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SYNTHESES AND CHEMICAL INVESTIGATIONS OF POSSIBLE
SINGLET DIATOMIC SULFUR PRECURSORS

by

Douglas Lee Smith

A Thesis 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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I hereby recommend that this dissertation prepared under my
direction by Douglas Lee Smith
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degree of Doctor of Philosophy

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Douglas L. Smith

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ABSTRACT

Analogy to singlet diatomic oxygen chemistry leads to the consideration of several methods for the chemical generation of singlet diatomic sulfur. The most promising among these methods are the oxidation of sodium disulfide with bromine and the pyrolysis or photolysis of 3,6-epidithio-1,4-cyclohexadienes.

Bromine oxidizes sodium disulfide to sulfur. This oxidation conducted in the presence of any of several potential trapping reagents (olefins substituted with either electron-donating or electron withdrawing substituents, cyclic dienes, or electron-poor acetylenes) failed to produce adducts which could be attributed to the intermediacy of singlet diatomic sulfur. The lone exception was the reaction conducted in the presence of dimethyl acetylenedicarboxylate, which produced small amounts of tetramethyl thiophenetetracarboxylate in addition to an unidentified polymer.

Synthetic schemes are discussed which concern the construction of 3,6-epidithio-1,4-cyclohexadienes of the following forms: (i) dihydrobenzenes with the disulfide bridge across the 1,4 positions, (ii) dihydronaphthalenes bridged in the 1,4 positions, and (iii) dihydroanthracenes bridged in the 9,10 positions. Progress toward such dihydrobenzenes was made via Diels-Alder reactions of *trans,trans*-1,4-Di(S-thioacetoxy)-1,3-butadiene with electron deficient acetylenes and double bond dienophiles. Adducts with maleic anhydride, diethyl azodicarboxylate, tetracyanoethylene, fumaryl chloride, and dimethyl acetylenedicarboxylate are described.

In conjunction with this synthetic approach, the trifluoromethanesulfonyl group was proposed to be a potent activating substituent for acetylenic dienophiles entering into Diels-Alder reactions with normal electron demand. Phenyltrifluoromethanesulfonylacetylene was prepared and kinetic data is presented which indicates the great dienophilicity of this acetylene as compared to other substituted phenylacetylenes.

Progress toward the synthesis of the above mentioned dihydroanthracenes was made through radical addition of thiolacetic acid to anthracene. However, displacement of various leaving groups with sulfur nucleophiles from the 9,10 positions of 9,10-dihydro-9,10-diphenylanthracenes, reaction of sulfur electrophiles with the anion radical or the dianion of 9,10-diphenylanthracene, and radical addition of various sulfur containing species to 9,10-diphenylanthracene all failed to produce the desired bridged species.

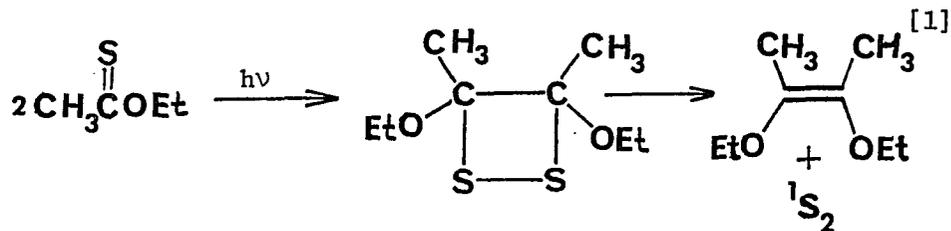
CHAPTER I

INTRODUCTION

Elemental sulfur heated at 450°C at a pressure of 0.1 torr gives a vapor which is 99% diatomic sulfur¹ in its ground state, i.e., $^3\Sigma_g^-$. With the exception of the lifetimes of the various excited states, the electronic states of this molecule are well characterized², and, in particular, several singlet excited states are observed. The lowest energy excited state is a singlet, $^1\Delta_g$, which lies 12.9 kcal above the ground state².

Apparently, neither the triplet ground state nor the singlet excited states of diatomic sulfur have been involved in rational organic synthesis. The advent of the interest in and the utility of the analogous singlet diatomic oxygen system³ makes the investigation of such sulfur species, particularly the singlets, very attractive and very timely. In addition, as with the singlet diatomic oxygen case, synthetic use would be enhanced by the ability to generate and trap the appropriate species in solution with the use of simple equipment and easily accessible reaction conditions, as opposed to generation and reaction in the vapor phase. Consequently, the purpose of this investigation is to seek methods suitable for the simple chemical generation of diatomic sulfur, with emphasis on the singlet species, and to seek reagents with which it may give useful reactions.

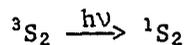
Note should be made of the fact that one report exists which claims the production of 1S_2 by the process outlined in Equation [1]⁴.



Although trapping was accomplished by the use of alicyclic dienes, many other mechanisms for product formation are possible under the reaction conditions used, and these were not considered in the report mentioned.

Thus, consideration needs to be given to other potential sources of $^1\text{S}_2$. Analogy with singlet diatomic oxygen chemistry prompts several considerations for possible methods of singlet diatomