9.9mmol) in 2ml of HMPT was added over 1/2 hr. After 3 days at room temperature, the mixture was poured into 200ml of water, and extracted with 3 x 20ml of ether. The combined extracts were washed with 2 x 25ml of water and 2 x 25ml of brine, and were dried over anhydrous magnesium sulfate. Removal of solvent gave 1.51g of yellow liquid. The mixture was vacuum distilled to give 0.63g of liquid with bp 72-75°/0.4mm, and 0.20g of liquid with bp 75°/0.4mm. Analytical glc showed both fractions to be mixtures with essentially the same composition. Preparative glc on 5% SE-30 was done to obtain pure samples of the C- and O-alkylated products.

Preparation of n-Hexyl Phenyl Sulfide

Sodium ethoxide (0.35g, 5.07mmol) was dissolved in 5ml of absolute ethanol, and a solution of thiophenol (0.51g, 4.56mmol) in 4ml of absolute ethanol was added over 20 min. The mixture was brought to reflux, and a solution of 1-bromohexane (0.74g, 4.50mmol) in 1ml of absolute ethanol was added over 5 min. The mixture was refluxed for 24 hr, then the excess ethanol was distilled off at atmospheric pressure. The residue was mixed with 20ml of water, and extracted with 2 x 10ml of ether. The extracts were washed with 10ml of water and 10ml of brine,

and were dried over anhydrous magnesium sulfate. Removal of solvent, followed by vacuum distillation of the residue, afforded 0.63g (72% yield) of n-hexyl phenyl sulfide as a colorless liquid, bp 80°/0.32mm.

Preparation of Barium Trichloromethanesulfonate

Barium hydroxide octahydrate (8.11g, 25.7mmol) and trichloromethanesulfonyl chloride (9.53g, 43.8mmol) were mixed with 60ml of water, and the mixture was stirred at room temperature for 18 hrs. Initially, the pH was 10, but had dropped to 7 by the end of the reaction. The mixture was filtered, and the solid washed with water. The washings and filtrate were combined, and evaporated to dryness. The crystalline white solid was leached with boiling acetone, and the mixture was filtered. The solvent was removed from the filtrate to yield 6.35g of the barium salt (54% yield).

An ir (KBr pellet) showed absorption bands at 1250, 1220, 1080, 840, and 810 cm^{-1}.

Preparation of Potassium Trichloromethanesulfonate

Potassium hydroxide (1.98g, 35.4mmol) and trichloromethanesulfonyl chloride (7.69g, 35.3mmol) were mixed with 30ml of water and the solution was stirred at room temperature for 4 days. The mixture was filtered, and the solid was washed with water. The washings and filtrate were combined, and the solvent was removed to give 4.41g crystalline white solid. This product was leached with boiling acetone, and again filtered. The solvent was removed from the filtrate to yield 2.87g of the potassium salt (34% yield).

An ir (KBr pellet) showed absorption bands at 1260, 1070, and 805 cm^{-1}.

Preparation of Trichloromethanesulfonic Acid

Potassium trichloromethanesulfonate (0.74g, 3.12mmol) was dissolved in 10ml of water and placed on a 1 x 35cm column prepared with a 100x excess of Dowex 50W-X8 resin (50-100 mesh, H^+ form). Water was used as eluting solvent, and the eluent was collected until neutral fractions were obtained. Lyophilization of the solution yielded a brownish-white solid, which was leached with acetone. Removal of solvent gave 0.69g of solid (slightly more than theoretical).

A portion of the solid was titrated against standard aqueous sodium hydroxide solution. Results indicated the solid was 85.9% trichloromethanesulfonic acid by weight.

An ir (KBr pellet) showed bands at 3400, 1270, 1200, 1055, and 800 cm^{-1}. By means of comparison, the SO_2 bands of trifluoromethanesulfonic acid (neat) absorb in the ir at 1274 and 1031 cm^{-1}.

Preparation of Trichloromethanesulfonic Acid Anhydride

Two methods were used to prepare this compound.

Procedure A

Trichloromethanesulfonic acid (0.34g, 85%, 1.45mmol) was dissolved in 5ml of 1,2-dimethoxyethane, and 1g of phosphorus pentoxide was added in one portion. The mixture was stirred at room temperature for 15 hr, then it was vacuum distilled. The 1,2-dimethoxyethane distilled over easily, but no higher boiling material would distill out.

At a bath temperature of 150°, the material began to froth up into the distilling head. The distillation was stopped, and the head was washed out with 1,2-dimethoxyethane. The solvent was removed from the resulting solution to give 0.27g of brown liquid. The ir spectrum (KBr pellet) showed bands at 1245, 1065, and 800 cm^{-1}, which are consistent with that expected for the acid anhydride. Yield was 97%.

For comparison, trifluoromethanesulfonic acid anhydride (neat) shows SO_2 band absorptions at 1471-1460 (d) and 1131 cm^{-1}.

Procedure B

Trichloromethanesulfonic acid (0.59g, 85%, 2.51mmol) was dissolved in 3ml of CH_3CN, and 2g of phosphorus pentoxide was added in one portion. The mixture was stirred at room temperature for 2 days, then vacuum distilled. As before, nothing distilled over after the solvent until the mixture began to froth and char. A small amount of oil (0.07g) was washed out of the distilling head. This oil later solidified, and had an ir spectrum identical to that previously obtained. Yield was 11%.

Reaction of N,N-Di-iso-propyltrichloromethanesulfenamide with Ozone

N,N-Di-iso-propyltrichloromethanesulfenamide (0.08g, 0.33mmol) was dissolved in 10ml of CH_2Cl_2, and the solution was cooled to -78°. Ozone was bubbled through the solution; after only a few seconds, the solution acquired a blue color, and after 1 min, passage of the gas was discontinued. After the solution was removed from the cooling bath, the color began to fade, and was gone in 5 min. Removal of solvent

from the solution gave 0.08g of colorless liquid, which ir, nmr, and mass spectral analysis showed to be the starting sulfenamide. None of the sulfonamide oxidation product was found.

Reaction of N-n-Hexyltrichloromethanesulfenamide with Active Manganese Dioxide

According to the method of Glander and Golloch (56), N-n-hexyltrichloromethanesulfenamide (1.02g, 4.0mmol) was dissolved in 25ml of benzene, and 2.67g (30.8mmol) of active manganese dioxide (prepared by the method of Attenburrow et al. [57]) was added. The mixture was heated at 70° for 40 hr, then filtered through Celite. The collected solid was washed with acetone, and the washings and filtrate were combined, and the solvent was removed to give 0.65g of brown liquid with some manganese dioxide in suspension. Preparative TLC on silica gel with benzene as the developing solvent gave a mixture of unreacted starting sulfenamide and decomposition products from this compound. None of the sulfonamide oxidation product was found.

Attempted Preparation of N-sec-Butyl-N-(trichloromethanesulfonyl)trifluoromethanesulfonimide

Two different starting points were used in the unsuccessful syntheses of this compound. The procedures followed are summarized below.

Procedure A

N-sec-Butyl-N-(trichloromethanesulfenyl)trifluoromethanesulfonamide was mixed with 2.1 equivalents of m-chloroperoxybenzoic acid in hexane, and the mixture was refluxed for 3 days. Work up was

followed by column chromatography on silica gel with benzene as eluting solvent, to give a mixture of unreacted starting material and N-sec-butyltrifluoromethanesulfonamide.

Procedure B

Following the procedure of Pan and Fletcher (61), one equivalent of N-sec-butyltrifluoromethanesulfonamide was mixed with one equivalent of thallous ethoxide in benzene. No reaction was apparent, even after refluxing for 4 hr. Work up gave a mixture of unreacted sulfonamide and thallous ethoxide.

Attempted Preparation of N-n-Hexyl-N-(trichloromethanesulfonyl)trifluoromethanesulfonimide

These unsuccessful syntheses were attempted from three different starting points: (a) from N-n-hexyl-N-(trichloromethanesulfenyl)-trifluoromethanesulfonamide, (b) from N-n-hexyltrifluoromethanesulfonamide, and (c) from N-n-hexyltrichloromethanesulfonamide. The procedures are outlined below.

From N-n-Hexyl-N-(trichloromethanesulfenyl)-trifluoromethanesulfonamide

Procedure A. One equivalent of N-n-hexyl-N-(trichloromethanesulfenyl)trifluoromethanesulfonamide was mixed with 2.1 equivalents of m-chloroperoxybenzoic acid in hexane, and the mixture was refluxed for 22 hr. Work up of the mixture followed by column chromatography on silica gel with benzene as eluting solvent gave a mixture. Ir, nmr, and mass spectral analysis seemed to indicate a mixture of unreacted starting material and N-n-hexyltrifluoromethanesulfonamide.

Procedure B. A CH_2Cl_2 solution of peroxytrifluoroacetic acid, prepared from trifluoroacetic anhydride and 90% hydrogen peroxide by the method of Emmons (58), was mixed with one-half equivalent of N-n-hexyl-N-(trichloromethanesulfenyl)trifluoromethanesulfonamide, and the mixture was refluxed for 1 hr. Work up gave only unreacted starting sulfonamide.

From N-n-Hexyltrifluoromethanesulfonamide

Procedure A. According to the method of Pan and Fletcher (61), one equivalent of N-n-hexyltrifluoromethanesulfonamide was mixed with one equivalent of thallous ethoxide in benzene. No reaction was observed, even after one week at room temperature. Work up gave only starting sulfonamide.

Procedure B. One equivalent of N-n-hexyltrifluoromethanesulfonamide was reacted with one equivalent of sodium hydride as a 57% oil dispersion in ether, and one equivalent of trichloromethanesulfonyl chloride was added. The mixture was stirred at room temperature for 15 hr, then worked up. Only unreacted sulfonamide was obtained.

Procedure C. Phenyl magnesium bromide was prepared from one equivalent of magnesium and one equivalent of bromobenzene in THF. One equivalent of N-n-hexyltrifluoromethanesulfonamide was added at room temperature, and then a THF solution of trichloromethanesulfonyl chloride. A precipitate formed immediately, but later changed to an oil. After 1/2 hr, the mixture was worked up to give only unreacted sulfonamide.

From N-n-Hexyltrichloromethanesulfonamide

Procedure A. One equivalent of N-n-hexyltrichloromethanesulfonamide was reacted with one equivalent of lithium hydride in ether, and one equivalent of trifluoromethanesulfonic acid anhydride was added while cooling in ice. After stirring at room temperature for 15 hr, the mixture was worked up to give N-n-hexyl-N-ethyltrichloromethanesulfonamide as the only product.

Attempted Preparation of N-t-Butyl-N,N-di(benzene)sulfonimide

Three unsuccessful attempts were made to prepare this compound; the procedures followed are outlined below.

Procedure A

N-t-Butyl-N-(benzenesulfenyl)benzenesulfonamide was dissolved in a mixture of hexane and CCl_4, and two equivalents of m-chloroperoxybenzoic acid were added. The mixture was refluxed for 3 hr, then cooled and filtered. Work up of the filtrate gave m-chlorobenzoic acid as the only identifiable product.

Procedure B

This procedure is the same as above, except that it was done in $CHCl_3$ at 0°. After 24 hr, no apparent reaction had taken place, so the temperature was raised to room temperature. After 96 hr, an nmr showed a mixture of m-chlorobenzoic acid and N-t-butylbenzenesulfonamide. Work up of the mixture gave only the above indicated mixture; m-chlorobenzoic acid and N-t-butylbenzenesulfonamide.

Procedure C

A solution of peroxytrifluoroacetic acid in a mixture of CCl_4 and CH_2Cl_2 was prepared from trifluoroacetic anhydride and 90% hydrogen peroxide by the method of Emmons (58). To the peracid solution was added a solution of N-t-butyl-N-(benzenesulfenyl)benzenesulfonamide in CCl_4, while cooling at 0°. Evolution of gas was noted during the addition. Nmr spectra were taken periodically, while keeping the reaction mixture at 0°. Immediately after mixing, the spectrum resembled a mixture of the starting compound, and N-t-butylbenzenesulfonamide. After 22-1/2 hr, no change was noted, and the temperature was increased to room temperature. No change was yet noted after 3-1/2 hr, so the mixture was worked up. The product mixture thus obtained was column chromatographed on silica gel with benzene as the eluting solvent. Only a minute amount of material was then obtained; it resembled N-t-butylbenzenesulfonamide.

Attempted Preparation of N-1-Adamantyl-N,N-di(benzene)sulfonimide

One unsuccessful attempt was made to prepare this compound. The procedure followed is outlined below.

N-1-Adamantyl-N-(benzenesulfenyl)benzenesulfonamide was dissolved in CH_2Cl_2, and added to a solution of two equivalents of peroxytrifluoroacetic acid, prepared from trifluoroacetic anhydride and 90% hydrogen peroxide by the method of Emmons (58), in CH_2Cl_2 cooled to -78°. The mixture was allowed to warm to -10°, and an nmr was taken; cleavage of the starting material to N-1-adamantylbenzenesulfonamide had taken place to some extent, but starting material was

apparently still present. After 2 days at -10°, the mixture was worked up to give a mixture of N-1-adamantylbenzenesulfonamide and another product in about equal proportion. Although the nmr of the product mixture still resembled a mixture of starting material and the sulfonamide resulting from N-sulfenyl group cleavage, no starting material could be seen on TLC (silica gel with benzene solvent). An ir of the mixture ($CHCl_3$ solution) showed a strong absorption band at 1770 cm^{-1}, characteristic of trifluoroacetates.

Attempted Preparation of N-(4-Nitrophenyl)-N-benzyltrifluoromethanesulfonamide

The unsuccessful syntheses of this compound were attempted from three different starting points: (a) sulfonylation of the amine, (b) nitration of the sulfonamide, and (c) sulfonylation followed by alkylation. A summary of these attempts is given below.

Sulfonylation of N-(4-Nitrophenyl)-N-benzylamine

Procedure A. Two equivalents of N-(4-nitrophenyl)-N-benzylamine, prepared by the method of Kehrmann and Tichwinski (104), were dissolved in CH_3CN, and the solution was cooled in ice. One equivalent of trifluoromethanesulfonic acid anhydride in CH_3CN was added, and the mixture was stirred at room temperature for 15 hr. After work up, TLC on silica gel, ir (KBr pellet), and nmr (deuteriochloroform solution) showed only starting material.

Procedure B. One equivalent of N-(4-nitrophenyl)-N-benzylamine was mixed in CH_3CN with one equivalent of sodium hydride as a 57% oil

dispersion. While cooling in ice, one equivalent of trifluoromethanesulfonic acid anhydride was added, and the mixture was stirred with cooling for 1 hr. After work up, as above, only starting amine was found. Only 43% of the starting material was recovered.

Procedure C. The procedure is the same as above, but cyclohexane was used as the solvent in place of CH_3CN. As before, no reaction was observed to have taken place.

Procedure D. This procedure is the same as above, except that the mixture was allowed to warm to room temperature and was stirred for 15 hr before work up. Again, no reaction was observed.

Nitration of N-Phenyl-N-benzyl(trifluoromethane)sulfonamide

Procedure A. N-Phenyl-N-benzyl(trifluoromethane)sulfonamide in a mixture of glacial acetic acid and concentrated sulfuric acid was treated at 5° with a mixture of concentrated nitric and sulfuric acids. After stirring at room temperature for 1 hr, the mixture was worked up to yield a mixture of polynitration products, which could not be separated by TLC on silica gel.

Procedure B. This procedure is the same as above, except that trifluoroacetic acid was used as solvent in place of glacial acetic acid. Work up after 1 hr at 0° gave a mixture of polynitration products and tars.

Procedure C. This procedure is identical to above, but here the reaction was followed by TLC on silica gel. After 1/4 hr at 0°, no starting material was present. Work up gave a mixture of polynitration products, tars, and cleavage to an amine (as indicated by ir).

Procedure D. Acetyl nitrate was prepared from concentrated nitric acid and acetic anhydride (106-108); while cooling this at 0°, one equivalent of N-phenyl-N-benzyl(trifluoromethane)sulfonamide in acetic anhydride was added. After 1/2 hr at 0°, only starting material was apparent by TLC on silica gel. The mixture was warmed to room temperature and checked periodically on TLC. After 9 days, no further change had taken place, and work up gave back only unreacted sulfonamide.

Procedure E. This procedure is the same as above, except that 90% fuming nitric acid was used to prepare the acetyl nitrate. As above, no reaction was noted at 0°, and the mixture was stirred at room temperature for several days before work up. Only unreacted starting sulfonamide was obtained.

Procedure F. One equivalent of nitrosonium fluoroborate (148-149) was suspended in nitromethane, and the mixture was cooled to 5-10°. One equivalent of N-phenyl-N-benzyltrifluoromethanesulfonamide in nitromethane was added, and the mixture was stirred at room temperature for 15 hr. Work up gave a mixture of polynitration products and tars.

Procedure G. This procedure is exactly the same as above, except that the reaction was carried out at -25°. After 1 hr, the

mixture was warmed to 0°, and kept at that temperature for an additional 1 hr. Work up gave only unreacted starting sulfonamide.

Sulfonylation of 4-Nitroaniline, Followed by Alkylation

Procedure A. 4-Nitrophenylamine (two equivalents) was suspended in ether and cooled to 0°. One equivalent of trifluoromethanesulfonic acid anhydride was added, and the mixture stirred at room temperature for 8 hr. Work up gave unreacted amine.

Procedure B. This procedure is the same as above, except that CH_3CN was used in place of ether as the solvent. The mixture was stirred at room temperature for 15 hr after mixing at 0°. Work up gave only starting amine.

Attempted Preparation of 3-Benzyl-3-trifluoromethanesulfonyl-1-phenyltriazene

Two unsuccessful attempts were made to prepare this compound. The procedures used are summarized below.

Procedure A

Benzenediazonium chloride was prepared from aniline, aqueous hydrochloric acid, and aqueous sodium nitrite. One equivalent of N-benzyltrifluoromethanesulfonamide was mixed with one equivalent of sodium hydroxide in water, and the diazonium salt solution (one equivalent) was added while cooling in ice. After 1/4 hr at 0°, the mixture was worked up. Only unreacted sulfonamide was identified from the product mixture.

Procedure B

Benzenediazonium chloride was prepared as before. Sodium carbonate was added to the diazonium salt solution, bringing the pH to 7, and the temperature was allowed to rise to 23°. N-Benzyltrifluoromethanesulfonamide (one equivalent) was added to the diazonium salt solution, and the mixture worked up after 3 hr. Unreacted starting sulfonamide and a little benzaldehyde were identified in the product mixture.

Attempted Preparation of 3-n-Hexyl-3-trifluoromethanesulfonyl-1-phenyltriazene

Two unsuccessful attempts were made to prepare this compound. The procedures are summarized below.

Procedure A

Benzenediazonium chloride was prepared from aniline, aqueous hydrochloric acid, and aqueous sodium nitrite. Excess solid sodium acetate was added. One equivalent of this solution was added to an aqueous solution containing one equivalent each of sodium hydroxide and N-n-hexyltrifluoromethanesulfonamide. Addition was carried out at 0°, and the mixture was kept cold for 15 hr before working up. Unreacted sulfonamide was the only identifiable product obtained.

Procedure B

Benzenediazonium chloride was prepared as before, then sodium carbonate was added to bring the pH to 7. To one equivalent of cold diazonium salt solution was added an aqueous solution containing one

equivalent each of sodium hydroxide and N-n-hexyltrifluoromethanesulfonamide. The mixture was kept below 0° during the addition, and was worked up after 3/4 hr. Unreacted sulfonamide was the only product identified from the product mixture.

Attempted Preparation of 3-Methyl-3-trifluoromethanesulfonyl-1-p-tolyltriazene

An unsuccessful attempt to prepare this compound was made using two equivalents of 3-methyl-1-p-tolyltriazene and one equivalent of trifluoromethanesulfonic acid anhydride in ether at 0°. The mixture was worked up after 1/4 hr to yield unreacted starting triazene.

Reaction of Trichloromethanesulfonic Acid Anhydride with Benzylamine

Trichloromethanesulfonic acid anhydride (0.07g, 0.19mmol) was dissolved in 1ml of CH_3CN, and 0.05g (0.42mmol) of benzylamine in 1ml of CH_3CN were added in one portion. After stirring at room temperature for 15 hr, the mixture was poured into 20ml of water and extracted with 2 x 15ml of ether. The combined extracts were washed with 2 x 15ml of water and 10ml of brine, and were dried over anhydrous magnesium sulfate. Removal of solvent gave 0.01g of colorless oil. Ir showed the desired product was not produced.

Reaction of Trichloromethanesulfonic Acid Anhydride with n-Hexylamine

Trichloromethanesulfonic acid anhydride (0.27g, 0.96mmol) in 1ml of 1,2-dimethoxyethane was added over 1 hr to an ice cold solution of 0.20g (1.99mmol) of n-hexylamine in 5ml of 1,2-dimethoxyethane.

After 1 hr, the mixture was poured into 40ml of water and extracted with 2 x 25ml of ether. The combined extracts were washed with 2 x 15ml of water and 20ml of brine, and were dried over anhydrous magnesium sulfate. Removal of solvent gave 0.06g of yellow oil. Nmr showed 1,2-dimethoxyethane and the presence of an n-hexyl group (0.95-1.38δ,m), and ir indicated a possible sulfonyl functionality (1240 and 1203 cm^{-1}), but no amino group. No sulfonamide product was evident.

Reaction of Trichloromethanesulfonyl Chloride with Phenol

Potassium hydroxide (0.74g, 85%, 11.2mmol) was dissolved in 20ml of water, and 1.07g (11.2mmol) of phenol were added. Trichloromethanesulfonyl chloride (2.42g, 11.1mmol) was added, and the mixture was stirred at room temperature for 3 days. The mixture consisted of two layers; 15ml of $CHCl_3$ were added, and the layers were separated. The aqueous layer was washed with 2 x 5ml of $CHCl_3$, and the extracts added to the organic layer. The combined organic layers were washed with 2 x 10ml of water, and 10ml of brine, and were dried over anhydrous magnesium sulfate. Removal of solvent gave 1.01g of brown oil.

Preparative TLC on silica gel with benzene as developing solvent gave a mixture of products. No phenyl ester was observed, but a mixture of chlorinated phenols was suggested by ir spectra.

Reaction of Trichloromethanesulfonyl Chloride with Sodium Phenolate

Sodium hydride (0.44g, 57% oil dispersion, 10mmol) was washed with benzene, then suspended in 20ml of benzene. To this was then added

over 1/4 hr a solution of phenol (0.94g, 10mmol) in 5ml of benzene. The mixture was stirred for 1/4 hr additional, then trichloromethanesulfonyl chloride (2.19g, 10mmol) in 3ml of benzene was added over 1/4 hr. The mixture was stirred at room temperature for 15 hr, then 10ml of water were added, and the layers were separated. The aqueous layer was washed with 3 x 10ml of ether, and the extracts were combined with the organic layer, and were washed with 2 x 20ml of water, and 20ml of brine. The organic solution was then dried over anhydrous magnesium sulfate, and the solvent was removed to give 1.85g of brown liquid. Preparative TLC on silica gel with benzene as developing solvent gave a mixture of products, none of which was the phenyl ester.

Reaction of Trichloromethanesulfonyl Chloride with Silver Trifluoromethanesulfonate

Silver trifluoromethanesulfonate (1.57g, 6.1mmol), prepared by the method of Gramstad and Haszeldine (29), was dissolved in 15ml of benzene, and a solution of trichloromethanesulfonyl chloride (1.29g, 6.1mmol) in 4ml of benzene was added over 5 min. No reaction was immediately apparent, but after 1/4 hr at room temperature, a brown solid began to form. After 3 hr, only a small amount of the solid had formed, so the mixture was stirred for an additional 12 hr. No additional solid had formed after this time, and the mixture was then refluxed for 3 days. The mixture was filtered free of 0.32g of grayish solid, and the brown solution was rotary evaporated to yield 2.37g of brown solid. The precipitate collected was insoluble in water and acetone, but soluble in ammonium hydroxide solution; but the addition

of dilute aqueous hydrochloric acid to the ammoniacal solution did not reprecipitate the solid. Ir (KBr pellet) spectra of both the products obtained indicated a mixture of starting materials, with no indication of the mixed anhydride having been formed.

Reactions of N-Cyano-N-phenyltrifluoromethanesulfonamide with Sodium di-t-butylphenolate

Two reactions were carried out, using different solvents and temperatures.

Procedure A

Sodium hydride (0.05g, 57% oil dispersion, 1.17mmol) was washed with ether and suspended in 1ml of HMPT. While cooling in ice, a solution of 0.21g (1.0mmol) of di-t-butylphenol in 0.75ml of HMPT was added over 1/2 hr. After stirring an additional 1/4 hr, a solution of 0.25g (1.0mmol) of N-cyano-N-phenyltrifluoromethanesulfonamide in 0.75ml of HMPT was added over 1/2 hr. The mixture was stirred at room temperature for 15 hr, then poured into 75ml of water. After extracting with 2 x 25ml of ether, the combined extracts were washed with 2 x 10ml of water and 20ml of brine, and were dried over anhydrous magnesium sulfate. Removal of solvent gave 0.38g of brown oil, which ir and nmr showed to be a mixture of original phenol and sulfonamide, with possibly some N-phenyltrifluoromethanesulfonamide. No desired product was seen.

Procedure B

Sodium hydride (0.04g, 57% oil dispersion, 1.03mmol) was washed with ether, then suspended in 1ml of toluene. While cooling in ice, a

solution of 0.10g (0.48mmol) of di-t-butylphenol in 0.75ml of toluene was added over 1/2 hr. After stirring for an additional 1/2 hr, a solution of 0.11g (0.42mmol) of N-cyano-N-phenyltrifluoromethanesulfonamide in 0.75ml of HMPT was added over 1/2 hr. The mixture was stirred at room temperature for 3 days, then a small sample was removed, mixed with a little water, and extracted with benzene. The benzene layer was spotted on a silica gel TLC plate, and eluted with 1,4-dioxane. No reaction product was seen, so the temperature of the remaining reaction mixture was raised to 50°. After 24 hr, another aliquot was treated as above, and the result was the same. The entire reaction mixture was then poured into 50ml of water, and extracted with 2 x 10ml of benzene. The combined organic layers were washed with 2 x 5ml of water and 10ml of brine, and were dried over anhydrous magnesium sulfate. Removal of solvent gave 0.07g of brown oil. An ir spectrum of the product showed unreacted di-t-butylphenol, and decomposition products. No evidence of the starting sulfonamide or of the desired product was noted.

Reaction of N-Cyano-N-phenyltrifluoromethanesulfonamide with Sodium Phenolate

Sodium hydride (0.04g, 57% oil dispersion, 0.85mmol) was washed with ether, and suspended in 1ml of HMPT. While cooling in ice, a solution of 0.08g (0.84mmol) of phenol in 0.6ml of HMPT was added over 1/4 hr. After stirring for an additional 1/4 hr, a solution of 0.21g (0.85mmol) of N-cyano-N-phenyltrifluoromethanesulfonamide in 0.6ml of HMPT was added over 1/4 hr. The mixture was stirred at room temperature for 15 hr, then poured into 40ml of water. It was extracted with

2 x 15ml of hexane, and the combined extracts were washed with 2 x 10ml of water and 10ml of brine, and were dried over anhydrous magnesium sulfate. Removal of solvent gave 0.05g colorless oil. Ir showed the presence of hydroxyl and trifluoromethanesulfonyl groups (1422, 1212, and 1142 cm^{-1}), but not of cyanate. The aqueous layers from the hexane extractions were acidified with 5N hydrochloric acid and extracted with hexane. Work up as above gave 0.09g of slightly yellow oil. Ir of this product showed the presence of hydroxyl and trifluoromethanesulfonyl groups, but was different overall from the spectrum obtained above. Again, no product was seen.

Reaction of N-Cyano-N-phenyltrifluoromethanesulfonamide with HMPT

N-Cyano-N-phenyltrifluoromethanesulfonamide (0.07g, 0.27mmol) was dissolved in 1ml of HMPT, and the solution was stirred at room temperature for 24 hr. A few drops of the reaction mixture were mixed with 10ml of water, the solution was made acid with a drop of 5N hydrochloric acid, and then extracted with ether. The ethereal solution was spotted on a silica gel TLC plate, and the plate was developed with 1,4-dioxane. None of the original sulfonamide was seen.

The remaining reaction mixture was poured into 40ml of water, and extracted with 6 x 5ml of ether. The extracts were washed with water and brine, and were dried over anhydrous magnesium sulfate. Removal of solvent gave 0.05g of colorless liquid. Ir and nmr showed only aliphatic groupings to be present, with no starting material.

A repeat of the experiment using 0.037g of the sulfonamide in 1ml of HMPT gave, after 4 days at room temperature, 0.027g of unreacted sulfonamide as the only product.

Reaction of N-Cyano-N-phenyltrifluoromethanesulfonamide with CH_3CN

N-Cyano-N-phenyltrifluoromethanesulfonamide (0.04g, 0.14mmol) was dissolved in 1ml of CH_3CN, and the solution was stirred at room temperature for 4 days. The mixture was poured into 50ml of water, and extracted with 3 x 10ml of ether. The extracts were washed with 2 x 10ml of water and 10ml of brine, and were dried over anhydrous magnesium sulfate. Removal of solvent gave 0.06g of brown liquid. Ir indicated decomposition products; no unreacted starting material was observed.

Reaction of N-Cyano-N-hexyltrifluoromethanesulfonamide with Diethyl Sodiomalonate

Sodium hydride (0.05g, 57% oil dispersion, 1.0mmol) was washed with ether, and suspended in 5ml of HMPT. Diethyl malonate (0.16g, 1.0mmol) in 0.75ml of HMPT was added over 1/4 hr at room temperature. After 1/2 hr additional, the mixture was cooled in ice, and a solution of 0.26g (1.0mmol) of N-cyano-N-hexyltrifluoromethanesulfonamide in 0.75ml of HMPT was added over 1/2 hr. The mixture was allowed to warm to room temperature slowly. After 11 hr, a small sample of the reaction mixture was spotted on a silica gel TLC plate, and developed in benzene. Unreacted starting material was observed. Glc (5% SE-30) gave the same results. The reaction was continued at 50°, with periodic testing by both TLC and glc. After 4 days, no reaction had

apparently taken place, so the temperature was raised to 95°. After 2 days, all the starting materials appeared to be gone, so the reaction mixture was cooled, poured into 40ml of water, and extracted with 3 x 10ml of hexane. The extracts were washed with 2 x 10ml of water and 10ml of brine, and were dried over anhydrous magnesium sulfate. Removal of solvent gave 0.12g of yellow liquid. Ir and nmr spectra of this product indicated a mixture of N-n-hexyltrifluoromethanesulfonamide and N,N-di-n-hexyltrifluoromethanesulfonamide.

The above aqueous layer was acidified with dilute hydrochloric acid, and was reextracted with hexane. The extracts were treated as above, and solvent was removed to yield 0.03g colorless liquid. Ir and nmr spectra indicated mainly N,N-di-n-hexyltrifluoromethanesulfonamide. No diethyl cyanomalonate or diethyl n-hexylmalonate were found.

Reaction of N-n-Hexyltrifluoromethanesulfonamide with 2-Carbomethoxy-1-cyclopentenyl-1-trifluoromethanesulfonate

Sodium hydride (0.07g, 57% oil dispersion, 1.64mmol) was washed with ether, then suspended in 3ml of HMPT. At room temperature, a solution of 0.27g (1.17mmol) of N-n-hexyltrifluoromethanesulfonamide in 1.5ml of HMPT was added over 1/2 hr. The mixture was stirred for an additional 1/4 hr, then a solution of 2-carbomethoxy-1-cyclopentenyl-1-trifluoromethanesulfonate (0.47g, 1.61mmol) in 1ml of HMPT was added over 5 min. At intervals, 1.5ml aliquots of the reaction mixture were added to 2ml of saturated aqueous sodium bicarbonate, and extracted with 10ml of water and 10ml of brine, and were dried over anhydrous

magnesium sulfate. The solvent was removed, and the product mixture analyzed on glc (10% carbowax 20M): aliquot 1 was taken after 1/2 hr, 2 after 5 hr, 3 after 20 hr, 4 after 1 week. In each case, a mixture of the starting materials was obtained, indicating no reaction had taken place.

Reaction of N,N-di-n-Hexyltrifluoromethanesulfonamide with 2-Carbomethoxycyclopentanone Potassium Salt

2-Carbomethoxycyclopentanone potassium salt (0.04g, 0.2mmol) and N,N-di-n-hexyltrifluoromethanesulfonamide (0.07g, 0.21mmol) were dissolved in 1ml of HMPT, and the mixture was stirred at room temperature for 6 days. It was then poured into 5ml of saturated aqueous sodium bicarbonate and extracted with 3 x 4ml of ether. The extracts were combined, and were washed with 2 x 5ml of water and 2 x 5ml of brine, and were dried over anhydrous magnesium sulfate. Removal of solvent gave a mixture which glc (10% carbowax 20M) showed to consist of 2-carbomethoxycyclopentanone and the starting sulfonamide.

Reaction of 2-n-Hexyl-2-carbomethoxycyclopentanone with 2-Carbomethoxycyclopentanone Potassium Salt

2-Carbomethoxycyclopentanone potassium salt (0.09g, 0.51mmol) and 2-n-hexyl-2-carbomethoxycyclopentanone (0.13g, 0.57mmol) were dissolved in 2ml of HMPT. The mixture was stirred at room temperature for 45 hr, then it was poured into 5ml of saturated aqueous sodium bicarbonate, and extracted with 2 x 10ml of ether. The combined extracts were washed with 2 x 5ml of water and 10ml of brine, and were dried over anhydrous magnesium sulfate. Removal of solvent gave a

mixture which glc (10% carbowax 20M) showed to consist of 2-carbomethoxycyclopentanone and 2-n-hexyl-2-carbomethoxycyclopentanone. No O-alkylated product was noted.

Reaction of N,N-Di-iso-Propyltrifluoromethanesulfonamide with Diethyl Sodiomalonate

Sodium hydride (0.3g, 57% oil dispersion, 7.1mmol) was washed with ether, and suspended in 1ml of HMPT. While cooling in ice, a solution of 1.21g (7.0mmol) of diethyl malonate in 2ml of HMPT was added over 1 hr. After stirring at room temperature for 1 hr additional, the mixture was again cooled, and a solution of 0.76g (3.26mmol) of N,N-di-iso-propyltrifluoromethanesulfonamide in 3ml of HMPT was added over 1/4 hr. After 24 hr at room temperature, 0.1ml of the reaction mixture was mixed with 6ml of water and extracted with 0.5ml of CCl_4. A portion of the CCl_4 solution was spotted on a silica gel TLC plate and developed with benzene. Only starting materials were observed. The reaction was continued for an additional 7 days, then tested again. No change was noted, and the temperature was increased to 40°. After 8 days, still no reaction was noted, and the temperature was increased to 70°. After 4 days, there was still no apparent reaction, and the temperature was increased to 125°. After 24 hr, the mixture was poured into 75ml of water and extracted with 2 x 25ml of ether. The extracts were washed with water and brine, and were dried over anhydrous magnesium sulfate. Removal of solvent gave 0.55g of yellow liquid. Analytical and preparative glc (5% SE-30) showed a mixture of unreacted starting materials: diethyl malonate and N,N-di-iso-propyltrifluoromethanesulfonamide.

Reaction of N-Phenyl-N-benzyltrifluoromethanesulfonamide with One Equivalent of Sodium Cyanide

To a solution of 0.05g (1.08mmol) of sodium cyanide in 10ml of HMPT was added over 1/2 hr a solution of 0.31g (0.99mmol) of N-phenyl-N-benzyltrifluoromethanesulfonamide in 1ml of HMPT. After stirring at room temperature for 14 hr, no odor of benzyl cyanide was noted. A 2ml aliquot of the mixture was poured into 10ml of water and extracted with 2 x 10ml of ether. The extracts were washed with 5ml of water and 10ml of brine, and were dried over anhydrous magnesium sulfate. After removing solvent, an ir spectrum showed unreacted sulfonamide. The reaction temperature was raised to 50°. After an additional 18 hr, no odor of benzyl cyanide was noted, and the temperature was raised to 100°. After 24 hr at this temperature, none of the cyanide was yet noted, so the mixture was saturated with sodium cyanide, and heated to reflux for 20 hr. The entire reaction mixture was worked up as above, giving 0.02g of brown oil with an odor like that of benzyl cyanide. Ir showed a nitrile band at 2205 cm^{-1}, but the presence of benzyl cyanide could not be confirmed.

Reaction of N-Phenyl-N-benzyltrifluoromethanesulfonamide with Excess Sodium Cyanide

To a solution of 0.33g (1.04mmol) of N-phenyl-N-benzyltrifluoromethanesulfonamide in 2ml of HMPT were added 0.5g (10mmol) of sodium cyanide in one portion, and the solution was stirred at 100° for 15 hr. Although the mixture had turned dark brown, no odor of benzyl cyanide was noted. The mixture was heated at 150° for an additional 15 hr, then poured into 30ml of water and extracted with

2 x 10ml of ether. The combined extracts were washed with 2 x 10ml of water and 2 x 10ml of brine, and were dried over anhydrous magnesium sulfate. Solvent was removed to give 0.08g of brown oil. Ir showed a nitrile band at 2190 cm^{-1}, but not in the correct position for benzyl cyanide (2250 cm^{-1}). No benzyl cyanide was observed in the nmr.

Reaction of N-Phenyl-N-benzyltrifluoromethanesulfonamide with Excess Diethyl Sodiomalonate

Sodium hydride (0.38g, 57% oil dispersion, 9.45mmol) was washed with ether, and suspended in 1ml of HMPT. While cooling in ice, a solution of 1.36g (8.48mmol) of diethyl malonate in 1ml of HMPT was added over 1 hr. To this was then added over 1 hr a solution of 0.32g (1.02mmol) of N-phenyl-N-benzyltrifluoromethanesulfonamide in 1ml of HMPT. The mixture was heated at 150° for 20 hr, then poured into 50ml of water and extracted with 2 x 15ml of ether. The combined extracts were washed with 2 x 10ml of water and 10ml of brine, and were dried over anhydrous magnesium sulfate. Removal of solvent gave 0.23g of greenish liquid. Analytical glc (5% SE-30) showed that diethyl benzylmalonate was produced in 41% yield. Identity of the compound was confirmed by spectra taken of material obtained by preparative glc and compared to the spectra of an authentic sample.

Reaction of N-(4-Fluorophenyl)-N-benzyl(trifluoromethane)-sulfonamide with Excess Diethyl Sodiomalonate

Sodium hydride (0.04g, 57% oil dispersion, 1.04mmol) was washed with ether, and suspended in 1ml of HMPT. While cooling ice, a solution of 0.16g (1.03mmol) of diethyl malonate in 1ml of HMPT was added over 1/2 hr. After stirring for 1 hr, a solution of 0.21g (0.64mmol)

of N-(4-fluorophenyl)-N-benzyl(trifluoromethane)sulfonamide in 0.5ml of HMPT was added over 1/2 hr. After stirring at room temperature for 2 days, 0.1ml of the reaction mixture was removed and mixed with 1ml of water. This was extracted with ether, and the ethereal solution was analyzed on glc (5% SE-30). Only starting materials were noted, and the temperature of the reaction was raised to 80°. After 24 hr, still no reaction was indicated by glc analysis, and the temperature of the mixture was raised to 110°. No reaction was apparent after 24 hr at this temperature, and the temperature was increased to 165°. After 24 hr, the dark reaction mixture was poured into 50ml of water and extracted with 2 x 10ml of ether. The extracts were washed with 2 x 10ml of water and 10ml of brine, and were dried over anhydrous magnesium sulfate. Removal of solvent gave 0.13g of yellow liquid. Glc indicated the same results as before; ir and nmr indicated some decomposition products in addition to the starting materials.

Reaction of Various N-Alkyl-N,N-di(trifluoromethane)-sulfonimides with Sodium Cyanide in HMPT

The N-alkyl-N,N-di(trifluoromethane)sulfonimides were allowed to react with sodium cyanide in HMPT under the same conditons. A specific example is given below.

Sodium cyanide (0.03g, 0.60mmol) was dissolved in 0.3ml of HMPT, and the solution was cooled in ice. A solution of 0.18g (0.57mmol) of N-iso-butyl-N,N-di(trifluoromethane)sulfonimide in 0.6ml of HMPT was added over 1/2 hr, and the mixture was allowed to warm to room temperature. After stirring for 4 days, the mixture was poured into 20 ml of water, and extracted with 3 x 10ml of ether. The

combined extracts were washed with 2 x 10ml of water and 10ml of brine, and were dried over anyhydrous magnesium sulfate. After filtering off the drying agent, the solution was diluted to 25.0ml with ether in a volumetric flask. Analytical glc at 75° on 10% SE-30 indicated a 10% yield of iso-butyl cyanide, along with unreacted N-iso-butyl-N,N-di(trifluoromethane)sulfonimide, N-iso-butyltrifluoromethane-sulfonamide, and N,N-di-iso-butyltrifluoromethanesulfonamide. The ether was distilled off at atmospheric pressure, and the residue was again dissolved in ether and diluted to 1.0ml in a volumetric flask. Analytical glc under the same conditions now showed only a 4% yield of the cyanide. The volatility of the product resulted in a greatly reduced isolated yield of the product.

In each case, samples of the product cyanides were obtained by preparative glc. Their ir and nmr spectra, and glc retention times, were compared with those of authentic samples prepared by the general method of Friedman and Shechter (150).

Reaction of Various N-Alkyl-N,N-di(trifluoromethane)-sulfonimides with Potassium Iodide in HMPT

The N-alkyl-N,N-di(trifluoromethane)sulfonimides were allowed to react with potassium iodide in HMPT under the same conditions. A specific example is given below.

Potassium iodide (0.20g, 1.21mmol) was dissoved in 2ml of HMPT, and the solution was cooled in ice. A solution of 0.45g (1.17mmol) of N-(2-phenethyl)-N,N-di(trifluoromethane)sulfonimide in 1.5ml of HMPT was added over 1/2 hr, and the solution was allowed to warm to room temperature. After 4 days, the mixture was poured into 50ml of water,

and extracted with 3 x 20ml of ether. The combined extracts were washed with 2 x 10ml of water and 10ml of brine, and were dried over anhydrous magnesium sulfate. The drying agent was filtered off, and the solution diluted to 25.0ml with ether in a volumetric flask. Analytical glc at 125° on 10% SE-30 indicated a 53% yield of 2-phenethyl iodide, among other products. The ether was removed by distillation at atmospheric pressure, and the residue was dissolved in CCl_4 and diluted to 1.0ml in a volumetric flask. Analytical glc under the same conditions still showed a yield of 53%. N-(2-Phenethyl)trifluoromethanesulfonamide was also found to be a product.

In each case, samples of the product iodides were obtained by preparative glc. Their ir and nmr spectra, and glc retention times were compared with those of authentic samples. iso-Butyl, 2-phenethyl, and 2-carbomethoxyethyl iodides were prepared by the general method of Rydon (151). Ethyl iodoacetate was prepared by the method of Hass and Huffman (152).

Reaction of Various N-Alkyl-N,N-di(trifluoromethane)-sulfonimides with Diethyl Sodiomalonate in HMPT

The N-alkyl-N,N-di(trifluoromethane)sulfonimides were allowed to react with diethyl sodiomalonate under the same conditions. A specific example is given below.

Sodium hydride (0.10g, 57% oil dispersion, 2.44mmol) was washed with ether, then suspended in 1.0ml of HMPT, and the solution was cooled in ice. A solution of 0.36g (2.25mmol) of diethyl malonate in 1.0ml of HMPT was added over 3/4 hr. The mixture was stirred with cooling for a further 1 hr, then a solution of 0.74g (1.95mmol) of

N-(2-methoxyethyl)-N,N-di(trifluoromethane)sulfonimide in 2.0ml of HMPT was added over 1 hr, while still cooling in ice. The mixture was allowed to come to room temperature, and was stirred for 3 days. The mixture was poured into 60ml of water, and was extracted with 3 x 30ml of ether. The combined extracts were washed with 2 x 20ml of water and 10ml of brine, and were dried over anhydrous magnesium sulfate. The solvent was removed to give 0.43g of yellow liquid, which was dissolved in CCl_4 and diluted to 1.0ml in a volumetric flask. Analytical glc at 105° on 10% SE-30 indicated a 51% yield of diethyl 2-methoxyethyl malonate. N,N-Di(2-methoxyethyl)trifluoromethanesulfonamide was also found as a product.

In each case, samples of the product diethyl malonates were obtained by preparative glc. Their ir and nmr spectra, and glc retention times, were compared with those of authentic samples. Diethyl iso-propyl, iso-butyl, 2-butyl, 2-methoxyethyl, and 2-phenethyl malonates were prepared by the general method of Marvel (153). Diethyl 2-carbethoxymethyl malonate was prepared by the method of Conrad (154).

Reaction of N-Benzyl-N,N-di(trifluoromethane)-sulfonimide with Potassium Acetate in HMPT

Potassium acetate (0.08g, 0.80mmol) was dissolved in 0.3ml of HMPT, and the solution was cooled in ice. A solution of 0.27g (0.74 mmol) of N-benzyl-N,N-di(trifluoromethane)sulfonimide in 0.6ml of HMPT was added over 1/2 hr. The mixture was stirred at room temperature for 4 days, then poured into 30ml of water and extracted with 3 x 10ml of ether. The combined extracts were washed with 2 x 10ml of water and 10ml of brine, and were dried over anhydrous magnesium sulfate. The

solvent was removed, and the residue was dissolved in CCl_4 and diluted to 1.0ml in a volumetric flask. Analytical glc at 145° on 10% SE-30 showed only a trace of benzyl acetate. N,N-Di-benzyltrifluoromethanesulfonamide was also found to be a product.

Reaction of N-n-Hexyl-N,N-di(trifluoromethane)sulfonimide with Various Nucleophiles in HMPT

N-n-Hexyl-N,N-di(trifluoromethane)sulfonimide was allowed to react with a series of nucleophiles in HMPT at room temperature. Experimental details are given below.

Reaction with 2-Carbomethoxycyclopentanone Potassium Salt

2-Carbomethoxycyclopentanone potassium salt (0.35g, 1.93mmol), prepared in 96% yield by the method of Mayer and Alder (102) for the salt of the ethyl ester, was dissolved in 2ml of HMPT, and the solution was flushed with dry nitrogen, and cooled in ice. A solution of N-n-hexyl-N,N-di(trifluoromethane)sulfonimide (0.69g, 1.90mmol) in 1.5ml of HMPT was added over 1-1/2 hr. The reaction mixture was allowed to come to room temperature. After 40 hr, one-half of the reaction mixture was poured into 5ml of saturated aqueous sodium bicarbonate, and extracted with 5 x 4ml of ether. The combined extracts were washed with 2 x 8ml of water and 2 x 8ml of brine, and were dried over anhydrous magnesium sulfate. Removal of solvent gave 0.22g of product mixture. A 0.06g portion of the product mixture was diluted to 2.0ml with ether in a volumetric flask. Analytical glc at 120° on

10% carbowax 20M showed a mixture of 2-carbomethoxy-1-cyclopentenyl-1-trifluoromethanesulfonate (VI), 3-carbomethoxy-2-cyclopentenyl-2-trifluoromethanesulfonate (V), N-n-hexyltrifluoromethanesulfonamide, N,N-di-n-hexyltrifluoromethanesulfonamide, and 2-carbomethoxycyclopentanone n-hexyl enol ether. The amount of the O-alkylation product present represented a yield of 8%.

After 23 hr, the remainder of the reaction mixture was worked up exactly as above, yielding 0.33g of liquid. A 0.07g portion of this mixture was diluted to 2.0ml with ether in a volumetric flask. Analytical glc under the same conditions as above showed a mixture of the same products as above, but in different proportions. The amount of the O-alkylated product now represented a 39% yield.

Samples of each product were obtained by preparative glc, and their ir and nmr spectra, and glc retention times, were compared with those of authentic samples.

2-n-Hexyl-2-carbomethoxycyclopentanone and 2-carbomethoxycyclopentanone n-hexyl enol ether were obtained as a mixutre from 1-bromohexane and 2-carbomethoxycyclopentanone potassium salt by the general method of Pond and Cargill (155).

Reaction with Ethyl Sodioacetoacetate

Sodium hydride (0.04g, 57% oil dispersion, 0.86mmol) was washed with ether, then suspended in 1ml of HMPT. The mixture was cooled in ice, and flushed with dry nitrogen. A solution of 0.10g (0.80mmol) of ethyl acetoacetate in 1ml of HMPT was added over 1/2 hr, and the solution was stirred at room temperature for 1 hr. The mixture was again

cooled in ice, and a solution of 0.28g (0.77mmol) of N-n-hexyl-N,N-di(trifluoromethane)sulfonimide in 1ml of HMPT was added over 1 hr, and the mixture was allowed to come to room temperature. After 15 hr, about one-half of the mixture was poured into 4ml of saturated aqueous sodium bicarbonate, and was extracted with 4 x 4ml of ether. The combined extracts were washed with 3 x 5ml of water and 3 x 5ml of brine, and were dried over anhydrous magnesium sulfate. Removal of solvent gave 0.07g of yellow liquid. Analytical glc of the product mixture at 115° on 10% carbowax 20M showed a mixture of ethyl acetoacetate, N-n-hexyltrifluoromethanesulfonamide, N,N-di-n-hexyltrifluoromethanesulfonamide, and ethyl acetoacetate n-hexyl enol ether.

After 1 week, the remainder of the reaction mixture was worked up exactly as above. Analytical glc under the same conditions showed the same product mixture in the same proportions. Although the amount of O-alkylation product was not quantitatively determined, its yield was estimated to be 30%.

Samples of each product were obtained by preparative glc, and their ir and nmr spectra, and glc retention times, were compared with those of authentic samples.

Ethyl n-hexylacetoacetate and ethyl acetoacetate n-hexyl enol ether were obtained as a mixture from 1-bromohexane and ethyl acetoacetate by the general method of le Noble and Puerta (156).

Reaction with Potassium Acetate

Potassium acetate (0.10g, 1.03mmol) was dissolved in 1ml of HMPT, and the solution was cooled in ice and flushed with dry nitrogen.

A solution of 0.37g (1.01mmol) of N-n-hexyl-N,N-di(trifluoromethane)-sulfonimide in 1ml of HMPT was added over 1 hr. The mixture was allowed to come to room temperature. After 3 days, the mixture was poured into 20ml of water, and was extracted with 4 x 5ml of ether. The combined extracts were washed with 3 x 5ml of water and 3 x 5ml of brine, and were dried over anhydrous magnesium sulfate. Removal of solvent gave 0.07g of yellow liquid. TLC on silica gel with CCl_4 as developing solvent showed three products in addition to N-n-hexyltrifluoromethane-sulfonamide. The product mixture was dissolved in 5ml of CCl_4, and was extracted with 5ml of 10% aqueous sodium hydroxide, 2 x 5ml of water, and 5ml of brine. After drying over anhydrous magnesium sulfate, removal of solvent gave 0.02g of yellow oil. Analytical glc at 140° on 19% SE-30 showed only N,N-di-n-hexyltrifluoromethanesulfonamide and a little N-n-hexyltrifluoromethanesulfonamide as the only products. Ir and nmr spectra indicated the same product mixture.

Reaction with Sodium Thiophenoxide

Sodium hydride (0.04g, 57% oil dispersion, 0.092mmol) was washed with ether, and suspended in 0.5ml of HMPT. The mixture was cooled in ice and flushed with dry nitrogen. A solution of 0.09g (0.77mmol) of thiophenol in 0.5ml of HMPT was added over 3/4 hr, and the mixture was further stirred for 1/4 hr. A solution of 0.28g (0.76mmol) of N-n-hexyl-N,N-di(trifluoromethane)sulfonimide in 0.5ml of HMPT was then added over 1 hr. After 3 days, the mixture was poured into 50ml of water, and extracted with 3 x 20ml of ether. The combined extracts were washed with 2 x 10ml of water and 10ml of brine, and were dried over

anhydrous magnesium sulfate. Removal of solvent gave 0.16g of yellow liquid. The mixture was dissolved in CCl_4 and diluted to 1.0ml in a volumetric flask. Analytical glc at 130° on 5% SE-30 showed a mixture of N-n-hexyltrifluoromethanesulfonamide, N,N-di-n-hexyltrifluoromethanesulfonamide, diphenyldisulfide, and phenyl-n-hexyl sulfide, which was present in 15% yield. Samples of each product were obtained by preparative glc, and their ir and nmr spectra and glc retention times were compared with those of authentic samples.

Reaction with Sodium Azide

Sodium azide (0.07g, 1.01mmol) was dissolved in 1ml of HMPT, and the mixture was cooled in ice and flushed with dry nitrogen. A solution of 0.29g (0.80mmol) of N-n-hexyl-N,N-di(trifluoromethane)sulfonimide in 1ml of HMPT was added over 1 hr. Evolution of gas was noted during the addition. The mixture was allowed to warm to room temperature. After 3-1/2 days, the mixture was poured into 50ml of water, and extracted with 3 x 20ml of water and 10ml of brine, and were dried over anhydrous magnesium sulfate. Removal of solvent gave 0.14g of colorless liquid. The product mixture was dissolved in CCl_4 and diluted to 1.0ml in a volumetric flask. Analytical glc at 150° on 5% SE-30 showed only N-n-hexyltrifluoromethanesulfonamide and N,N-di-n-hexyltrifluoromethane sulfonamide.

Reaction with Acetylacetonatothallium (I)

Acetylacetonatothallium (I) (0.31g, 1.01mmol), prepared by the method of Taylor, Hawks, and McKillop (157), was suspended in 1ml of HMPT, and the solution was cooled in ice and flushed with dry nitrogen.

A solution of 0.37g (1.01mmol) of N-n-hexyl-N,N-di(trifluoromethane)-sulfonimide in 1ml of HMPT was added over 1/2 hr. The mixture was allowed to come to room temperature and was stirred for 4 days. The mixture was poured into 50ml of water, and was extracted with 3 x 20ml of ether. The combined extracts were washed with 2 x 10ml of water and 10ml of brine, and were dried over anhydrous magnesium sulfate. Removal of solvent gave 0.23g of yellow liquid, which was dissolved in CCl_4 and diluted to 1.01ml in a volumetric flask. Analytical glc at 145° on 5% SE-30 showed a mixture of N-n-hexyltrifluoromethanesulfonamide, N,N-di-n-hexyltrifluoromethanesulfonamide, and 2,4-pentanedione n-hexyl enol ether, which was present in 45% yield. Samples of each product were obtained by preparative glc, and their ir and nmr spectra, and glc retention times, were compared with those of authentic samples.

Reaction with Malononitrile Sodium Salt

Sodium hydride (0.05g, 57% oil dispersion, 1.1mmol) was washed with ether and suspended in 0.5ml of HMPT. The mixture was cooled in ice and flushed with dry nitrogen. A solution of 0.07g (1.04mmol) of malononitrile in 0.5ml of HMPT was added over 40 min. After stirring with cooling for an additional 20 min, a solution of 0.37g (1.01mmol) of N-n-hexyl-N,N-di(trifluoromethane)sulfonimide in 1ml of HMPT was added over 40 min. The mixture was allowed to warm to room temperature, and was stirred for 3 days. The mixture was poured into 50ml of water, and was extracted with 3 x 20ml of ether. The combined extracts were washed with 2 x 10ml of water and 10ml of brine, and were dried over anhydrous magnesium sulfate. Removal of solvent gave 0.17g of

yellowish liquid, which was dissolved in CCl_4 and diluted to 1.0ml in a volumetric flask. Analytical glc at 145° on 5% SE-30 showed a mixture of N-n-hexyltrifluoromethanesulfonamide and N,N-di-n-hexyltrifluoromethanesulfonamide as the only products.

Reactions with Phenyl Magnesium Bromide

Two reactions were run with this reagent:

With Toluene as the Solvent. Magnesium turnings (0.22g, 9.0mmol) were suspended in 5 ml of ether, and bromobenzene (1.42g, 9.0mmol) in 1ml of ether was added portionwise to generate the Grignard reagent. Heating and a crystal of iodine were needed to initiate and maintain the reaction. When the formation of the reagent was complete, a solution of 1.62g (4.45mmol) of N-n-hexyl-N,N-di(trifluoromethane)-sulfonimide in 1ml of toluene was added over 10 min. The ether was removed by distillation, and the solvent was replaced by toluene. After heating at 90° for 2 hr, the mixture was poured onto 20g of ice and 10ml of 6N hydrochloric acid. The layers were separated, and the aqueous layer was washed with a little ether. The combined organic layers were washed with 10ml of water and 10ml of brine, and were dried over anhydrous magnesium sulfate. Removal of solvent gave 1.85g of red-orange liquid. The product was dissolved in benzene and diluted to 10.0ml in a volumetric flask. Analytical glc at 145° on 10% SE-30 showed a mixture of the starting sulfonimide, and traces of other unidentifiable products.

With 1,4-Dioxane as the Solvent. Phenyl magnesium bromide (5.61mmol) was prepared as above from magnesium turnings and bromobenzene in 1,4-dioxane. The Grignard reagent solution was brought to reflux, and a solution of N-n-hexyl-N,N-di(trifluoromethane)sulfonimide in 1ml of 1,4-dioxane was added over 10 min. After refluxing for 1 hr the solution was poured into 15ml of 6N hydrochloric acid and 5ml of water. The mixture was then extracted with 3 x 20ml of ether, and the layers were separated; the aqueous layer was washed once with ether. The combined extracts were washed with 2 x 10ml of water and 10ml of brine, and were dried over anhydrous magnesium sulfate. Removal of solvent gave 1.71g of red-brown liquid, which was dissolved in CCl_4 and diluted to 5.0ml in a volumetric flask. Analytical glc at 145° on 10% SE-30 showed a mixture of unreacted bromobenzene and N-n-hexyl-N,N-di(trifluoromethane)sulfonimide, N-n-hexyltrifluoromethanesulfonamide, N,N-di-n-hexyltrifluoromethanesulfonamide, and biphenyl. A sample of biphenyl was obtained by preparative glc, and its ir and nmr spectra and glc retention time were compared with those of an authentic sample.

Reactions with Water

Eight reactions were run, varying the amount of water, the reaction temperature, and the reaction time:

With One Equivalent of Water, at Room Temperature. N-n-Hexyl-N,N-di(trifluoromethane)sulfonimide (0.17g, 0.48mmol) was dissolved in 0.5ml of HMPT, and 8.65µl (0.48mmol) of water were added in one portion. The mixture was stirred at room temperature for 6 days, then poured into 30ml of water and extracted with 4 x 6ml of ether. The combined

extracts were washed with 10ml of brine, and were dried over anhydrous magnesium sulfate. Removal of solvent gave 0.14g of yellow liquid, which was diluted to 1.0ml with $CHCl_3$ in a volumetric flask. Analytical glc at 125° on 10% SE-30 showed a mixture of unreacted N-n-hexyl-N,N-di(trifluoromethane)sulfonimide, N-n-hexyltrifluoromethanesulfonamide, N,N-di-n-hexyltrifluoromethanesulfonamide, and n-hexyltrifluoromethanesulfonate. The yield of ester was about 90%: it began to hydrolyze shortly after isolation of the product mixture. A sample of the sulfonate ester was obtained by preparative glc. Its ir spectrum (CCl_4 solution) showed bands at 2945, 1228, 1190, 1145, and 850 cm^{-1}. Its nmr spectrum (CCl_4 solution) showed signals at 0.91-1.38δ (m, 11H), and 3.22δ (t, J=7, 2H). These spectra were identical with those of an authentic sample, prepared in low yield by the general method of Su, Sliwinski, and Schleyer (158). This sample also hydrolyzed rapidly.

Upon standing, the $CHCl_3$ solution of the product mixture separated into two layers. The lower layer was removed, and was found to be insoluble in CCl_4 and D_2O, but soluble in ether and acetone. An nmr (hexadeuterioacetone solution) showed signals at 0.89-1.38δ (m, 11H), 2.80-2.95δ (d, J=10, 18H), and 4.32δ (m, 2H). An ir spectrum (neat) showed absorption bands at 2950, 1465, 1355, 1310, 1225, 1190, 1140, 1060, and 1000 cm^{-1}. These spectra are consistent with the compound: tris(dimethylamino)-n-hexyloxyphosphonium N,N-di(trifluoromethane)sulfonimide (VII).

With Ten Equivalents of Water, at 45°. N-n-Hexyl-N,N-di(trifluoromethane)sulfonimide (0.16g, 0.425mmol) was dissolved in 0.5ml

of HMPT, and 76.5µl (4.25mmol) of water were added in one portion. The mixture was heated at 45° for 5 days, then poured into 40ml of water, and extracted with 4 x 6ml of ether. The combined extracts were washed with 10ml of water and 10ml of brine, and were dried over anhydrous magnesium sulfate. Removal of solvent gave 0.06g of yellow oil. The product was dissolved in CCl_4, and diluted to 1.0ml in a volumetric flask. A separate yellow layer separated during glc analysis. Analytical glc at 95° on 10% Ucon 50LB 550X showed a mixture of N-n-hexyl-N,N-di(trifluoromethane)sulfonimide, N-n-hexyltrifluoromethanesulfonamide, and n-hexanol. The yield of alcohol was 71% by glc. The separate layer which formed in the CCl_4 solution was isolated, and found to be the phosphonium salt (VII) described above.

With Five Equivalents of Water, at 45°. This reaction is the same as above, except that only five equivalents of water were used in place of ten. The mixture was allowed to react for the same length of time, and was worked up in the same manner. Glc analysis under the same conditions showed only n-hexanol in 0.2% yield. Some of the phosponium salt (VII) was also present.

With Twenty Equivalents of Water, at 45°. This reaction is the same as above, except that twenty equivalents of water were used in place of ten. The mixture was allowed to react for the same length of time, and was worked up in the same manner. Glc analysis under the same conditions showed n-hexyltrifluoromethanesulfate, and n-hexanol (44% yield). Again, some of the phosphonium salt (VII) was also found.

With Ten Equivalents of Water, at 75°. This reaction is the same as above, except that it was carried out at 75° instead of 45°. The reaction was allowed to proceed for the same length of time, and was worked up in the same manner. Glc analysis under the same conditions showed only n-hexanol in 49% yield. No phosphonium salt was found.

With Twenty Equivalents of Water, at 75°. This reaction is the same as above, except that twenty equivalents of water were used in place of ten, and the reaction was allowed to proceed for only 4 days instead of 5 days, but was worked up in the same manner. Glc analysis under the same conditions showed n-hexyltrifluoromethanesulfonate, and n-hexanol (25% yield). No phosphonium salt was found.

With Twenty Equivalents of Water, at 75°. This reaction is the same as above, except that the reaction was allowed to proceed for 7 days instead of 4 days. It was worked up in the same manner, and glc analysis under the same conditions showed a mixture of n-hexyltrifluoromethanesulfonate and n-hexanol (34% yield). No phosphonium salt was found.

With Twenty Equivalents of Water, at 75°; with One Equivalent of Calcium Carbonate. This reaction is the same as above, except that twenty equivalents of water were used in place of ten, and one equivalent of calcium carbonate was also added. The mixture was allowed to react for the same length of time, and was worked up in the same manner. Glc analysis under the same conditions showed a mixture of . .

n-hexyltrifluoromethanesulfonate and n-hexanol (35% yield). Some of the phosphonium salt (VII) was also found.

Reactions with HMPT

Four reactions were carried out to determine the products of the interaction of N-n-hexyl-N,N-di(trifluoromethane)sulfonimide with HMPT:

1. N-n-Hexyl-N,N-di(trifluoromethane)sulfonimide (0.26g, 0.72mmol) was dissolved in 1.0ml of HMPT, the flask was flushed with dry nitrogen, and the solution was stirred at room temperature for 47 hr. The mixture was poured into 5ml of water, and extracted with 4 x 5ml of ether. The combined extracts were washed with 2 x 5ml of water and 2 x 5ml of brine, and were dried over anhydrous magnesium sulfate. Removal of solvent gave 0.11g of colorless oil. Analytical and preparative glc at 120° on 10% carbowax 20M showed a mixture of N-n-hexyltrifluoromethanesulfonamide and n-hexyltrifluoromethanesulfonate. Nmr spectra of the crude product mixture indicated the presence of tris(dimethylamino)-n-hexyloxyphosphonium N,N-di(trifluoromethane)sulfonimide (VII): 0.89-1.35δ(m), 2.65-2.8δ(d, J=10), and 4.10δ(m).
2. N-n-Hexyl-N,N-di(trifluoromethane)sulfonimide (0.24g, 0.65mmol) was dissolved in 0.6ml of HMPT, the flask was flushed with dry nitrogen, and the mixture was stirred at room temperature. An nmr spectrum taken immediately after mixing showed the sulfonimide methylene signal at 4.20δ(t, J=7). After 6 hr, the signal had shifted to 4.3δ, and was no longer a clearly

resolved triplet. After 17-1/2 hr, the signal had shifted to 4.35δ, and was now a quartet. No indication of the sulfonimide was found; formation of the phosphonium salt (VII) appeared to be quantitative.

3. N-n-Hexyl-N,N-di(trifluoromethane)sulfonimide (0.22g, 0.61mmol) was dissolved in 0.6ml of HMPT, the flask was flushed with dry nitrogen, and the solution was stirred at room temperature for 1 day to allow the phosphonium salt (VIII) to form. This solution was then poured into an ice cold solution of 0.20g (1.11mmol) of potassium hexafluorophosphate in 3 ml of water. A brownish oil formed immediately; the oil would not solidify, even upon cooling to -10° for several days. The aqeuous solution was decanted from the oil, and acetone was added. The oil dissolved easily. The acetone was removed, and the oil was dried in a vacuum oven at room temperature, but could not be induced to crystallize. An nmr of the oil (hexdeuterioacetone solution) showed signals at 0.89-1.90δ(m, 11H), 2.80-2.98δ (d, J=10, 18H), 4.32δ(m, 2H). The ir (neat) showed absorption bands at 2925, 1490, 1480, 1350, 1310, 1225, 1185, 1140, 1060, 1000, and 840 cm^{-1}. These spectra, again, support the structure of the tris(dimethylamino)-n-hexyloxyphosphonium salt (VII).

4. The preparation of an HMPT solution of the phosphonium salt (VII) was carried out as described above using 0.15g (0.42mmol) of the sulfonimide in 0.4ml of HMPT. While cooling the phosphonium salt solution in ice, a solution of 0.34g (1.0mmol) of sodium tetraphenylboron in 10ml of water was added over 5 min.

A voluminous precipitate rapidly formed. After stirring with cooling for 1/2 hr, the white precipitate was removed by suction filtration and dried in air to give 0.18g of material with mp 160-161°. The yield was 73%. This crude product was recrystallized from absolute methanol to give a first crop of colorless needles of 0.16g with mp 169-196.5°. A second crop of colorless needles of 0.01g was obtained, having mp 168-168.5°. Total purified yield was 69%.

An ir spectrum (KBr pellet) showed bands at 3050, 2925, 1575, 1475, 1450, 1420, 1300, 1180, 1155, 1050, 1030, and 995 cm^{-1}. The nmr of the salt (hexadeuterioacetone solution) showed signals at 0.70-1.88δ (m, 11H), 2.70-2.87δ(d, J=10, 18H), 4.23δ(m, 2H), 6.89δ(m, 12H), and 7.14δ(m, 8H). Spin decoupling experiments were also performed: irradiation in the 1.63δ region caused the quartet at 4.23δ to collapse to a doublet with J=6. Also, irradiation at 4.23δ produced a simplification in the multiplet at 1.63δ.

Elemental microanalysis gave %C = 73.85, %H = 8.82, and %N = 7.30 (calculated: %C = 74.10, %H = 8.76, %N = 7.23). These spectral and analysis data all agree with the structure of VII as the tetraphenylboron salt.

Reactions of N-n-Hexyl-N,N-di(trifluoromethane)-sulfonimide with Various Nucleophiles, via the Tris(dimethylamino)-n-hexyloxyphosphonium Salt (VII) in HMPT

N-n-Hexyl-N,N-di(trifluoromethane)sulfonimide was allowed to react with HMPT to form the tris(dimethylamino)-n-hexyloxyphosphonium salt (VII). The HMPT solution of this salt was then allowed to react

with other various nucleophiles at room temperature. Experimental details are given below.

Reaction with Sodium Cyanide

Three reactions were carried out, differing in length of reaction time:

1. N-n-Hexyl-N,N-di(trifluoromethane)sulfonimide (0.24g, 0.655mmol) was dissolved in 0.6ml of HMPT, the flask was flushed with dry nitrogen, and the solution was stirred at room temperature for 20 hr. Sodium cyanide (0.04g, 0.773mmol) was added in one portion, and stirring at room temperature was continued. After 4-1/2 hr, an nmr showed a diminishing of the signal at 4.35δ, indicating that most of the tris(dimethylamino)-n-hexyloxyphosphonium salt (VII) had reacted, but some was still present. Monitoring by nmr continued; after 194 hr no further change was noted, and the solution was poured into 35 ml of water, and extracted with 3 x 10ml of ether. The combined extracts were washed with 10ml of water and 10ml of brine, and were dried over anhydrous magnesium sulfate. Removal of solvent gave 0.10g of yellow oil. An attempt to dissolve this product in CCl_4 resulted in the precipitation of a yellowish solid. The mixture was filtered free of the solid, which was identified as unreacted phosphonium salt by its ir and nmr spectra, and the filtrate was diluted to 1.0ml with CCl_4 in a volumetric flask. Analytical glc at 110° on 10% SE-30 showed a mixture of n-hexyl cyanide and

N,N-di-n-hexyltrifluoromethanesulfonamide. Samples of each product were obtained by preparative glc, and their ir and nmr spectra and glc retention times were compared with those of authentic samples. The yield of n-hexyl cyanide was 36%.

2. This reaction was the same as that described above, except that the mixture was stirred at room temperature for 4 days after adding the sodium cyanide to the phosphonium salt solution instead of 8 days. Work up was carried out in exactly the same manner, as was glc analysis. A 58% yield of n-hexyl cyanide was obtained by glc; N,N-di-n-hexyltrifluoromethanesulfonamide was also found.

3. This reaction was carried out in exactly the same manner as above, but on twice the scale. Work up and analytical glc were the same, and a 72% yield of n-hexyl cyanide was obtained. The CCl_4 solution used for glc analysis was concentrated, and the residue was bulb-to-bulb distilled at 0.35mm pressure and at an air bath temperature of 90° to isolate the n-hexyl cyanide from the N,N-di-n-hexyltrifluoromethanesulfonamide also present. A 59% isolated yield of n-hexyl cyanide was obtained.

Reaction with Diethyl Sodiomalonate

An HMPT solution of the tris(dimethylamino)-n-hexyloxyphosphonium salt (VII) was prepared as described above from 0.24g (0.670 mmol) of N-n-hexyl-N,N-di(trifluoromethane)sulfonimide in 0.6ml of HMPT. Diethyl sodiomalonate was prepared by adding 0.13g (0.805mmol) of diethyl malonate in 0.2ml of HMPT to 0.03g (0.807mmol, 57% oil

dispersion, washed in ether) of sodium hydride suspended in 0.2ml of HMPT and cooled in ice, over a 3/4 hr period. The mixture was stirred with cooling for an additional 1 hr, then the phosphonium salt solution was added with cooling over 1/2 hr. After stirring at room temperature for 4 days, the mixture was worked up as described above. Analytical glc at 165° on 10% SE-30 showed a mixture of diethyl malonate, N,N-di-n-hexyltrifluoromethanesulfonamide, and diethyl n-hexylmalonate (87% yield). Samples of each product were obtained by preparative glc, and their ir and nmr spectra and glc retention times were compared with those of authentic samples.

Reaction with Malononitrile Sodium Salt

An HMPT solution of the tris(dimethylamino)-n-hexyloxyphosphonium salt (VII) was prepared as described above from 0.20g (0.56mmol) of N-n-hexyl-N,N-di(trifluoromethanesulfonimide in 0.5ml of HMPT. Malononitrile sodium salt was prepared by adding 0.04g (0.65mmol) of malononitrile in 0.2ml of HMPT to a cooled suspension of 0.03g (0.65mmol, 57% oil dispersion, washed with ether) over 3/4 hr. The mixture was further stirred with cooling for 1/2 hr, then the malononitrile salt solution was added to the phosphonium salt solution over 1/2 hr, while cooling in ice. After stirring at room temperature for 4 days, the mixture was worked up as described above. Analytical glc at 150° on 10% SE-30 showed a mixture of N,N-di-n-hexyltrifluoromethanesulfonamide, n-hexylmalononitrile (24% yield), and di-n-hexylmalononitrile (19% yield). Samples of each product were obtained by preparative glc, and their ir and nmr spectra and glc retention times

were compared with those of authentic samples. A mixture of n-hexylmalononitrile and di-n-malononitrile was prepared by the general method of Bloomfield (159).

Reaction with Sodium Azide

An HMPT solution of the tris(dimethylamino)-n-hexyloxyphosphonium salt (VII) was prepared as described above from 0.22g (0.614 mmol) of N-n-hexyl-N,N-di(trifluoromethane)sulfonimide in 0.6ml of HMPT. Sodium azide (0.05g, 0.7mmol) was added in one portion, and the mixture was stirred at room temperature for 4 days, then worked up as described above. Analytical glc at 135° on 10% SE-30 showed a mixture of n-hexylazide (14% yield) and N-n-hexyltrifluoromethanesulfonamide. No N,N-di-n-hexyltrifluoromethanesulfonamide was found. Samples of each product were obtained by preparative glc, and their ir and nmr spectra and glc retention times were compared with those of authentic samples. An authentic sample of n-hexylazide was prepared by the method of Henkel and Weygand (160).

Reaction with 1,3-Dithiane Lithium Salt

An HMPT solution of the tris(dimethylamino)-n-hexyloxyphosphonium salt (VII) was prepared as described above from 0.2g (0.556 mmol) of N-n-hexyl-N,N-di(trifluoromethane)sulfonimide in 0.5ml of HMPT. The 1,3-dithiane lithium salt was prepared by adding 0.34ml (0.5mmol, 1.6M hexane solution) of n-butyl lithium to 0.07g (0.60mmol) of 1,3-dithiane in 0.5ml of THF, cooled to -78°, over a period of 1/2 hr. The mixture was warmed to 0°, and the THF removed by a stream of

dry nitrogen; 0.5ml of HMPT were then added. The lithium salt solution was then added to the phosphonium salt solution, with cooling in ice, over a period of 1/2 hr. After stirring at room temperature for 4 days, the mixture was worked up as described above. Analytical glc at 135° on 10% SE-30 showed a mixture of 1,3-dithiane, N,N-di-n-hexyltrifluoromethanesulfonamide, and 2,2-di-n-1,3-dithiane (11% yield). Samples of each product were obtained by preparative glc and their ir and nmr spectra and glc retention times were compared with those of authentic samples.

Reaction with Phenyl Copper

An HMPT solution of the tris(dimethylamino)-n-hexyloxyphosphonium salt (VII) was prepared as described above from 0.21g (0.564mmol) of N-n-hexyl-N,N-di(trifluoromethane)sulfonimide in 0.5ml of HMPT. An ether solution of phenyl copper was prepared by the method of Costa et al. (126) from 0.11g (0.805mmol) of cuprous bromide and 0.44ml (0.7mmol, 1.6M in ether-benzene) of phenyl lithium. Without isolating the phenyl copper from the ethereal solution, it was cooled to -20°, and the phosphonium salt solution, diluted to 1.5ml with ether, was added over 5 min. After stirring at room temperature for 4 days, the mixture was poured into 5ml of 6N hydrochloric acid, and extracted with 3 x 10ml of ether. The extracts were dried over anhydrous magnesium sulfate, and the solvent was removed. Analytical glc at 175° on 10% SE-30 showed several peaks, none of them major. Bulb-to-bulb distillation at 0.35mm pressure at an air bath temperature of 90-97° gave a small amount of material, which gave six bands on TLC (silica gel, with

benzene as eluting solvent). The three major bands were isolated by preparative TLC (same conditions as above), and ir spectra were taken of the isolated products. One of the products was identified as benzoic acid by comparison of ir spectra, but none of the other products was conclusively identified; 1-phenyl hexane was not found in the products.

Reactions with Water

Four reactions were carried out, varying temperature and amount of water used:

With Five Equivalents of Water, at Room Temperature for 4 Days. An HMPT solution of the tris(dimethylamino)-n-hexyloxyphosphonium salt (VII) was prepared as described above from 0.20g (0.557mmol) of N-n-hexyl-N,N-di(trifluoromethane)sulfonimide in 0.5ml of HMPT. Water (50.1µl, 2.8mmol, 5x excess) was added in one portion and the mixture was stirred at room temperature for 4 days. The mixture was poured into 45ml of water, and extracted with 4 x 10ml of ether. The combined extracts were washed with 10ml of water and 10ml of brine, and were dried over anhydrous magnesium sulfate. Removal of solvent gave 0.23g of colorless liquid, which was insoluble in CCl_4, but soluble in acetone. The product was diluted to 1.0ml with acetone; analytical glc at 95° on 10% Ucon 50LB 550X showed a 9% yield of n-hexanol. Analytical glc at 125° on 10% SE-30 also showed the presence of n-hexyltrifluoromethanesulfonate.

With Five Equivalents of Water, at Room Temperature, for 18 Days. The procedure followed here was exactly the same as that indicated above except that the mixture was stirred at room temperature for 18 days instead of 4 days before working it up. Analytical glc under the same conditions showed a 13% yield of n-hexanol. Some n-hexyltrifluoromethanesulfonate was present as well.

With Five Equivalents of Water, at 45°, for 5 Days. This procedure is the same as that described above, except that the mixture was stirred at 45° for 5 days instead of at room temperature for 4 days. Analytical glc under the same conditions showed a 43% yield of n-hexanol. Some n-hexyltrifluoromethanesulfonate was also found.

With Ten Equivalents of Water, at 45°, for 7 Days. This procedure is the same as that described above, except that ten equivalents of water were used instead of only five, and the mixture was heated at 45° for 7 days, instead of remaining at room temperature for 4 days. Analytical glc under the same conditions showed a 47% yield of n-hexanol. Another, unidentified, peak was found in the glc analysis, but in much smaller amount than the alcohol.

Isolation of Tris(dimethylamino)-n-hexyloxyphosphonium tetraphenylboron from the Reaction of N-n-Hexyl-N,N-di(trifluoromethane)sulfonimide with Sodium Azide in HMPT

A solution of 0.08g (1.29mmol) of sodium azide in 1.25 ml of HMPT was cooled in ice, and a solution of 0.44g (1.21mmol) of N-n-hexyl-N,N-di(trifluoromethane)sulfonimide in 0.25ml of HMPT was added over 15 min. After stirring at room temperature for 5 days, the mixture

was poured into 50ml of water and extracted with 3 x 15ml of ether. The combined extracts were washed with 2 x 10ml of brine and were dried over anhydrous magnesium sulfate. Removal of solvent gave 0.30g of yellow liquid. Analytical glc of the product on 10% SE-30 at 150° indicated a mixture of n-hexyl azide (4% yield), N-n-hexyltrifluoromethanesulfonamide, and N,N-di-n-hexyltrifluoromethanesulfonamide.

One-half of the original aqueous layer from the reaction work up was acidified with 6N hydrochloric acid, and extracted with 2 x 20ml of ether. Only 0.01g of liquid was obtained after work up of the ether extracts, and glc (same conditions as above) showed only a trace of N-n-hexyltrifluoromethanesufonamide present.

The other half of the original aqueous layer was mixed with a solution of 0.50g (1.4mmol) of sodium tetraphenylboron in 5ml of water. An immediate white precipitate formed, which changed to an oil. The oil was removed by extraction with ethyl acetate. The combined extracts were washed repeatedly with water, and once with brine, and were dried over anhydrous magnesium sulfate. Removal of solvent gave 0.57g of yellowing solid. The ir (KBr pellet) of the solid was identical with that of tris(diethylamino)-n-hexyloxyphosphonium tetraphenylboron. An nmr (hexadeuterioacetone solution) showed the phosphonium salt with a small amount of some impurity. No further purification was carried out.

The aqueous layer from the precipitation of the phosphonium salt was acidified with 6N hydrochloric acid and extracted with ether. Work up of the ether extracts gave 0.03g of brown solid/oil, which glc

(same conditions as above) showed to contain no N-n-hexyltrifluoromethanesulfonamide.

Attempts to Trap N-n-Hexyltrifluoromethanesulfonamide from the Equilibrium Between HMPT and N-n-Hexyl-N,N-di(trifluoromethane)sulfonimide

Two attempts were made to trap N-n-hexyltrifluoromethanesulfonamide as N-methyl-N-n-hexyltrifluoromethanesulfonamide from the rapid equilibrium between HMPT and N-n-hexyl-N,N-di(trifluoromethane)-sulfonimide. The only difference between the methods used was the choice of methylating agents. Details of the procedures are given below.

Procedure A

N-n-Hexyl-N,N-di(trifluoromethane)sulfonimide (0.18g, 0.51mmol) was dissolved in 1.0ml of HMPT, and the solution was cooled in ice. Methyl iodide (0.71g, 5.0mmol) was added quickly, and the mixture was stirred at room temperature for 5 days. The mixture was poured into 75ml of water, and extracted with 4 x 10ml of ether. The combined extracts were washed with 15ml of water and 15ml of saturated brine, and were dried over anhydrous magnesium sulfate. Solvent removal gave 0.11g of yellow liquid.

Upon mixing the product mixture with CCl_4, a separate yellow layer formed, yielding 0.05g of the phosphonium salt VII, as identified by its ir and nmr spectra. After removal of the phosphonium salt, the remainder of the CCl_4 solution of the product mixture was diluted to 1.0ml with the same solvent, and analyzed by glc. Analysis showed a

trace of unreacted sulfonimide, approximately 10% n-hexyl-trifluoromethanesulfonate (peak partially under solvent peak), a 10% yield of N-n-hexyltrifluoromethanesulfonamide, and a 33% yield of 1-iodohexane. No evidence of N-methyl-N-n-hexyltrifluoromethanesulfonamide was found. Samples of each product were obtained by preparative glc, and identified by comparison of their ir and nmr spectra and glc retention times with those of authentic samples.

Procedure B

This procedure is identical to that discussed above, except that methyl trifluoromethanesulfonate was used in place of methyl iodide as the methylating agent. Upon addition of the methyl trifluoromethanesulfonate, a gelatinous precipitate formed. After 5 days, work up was carried out as indicated above. During the washing of the combined ether extracts, an oil separated and was removed from the mixture by decantation. After drying, the oil solidified to a crystalline white solid with mp $> 310^{\circ}$. An ir (KBr pellet) showed absorption bands at 2935, 2850, 1445, 1345, 1300, 1205, 1175, 1115, 1025, and 990 cm^{-1}. As the product was insoluble in CCl_4, $CHCl_3$, CH_3CN, water, acetone, ether, benzene, carbon disulfide, trifluoroacetic acid, and dimethyl sulfoxide, an nmr was not available. However, the ir is consistent with the salt: tris(dimethylamino)methoxyphosphonium N,N-di(trifluoromethane)sulfonimide.

Removal of solvent from the dried ether extracts gave 0.09g of yellow oil. Upon mixing the product with CCl_4, a separate yellow

layer of phosphonium salt VII formed. Isolation of the salt layer gave 0.06g of the salt, which was identified by its ir and nmr spectra.

The remainder of the product mixture solution was diluted to 1.0ml with CCl_4 and analyzed by glc. The results indicated an approximately 10% yield (peak partially obscured by solvent) of n-hexyltrifluoromethanesulfonate, a 9% yield of unreacted sulfonimide, and a 22% yield of N-n-hexyltrifluoromethanesulfonamide. No evidence of N-methyl-N-n-hexyltrifluoromethanesulfonamide was found. Samples of each product were obtained by preparative glc, and identified by comparison of their ir and nmr spectra and glc retention times with those of authentic samples.

Reaction of N-n-Hexyltrifluoromethanesulfonamide Sodium Salt with the Product of the Reaction of HMPT with Trifluoromethanesulfonic Acid Anhydride

Sodium hydride (0.05g, 57% oil dispersion, 1.25mmol) was washed with ether, then suspended in 0.5ml of HMPT. While cooling the suspension in ice, a solution of N-n-hexyltrifluoromethanesulfonamide (0.27g, 1.17mmol) in 0.25ml of HMPT was added over 1/2 hr. The solution was warmed to room temperature and stirred for an additional 1/2 hr. The solution was again cooled in ice, and a suspension of 0.92g of the product of the reaction of HMPT with trifluoromethanesulfonic acid anhydride (presumably trifluoromethanesulfonylated HMPT) in 1.25ml of HMPT was added over 1/2 hr.

One hour after mixing, an nmr was taken: in addition to the solvent signals, absorptions were also noted at 4.45δ (small, but broad) and 7.80δ (large, but also broad). This pattern suggested

the presence of N-n-hexyltrifluoromethanesulfonamide. After allowing the mixture to react for an additional hour, an nmr showed a great increase in the size of the signal at 4.3-5.4δ, and a decrease in the signal now at 8.25δ. In addition, three other small, broad signals were observed in the region 5.8-7.5δ. An nmr taken 3-1/2 hr after mixing showed that the signal at approximately 5δ had diminished substantially; no further changes were noted for the next three hours.

After 6-1/2 hr, a 0.5ml portion (approximately 1/4 of the total) of the reaction mixture was removed and mixed with 30ml of water. After extracting with 4 x 10ml of ether, the combined extracts were washed with 10ml of water and 10ml of brine, and were dried over anhydrous magnesium sulfate. Removal of solvent gave 0.05g of yellowish liquid. Analysis by glc on 10% SE-30 showed the product to consist only of N-n-hexyltrifluoromethanesulfonamide; no sulfonimide was found. The amount of sulfonamide found corresponded to 78% of the amount initially used.

Twenty-one hours after mixing, another nmr showed a slight decrease in the 5δ signal. Another 0.5ml portion of the reaction mixture was removed, and mixed with a solution of 0.34g (1mmol) of sodium tetraphenylboron in 10ml of water. The solution immediately became milky, and a white precipitate fell out of solution. The solid was filtered, but the filtrate remained milky. Centrifugation of the filtrate yielded more material. An ir (KBr pellet) of the crude precipitate clearly demonstrated the presence of the phosphonium salt VII as the tetraphenylboron salt. An attempt to recrystallize the precipitate from methanol resulted in hydrolysis of the salt.

After forty-seven hours, no change was noted in the nmr. One-half of the remaining reaction mixture was worked up by the ether extraction procedure indicated above. Removal of solvent from the dried extracts gave 0.04g of yellowish liquid, which glc showed to contain a mixture of HMPT and N-n-hexyltrifluoromethanesulfonamide. The amount of sulfonamide found corresponded to only 63% of the total initially used. Again, no sulfonimide was found.

The other half of the reaction mixture was treated with an aqueous sodium tetraphenylboron solution as described above. The suspension which resulted was centrifuged to yield an oily solid, which nmr showed to consist of a mixture of N-n-hexyltrifluoromethanesulfonamide and other products. An ir (KBr pellet) of the solid portion of the product clearly showed the phosphonium salt VII as the tetraphenylboron salt. Again, attempts to recrystallize the salt resulted in complete hydrolysis.

Reaction of N-(2-Phenethyl)-N,N-di(trifluoromethane)-sulfonimide with Water in HMPT at 45°

N-(2-Phenethyl)-N,N-di(trifluoromethane)sulfonimide (0.32g, 0.828mmol) was dissolved in 0.8ml of HMPT, and 149.0 µl (8.28mmol, 10X excess) of water was added in one portion. The mixture was heated at 45° for 5 days, then poured into 50ml of water and extracted with 4 x 10ml of ether. The combined extracts were washed with 2 x 10ml of water and 10ml of brine, and were dried over anhydrous magnesium sulfate. Removal of solvent gave 0.35g of yellow liquid, which was then dissolved in CCl_4 and diluted to 1.0ml in a volumetric flask. A separate yellow layer formed, and was brought back into solution by the

addition of a little ether. The volume was adjusted to 1.0ml, and the solution analyzed by glc at 125° on 10% SE-30. The analysis indicated a 31% yield of 2-phenethyl alcohol. A sample of the product was obtained by preparative glc, and its ir and nmr spectra and glc retention time were compared with those of an authentic sample.

The ether was removed from the solution, and CCl_4 was added; the yellow layer which formed was removed. Nmr (hexadeuterioacetone solution) showed signals at 2.62-2.80δ (d, J=10); 3.42δ (m); 3.75δ (m); and 7.22δ (t, J=3). The ir (neat) showed absorption bands at 2910, 1350, 1270, 1180, 1135, 1050, and 985 cm^{-1}. These data suggested the compound: tris(dimethylamino)-2-phenethyloxyphosphonium N,N-di(trifluoromethane)sulfonimide (X).

Preparation of Tris(dimethylamino)-2-phenethyloxyphosphonium Tetraphenylboron (X)

N-(2-Phenethyl)-N,N-di(trifluoromethane)sulfonimide (0.26g, 0.665mmol) was dissolved in 0.7ml of HMPT, and the solution was stirred at room temperature for 3 days to allow the phosphonium salt (X) to form. A solution of 0.38g (1.1mmol) of sodium tetraphenylboron in 10ml of water was added over 5 min to the phosphonium salt solution, while cooling in ice. A voluminous white precipitate formed during the addition. After stirring with cooling for 1/2 hr, the mixture was filtered, and the solid washed with water. Air drying afforded 0.22g of white solid (51% crude yield). Methanol proved unsuitable for a recrystallizing solvent, but the product dissolved in 95% ethanol at reflux. Upon cooling in ice, however, only a very small amount of recrystallized product was obtained, even upon concentration of the

mother liquor. The mp=192-194°, and an ir (KBr pellet) showed absorption bands at 3050, 2990, 1475, 1455, 1305, 1175, 1150, 1060, and 1000 cm^{-1}. The ir spectrum is consistent with the structure of (X) as the tetraphenylboron salt.

Recovery of n-Hexanol from Aqueous HMPT Solution

n-Hexanol (0.11g, 1.10mmol) was mixed with 1ml of HMPT and 0.2ml of water, and the solution was stirred and heated at 75°. After 4 days, the mixture was poured into 30ml of water and extracted with 2 x 15ml of ether. The combined extracts were washed with 2 x 10ml of water and 10ml of brine, and were dried over anhydrous magnesium sulfate. Removal of solvent gave 0.08g of yellowish liquid. Glc (10% Ucon 50LB 550X and 10% SE-30) showed only n-hexanol. No di-n-hexyl ether or tris(dimethylamino)-n-hexyloxyphosphonium N,N-di(trifluoromethane)sulfonimide (VII) was seen. Only 70% of the alcohol was recovered.

Attempted Preparation of the Tris(dimethylamino)-n-hexyloxyphosphonium Salt (VII) from n-Hexylamine and HMPT

Four unsuccessful attempts were made to prepare this phosphonium salt. The procedures followed are outlined below.

Procedure A

n-Hexylamine was dissolved in a three-fold molar excess of HMPT, and the solution was cooled to 0°. One equivalent of nitrosyl hexafluorophosphate was added, and was accompanied by evolution of gas and a blue-green coloration of the reaction mixture. The mixture was

allowed to warm to room temperature over 1/2 hr, then an nmr was taken. No significant change was noted over that of a solution of n-hexylamine and HMPT alone. No change was noted even after heating the mixture at 95° for 1/2 hr. Work up of the mixture gave a mixture of n-hexylamine and HMPT.

Procedure B

This is similar to above, except that the amine was dissolved in CH_3CN, then cooled to -78°. One equivalent of the nitrosyl hexafluorophosphate was added, causing a blue-green color to form, then the solution was warmed slightly to about -20°, and one equivalent of HMPT was added. The solution was then warmed to 0°; the color faded gradually upon warming. Most of the CH_3CN was then removed under a stream of dry nitrogen, and replaced by HMPT, keeping the mixture at 0° throughout. The mixture was warmed to room temperature, and an nmr was taken. Only n-hexylamine and HMPT were seen in the nmr.

Procedure C

One equivalent each of n-hexylamine and HMPT were dissolved in CH_3CN and the solution was cooled to -40°. One equivalent of nitrosyl hexafluorophosphate was added, accompanied by the evolution of brown gas. The mixture was warmed to 0°, during which time the blue-green color faded. After 1/2 hr at 0°, the mixture was warmed to room temperature, and an nmr was taken. Only n-hexylamine and HMPT were found, along with the CH_3CN.

Procedure D

Following the procedure of Friedman and Chlebowski (161), one equivalent each of n-hexylamine and HMPT were dissolved in benzene, and one equivalent of iso-amyl nitrite was added. No evolution of gas was noted, and the solution was refluxed, with nmr spectra being taken periodically to follow the reaction. After 20 hr at reflux, the only reaction noted was a partial decomposition of the iso-amyl nitrite.

Recovery of N-n-Hexyltrifluoromethanesulfonamide from Aqueous HMPT Solution

N-n-Hexyltrifluoromethanesulfonamide (0.23g, 0.97mmol) was dissolved in 0.5ml HMPT, and the solution was added over 1/2 hr to an ice cold suspension of sodium hydride (0.05g, 57% oil dispersion, 1.11mmol) in 0.5ml HMPT. The mixture was stirred at room temperature overnight, then poured into 100ml of water and extracted with 3 x 15ml of ether. The combined extracts were washed with 15ml of brine, and were dried over anhydrous magnesium sulfate. Removal of solvent gave 0.23g of colorless liquid. The aqueous solution was reserved for later treatment. Analytical glc on 10% SE-30 at 130° showed two overlapping components were present in the product. The product mixture was dissolved in CCl_4, and extracted with 5% aqueous sodium hydroxide solution. The aqueous layer was acidified with 6N hydrochloric acid and again extracted with CCl_4. The extracts were washed with brine, and were dried over anhydrous magnesium sulfate. Removal of solvent gave 0.11g of colorless liquid. Analytical glc now showed only the N-n-hexyltrifluoromethanesulfonamide. The amount recovered was only

30%. It was estimated that up to as much as an additional 20% was lost during the purification procedure.

The original aqueous solution from the isolation extraction above was acidified with 6N hydrochloric acid, and extracted with 3 x 10ml of ether. The combined extracts were washed with brine and dried over anhydrous magnesium sulfate. Removal of solvent gave 0.06g of colorless liquid. Analytical glc showed only N-n-hexyltrifluoromethanesulfonamide was present; 12% of the original amount was recovered.

Recovery of the N-Phenyltrifluoromethanesulfonamide Anion from Aqueous HMPT Solutions

N-Phenyltrifluoromethanesulfonamide (0.2g, 0.89mmol) was converted to its sodium salt in 10ml of HMPT by adding one equivalent of sodium hydride (as a 57% oil dispersion). The mixture was poured into 200ml of water and acidified with a little 5N hydrochloric acid. The solution was extracted with 4 x 10ml of ether, and the extracts were washed with 3 x 10ml of water and 20ml of brine, and were dried over anhydrous magnesium sulfate. Removal of solvent gave a quantitative yield of the original sulfonamide, whose identity was confirmed by nmr.

Trifluoromethanesulfonylation of HMPT with Trifluoromethanesulfonic Acid Anhydride

Four attempts were made to prepare trifluoromethanesulfonylated HMPT as the trifluoromethanesulfonate salt.

Procedure A

Trifluoromethanesulfonic acid anhydride (3.57g, 12.68mmol) was dissolved in 30ml of CH_2Cl_2, and the solution was cooled in ice. Over 1/2 hr, HMPT (2.26g, 12.60mmol) was added. A gelatinous precipitate appeared during the addition, and the entire mixture eventually gelled. An additional 5ml of CH_2Cl_2 was added. After 3 days, the mixture was filtered, and the crystalline white solid was washed with CH_2Cl_2 and air dried. A total of 2.44g of product were obtained.

An ir (KBr pellet) showed absorption bands at 2925, 1490, 1465, 1315, 1260, 1220, 1155, 1050, 1028, 1010, 960, 767, and 750 cm^{-1}. The nmr (hexadeuterioacetone or trideuterioacetonitrile solutions) showed three signals rather than the expected two: 2.90, 3.08, and 3.17δ. The first and last signals appeared to constitute a doublet with J=12. While the ir was in reasonable agreement with the structure of the desired product, the nmr indicated the presence of some impurity, or some entirely unexpected compound as the only product. No definitive structural assignment was made.

Procedure B

This procedure is the same as above, except that the HMPT addition was carried out at -25° instead of at 0°, and the mixture was worked up after only 10 min at room temperature. The precipitate was filtered, washed, and dried as above, yielding 0.68g of crystalline white solid. An nmr (hexadeuterioacetone solution) showed the same product obtained above. The addition of a little water to the nmr sample showed the appearance of a doublet at 2.60-2.75δ, which is

consistent with HMPT. After 24 hr, the new doublet had increased greatly, and after 3 days, nearly all the original signal had disappeared.

Whatever product was initially formed, hydrolysis gave back HMPT as one of the products.

Procedure C

This procedure is the same as above except that CCl_4 was used in place of CH_2Cl_2 as the solvent, and the solution of trifluoromethanesulfonic acid anhydride was added to the HMPT solution. After stirring at 0° for 1/2 hr, the mixture was worked up as above. The product obtained was pasty in consistency, as if hygroscopic rather than wet with solvent. The nmr (hexadeuterioacetone solution) was different from the previously obtained products, having signals at 2.70-2.85 (d), 2.93, 3.03, 3.11, and 7.51δ. No structure was proposed for this product(s).

Procedure D

This procedure is the same as above except that benzene was used in place of CH_2Cl_2 as the solvent, and the mixture was worked up after only 20 hr at room temperature. Again, a pasty product was obtained, which nmr (hexadeuterioacetone solution) showed to be a mixture of HMPT and the same product obtained above.

Preparation of Dimethyl Adipate

Adipic acid (100.0g, 0.695mol) was added to 250 ml of absolute methanol and 1ml of conc. sulfuric acid was refluxed for

18 hr. The mixture was then vacuum distilled. The first fractions, containing methanol and water, were discarded. The yield of dimethyl adipate, bp 88°/1mm, was 118.2g (98% yield).

Preparation of 2-Carbomethoxycyclopentanone

In a manner similar to that employed by Pinkey (162) for the preparation of the ethyl ester, sodium hydride (8.5g, 57% oil dispersion, 0.2mol) was added to 100ml of toluene in a 3-neck flask fitted with a stirrer, a reflux condenser, and a dropping funnel. The slurry was heated at 50°, and 1ml of absolute methanol was added. Dimethyl adipate (17.5g, 0.1mol) in 80ml of toluene was added over 15 min. About 30 min after the addition, the mixture had become a thick gel, and an additional 125ml of toluene were added. After 15 hr, the mixture was poured into a solution of 150ml of diethyl ether and 25ml of methanol. Ice (200g) was added and the mixture was made acid to Congo red paper with 6N hydrochloric acid. The layers were separated, and the aqueous was washed once with 50ml of toluene, and then discarded. The combined organic layers were washed with 50ml of saturated aqueous sodium bicarbonate and 2 x 100ml of H_2O. The bulk of the solvent was removed by rotary evaporation, and the residue was vacuum distilled to yield 10.6g of product (73% yield) with bp 68°/0.7mm.

Preparation of Deuteriotrifluoromethanesulfonic Acid

Deuterium oxide (0.70g, 35.1mmol) was mixed with trifluoromethanesulfonic acid anhydride (10.05g, 37.3mmol), and the mixture was stirred at room temperature for five days. At this time, the mixture had become homogeneous, indicating that hydrolysis was complete.

Preparation of Pyridinium Deuteriotrifluoromethanesulfonate

Pyridine (1.59g, 20mmol) was dissolved in 25ml of CCl_4, and the solution was cooled in ice. Deuteriotrifluoromethanesulfonic acid (3.04g, 20mmol) in 1ml of CCl_4 was added over 30 min. After stirring for 2 hr, the mixture was filtered, and the product was washed with CCl_4. The salt was recrystallized from ethyl acetate to yield 3.86g (84% yield) of product.

Preparation of Triethylammonium Deuteriotrifluoromethanesulfonate

The salt was obtained in 84% yield using the same procedure described for the pyridinium salt.

Preparation of Pyridinium Trifluoromethanesulfonate

This salt was prepared from pyridine and trifluoromethanesulfonic acid by the same procedure described for the preparation of the deuterated salt. The yield was 78% after recrystallization from ethyl acetate.

Preparation of 1-Carbomethoxy-2-trimethylsiloxycyclopentene

The method used was a modification of that used by Kusnezowa, Rühlmann, and Gründermann (163): 2-Carbomethoxycyclopentanone (2.15g, 15.1mmol) and triethylamine (1.62g, 16.1mmol) were dissolved in 25ml of toluene, and the solution was heated to 65°. Trimethylsilyl chloride (1.75g, 16.1mmol) in 10ml of toluene was added over 15 min, and the mixture was stirred at 65° for 4 hr. The mixture was filtered through Celite, and the toluene was removed under vacuum. The residue

was vacuum distilled to give 2.51g (77% yield) of product with bp 60-61°/0.2mm.

An ir spectrum in CCl_4 solution showed absorptions at 2875, 1710, 1625, 1440, 1370, 1300, 1180, 1150, and 1045 cm^{-1}. An nmr spectrum in CCl_4 solution with external TMS standard showed the following signals: 0.10δ (s, 18H); 1.70δ (m, 2H); 2.30δ (m, 4H); and 3.48δ (s, 3H). The uv spectrum in cyclohexane solution showed λ_{max} at 241.0nm with ε 1.0×10^4.

Preparation of 2-Deuterio-2-carbomethoxycyclopentanone

1-Carbomethoxy-2-trimethylsiloxycyclopentene (2.51g, 11.7mmol) was dissolved in 6ml of CCl_4, and 0.83g (25mmol) of methanol-d_1, prepared by the method of Streitweiser, Verbit, and Stang (164), were added as a solution in 2ml of CCl_4 in one portion. After stirring at room temperature for 2 days, the mixture was vacuum distilled to give 1.62g (97% yield) of 2-deuterio-2-carbomethoxycyclopentanone with bp 50-52°/0.12mm. Comparison of the nmr integration ratio of the methyl (3.80δ, s, 1H) and methinyl (3.10δ, t, J=8, 3H) signals of 2-carbomethoxycyclopentanone with that of the product indicated more than 95% incorporation of deuterium into the 2-position.

Reactions of 2-Carbomethoxycyclopentanone with Trifluoromethanesulfonic Acid Anhydride and Various Bases in CCl_4

The procedure employed was similar to that of Stang and Dueber (103) for the preparation of vinyl trifluoromethanesulfonates, except that a series of amines were used as catalysts. Reaction time was determined by the length of time necessary for the characteristic

color change to occur, and varied from 1 to 5 days. A specific example is given.

Trifluoromethanesulfonic acid anhydride (3.73g, 13.1mmol) was rapidly added to a mixture of 2-carbomethoxycyclopentanone (1.73g, 12.0mmol) and pyridine (1.03g, 13.1mmol) in 30ml of CCl_4 cooled to -78°. As the mixture was allowed to warm to room temperature, the color began to darken, and solids began to form. After 3 days, the mixture was filtered, and the solids and tars were mixed with 40ml of water. The aqueous solution was extracted with 5ml of CCl_4; the extracts were combined with the filtrate, and the mixture was washed with 2 x 10ml of water, and was dried over anhydrous magnesium sulfate. Solvent was removed by rotary evaporation, and the residue was vacuum distilled to yield 0.90g of a mixture with bp $53-57^{\circ}$/0.3mm consisting of unreacted ester, and both isomers of the vinyl trifluoromethanesulfonate.

Preparative glc on 5% SE-30 permitted the isolation and characterization of each isomer. 2-Carbomethoxy-1-cyclopentenyl-2-trifluoromethanesulfonate (VI) showed nmr signals (CCl_4 solution) at 2.10δ (m, 2H); 2.78δ (t, J=7, 4H); 3.80δ (s, 3H). The ir (CCl_4 solution) showed bands at 2950, 1725, 1655, 1425, 1350, 1205, 1170, 1140, 1050, and 1000 cm^{-1}. The uv spectrum (cyclohexane solvent) showed λ_{max} at 198nm with ε 4.2 x 10^3. Elemental microanalysis gave 35.24% C, 3.29% H, and 11.62% S (calculated: 35.04% C, 3.31% H, and 11.69% S).

3-Carbomethoxy-2-cyclopentenyl-2-trifluoromethanesulfonate (V) showed nmr signals (CCl_4 solution) at 2.40δ (m, 5H); 3.70δ (s, 3H);

5.80δ (m, 1H). The ir spectrum (CCl_4 solution) showed absorption bands at 2950, 1740, 1650, 1420, 1330, 1205, 1170, 1060, and 970 cm^{-1}. The uv spectrum (cyclohexane solvent) showed λ_{max} at 220.5nm with ε 1.2 x 10^4. Elemental microanalysis gave 35.19% C, 3.23% H, and 11.60% S (calculated: 35.04% C, 3.31% H, and 11.69% S).

In each reaction, the yield of vinyl trifluoromethanesulfonates, and the ratio of isomers, was determined by quantitative glc on a 5% SE-30 column. A response factor was previously determined for each compound under the same analysis conditions.

Reaction of 2-Deuterio-2-carbomethoxycyclopentanone with Trifluoromethanesulfonic Acid Anhydride and Pyridine in Carbon Tetrachloride

The procedure followed was identical to the reaction with 2-carbomethoxycyclopentanone, except that 2-deuterio-2-carbomethoxy-cyclopentanone was used in its place.

Reaction of 2-Carbomethoxycyclopentanone with Trifluoromethanesulfonic Acid Anhydride and Pyridine in CH_2Cl_2

The procedure followed was identical to that done previously, but here CH_2Cl_2 was substituted for CCl_4 as solvent. A small change was noted in the ratio of vinyl trifluoromethanesulfonate isomers produced, as was expected.

Reactions of 2-Carbomethoxycyclopentanone with Trifluoromethanesulfonic Acid Anhydride and Various Bases, in the Presence of the Amine Salt of Deuteriotrifluoromethanesulfonic Acid in CH_2Cl_2

The reactions were run using pyridine and triethylamine as catalysts, in the presence of their deuteriotrifluoromethanesulfonate salts. A specific example is given below.

2-Carbomethoxycyclopentanone (1.74g, 12.0mmol), pyridine (0.48g, 6.0mmol), and pyridinium deuteriotrifluoromethanesulfonate (1.38g, 6.0mmol) were dissolved in 30ml of CH_2Cl_2, and the solution was cooled to -78°. Trifluoromethanesulfonic acid anhydride (1.70g, 6.0mmol) was added in one portion, and the mixture was allowed to warm to room temperature. After 5 days, the mixture was worked up as above. In addition, a sample of the unreacted ester was isolated by preparative glc on 5% SE-30. A portion of this sample was submitted for deuterium analysis by the falling drop method. A deuterium incorporation of 60.7% was reported. Another portion of the sample was analyzed by nmr: The ratio of the integration of the methyl (3.80δ, s, 3H) to the methine (3.10δ, t, J=8, 1H) signals in 2-carbomethoxycyclopentanone were determined and compared to the ratio obtained for the sample isolated from the reaction. The results indicate a 26.9% incorporation of deuterium into the unreacted ester. Mass spectral analysis was attempted on a third portion of the sample. Comparison of the (m/e) 142 (M^+) to (m/e) 143 (M^+) peak ratio in 2-carbomethoxycyclopentanone with the sample obtained from the reaction indicated a deuterium incorporation of only 6.6%.

Reaction of 2-Deuterio-2-carbomethoxycyclopentanone with Trifluoromethanesulfonic Acid Anhydride and Pyridine in the Presence of Pyridinium Trifluoromethanesulfonate in CH_2Cl_2

The reaction was carried out in the same manner as that used with 2-carbomethoxycyclopentanone in the presence of the amine deuterio salts, but here the 2-deuterio ester was used in the presence of the hydrogen acid salt of the amine.

Reaction of 2-Carbomethoxycyclopentanone with Trifluoromethanesulfonic Acid Anhydride and Trifluoromethanesulfonic Acid in CCl_4

To 2-carbomethoxycyclopentanone (1.78g, 12.3mmol) in 30ml of CCl_4 cooled to -78° were quickly added 3.81g (13.5mmol) of trifluoromethanesulfonic acid anhydride, and two drops of trifluoromethanesulfonic acid. The mixture warmed to room temperature slowly, and after three days, it was poured into 30ml of water and worked up in the same way as with the base-catalysed reactions.

APPENDIX A

VINYL TRIFLUOROMETHANESULFONATES

Although vinyl trifluoromethanesulfonates were unknown until being nearly simultaneously reported by Stang and Summerville (165) and Jones and Maness (166), several methods for their preparation can now be found in the literature (103, 167-171).

It was observed earlier that the cyclic vinyl trifluoromethanesulfonate esters, V and VI as indicated above, were among the products of the reaction of 2-carbomethoxycyclopentanone potassium salt with N-n-hexyl-N,N-di(trifluoromethane)sulfonimide in HMPT. In order to characterize and fully establish the identity of these compounds, it was necessary to prepare authentic samples, by an independent route, for comparison of spectral and physical properties.

Using a method similar to that of Stang and Dueber (103), 2-carbomethoxycyclopentanone was allowed to react with one equivalent each of pyridine and trifluoromethanesulfonic acid anhydride in carbon tetrachloride. After a few days, the dark reaction mixture was worked up. Distillation yielded a mixture of unreacted starting ester and two other compounds. Samples of each compound were obtained by preparative glc; ir, nmr, and uv spectra, and elemental microanalyses supported the structures assigned to compounds V and VI. Analytical glc indicated that the ratio of the conjugated isomer (VI) to unconjugated isomer (V) was 2.2:1.

Although the relatively high yield of thermodynamically less favorable unconjugated isomer produced here was unexpected, production of double bond isomers of vinyl trifluoromethanesulfonates has been reported (103). Stang and Dueber (103) have shown that the reaction of 3-methyl-2-butanone with one equivalent each of pyridine and trifluoromethanesulfonic acid anhydride in carbon tetrachloride produced a mixture of vinyl trifluoromethanesulfonates consisting of 90% of the more substituted isomer, and 10% of the less substituted olefin. Further, they have demonstrated that by substituting anhydrous sodium carbonate for pyridine and methylene chloride for carbon tetrachloride, the composition of the product mixture was changed to 70% of the more substituted, and 30% of the less substituted isomer.

The results of Stang and Dueber (103), together with the large amount of compound V produced in this work, suggested the possibility of controlling the ratio of vinyl trifluoromethanesulfonate isomers produced by varying the strength of the base used in the reaction. To test this hypothesis, the reaction of 2-carbomethoxycyclopentanone with trifluoromethanesulfonic acid anhydride in carbon tetrachloride was repeated, substituting a variety of bases for pyridine. The results of these experiments are given in Table 14.

The pK_a values reported in Table 14 do not in themselves provide an adequate comparison of the strengths of the bases used in these experiments; further clarification is necessary.

While the pK_a value of 1,8-diazabicyclo(5,4,0)undec-7-ene (DBU) has not been reported, amidines are known to be strong bases. For example, the pK_a value for N,N-diphenyl acetamidine is 8.3 (176); DBU,

Table 14. Results of the Reactions of 2-Carbomethoxycyclopentanone with Trifluoromethanesulfonic Acid Anhydride and Various Bases in Carbon Tetrachloride

Base	pK_a[a]	% Yield, VI + V[b,c]	Ratio, VI/V[b]
CF_3SO_3H	--	12	2.2
Triphenylamine	--[d]	11	3.3
Quinoxaline	0.6[e]	--[f]	1.1
8-Nitroquinoline	2.6[e]	18	2.2
2,6-Di-t-butylpyridine	3.58[g]	37	5.1
Pyridine	5.2[e]	28	2.2
Pyridine[h]	5.2[e]	9	2.3
Pyridine[i]	5.2[e]	8	1.4
2,6-Dimethylpyridine	6.8[e]	39	6.3
Triethylamine	10.67[j]	33	34.8
DBU[k]	--[l]	15	34.8

[a]Unless otherwise indicated, determined in aqueous solution at 20-25°.

[b]Based on quantitative glc by comparison with authentic samples.

[c]Products identified by comparison of ir and nmr spectra and glc retention times of isolated products with authentic samples.

[d]Not measurably basic in aqueous solution, reference 172.

[e]Reference 173.

[f]Only a trace of products were obtained.

[g]Determined in 50% aqueous ethanol, reference 174.

[h]Reaction run in methylene chloride solvent.

[i]Ester used here was 2-deuterio-2-carbomethoxycyclopentanone.

[j]Reference 175.

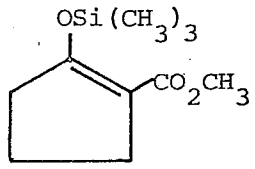
[k]DBU = 1,8-diazabicyclo[5,4,0]undec-7-ene.

[l]Value not reported.

therefore, is approximately as strong a base as triethylamine. The pK_a value for 2,6-di-t-butylpyridine was determined in 50% aqueous ethanol solution, while the other values in the table were determined in water solution. Further, Brown and Kanner (174) argue that the reported value is at least 1.4 pK_a units lower than expected due to solubility problems. Thus, this compound would realistically be expected to be a stronger base than pyridine, rather than weaker as its reported pK_a value would seem to suggest. Quinoxaline, due to its insolubility in the reaction medium, resulted in a very low yield of products. For this reason, the isomer ratio could not be accurately determined. And finally, while triphenylamine is reported to be too weak a base to be measured in aqueous solution (172), its base strength in the reaction medium may be quite different.

Bearing the above discussion in mind, the isomer ratios presented in Table 14 do follow a definite trend. The use of bases equal to or less than pyridine in strength produced isomer ratios of VI to V of 2.2:1. When much stronger bases, such as DBU, were used, this ratio increased dramatically to 34.8:1. Bases intermediate in strength between DBU and pyridine produced isomer ratios between these extremes.

A series of deuterium exchange reactions were also run with this system. Using a modification of the method of Kusnezowa et al. (163), 1-carbomethoxy-2-trimethylsiloxycyclopentene, XV, was prepared. By allowing this compound to react with methanol-d_1, prepared by the method of Streitweiser et al. (164), 2-deuterio-2-carbomethoxycyclopentanone was formed in 97% yield. Comparison of the nmr integration



XV

ratio of the methyl and methinyl signals indicated greater than 95% incorporation of deuterium into the 2-position.

The 2-deuterio-2-carbomethoxycyclopentanone was allowed to react with pyridine and trifluoromethanesulfonic acid anhydride in carbon tetrachloride, under exactly the same conditions as employed in earlier reactions. Analysis of the resulting product mixture showed an isomer ratio of only 1.4:1, apparently indicating a substantial deuterium isotope effect.

In another series of exchange reactions, one equivalent of the keto ester was allowed to react with one-half equivalent each of the base, trifluoromethanesulfonic acid anhydride, and the appropriate trifluoromethanesulfonic acid salt of the base used in the reaction. Unreacted keto ester was then isolated from the reaction product mixture by preparative glc, and the amount of exchange at the 2-position was determined by nmr. These results are given in Table 15.

The use of the base salts in these reactions necessitated changing the solvent from carbon tetrachloride to methylene chloride. The reaction of 2-carbomethoxycyclopentanone with pyridine and trifluoromethanesulfonic acid anhydride was run in this solvent, and a change of isomer ratio from 2.2:1 to 2.3:1 was noted.

Table 15. Results of the Reactions of 2-Carbomethoxycyclopentanone with Trifluoromethanesulfonic Acid Anhydride and Various Bases, in the Presence of the Base Deuteriotrifluoromethanesulfonic Acid Salts in Methylene Chloride

Base	% Yield VI + V[a,b]	% Deuterium Incorporation[c]	Ratio, VI/V[a]
Pyridine	14	22	2.3
Pyridine	37	20	2.2
Pyridine	9	79[d,e]	2.2
Triethylamine	27	0	36

[a]Based on quantitative glc by comparison with authentic samples.

[b]Products identified by comparison of ir and nmr spectra and glc retention times of isolated products with authentic samples.

[c]Ratio of methyl to methinyl signals in the nmr spectra of starting ester and unreacted ester isolated from products was used to determine incorporation into the 2-position.

[d]Ester used here was 2-deuterio-2-carbomethoxycyclopentanone, in the presence of pyridinium trifluoromethanesulfonate.

[e]Value represents the % hydrogen incorporation.

Deuteriotrifluoromethanesulfonic acid was prepared by mixing trifluoromethanesulfonic acid anhydride with slightly less than one equivalent of deuterium oxide, and stirring until a homogeneous solution was obtained. The pyridinium and triethylammonium salts of this acid were prepared by mixing one equivalent of the base with one equivalent of the acid in carbon tetrachloride solvent. Pyridinium trifluoromethanesulfonate was prepared by an analogous method.

The reaction of 2-deuterio-2-carbomethoxycyclopentanone with pyridine in the presence of pyridinium trifluoromethanesulfonate was carried out as described above. Analysis of the products showed an isomer ratio of 2.2:1, and the nmr of the recovered keto ester indicated that 79% of the deuterium had been replaced by hydrogen. When the reaction was run using 2-carbomethoxycyclopentanone in the presence of the deuteriotrifluoromethanesulfonate salt, the isomer ratio was the same, but the nmr showed only 21% incorporation of deuterium into the 2-position. It was uncertain whether this discrepancy was a result of the deuterium isotope effect noted above, or an artifact resulting from the work up of the product mixture or isolation of the unreacted keto ester.

Finally, the reaction of 2-carbomethoxycyclopentanone with triethylamine in the presence of triethylammonium deuteriotrifluoromethanesulfonate was run. The isomer ratio was found to be 36:1, but the nmr showed no incorporation of deuterium into the 2-position of the keto ester.

Although a correlation between base strength and isomer ratio is exhibited by the data in Table 14, the nature of this dependence is not clear.

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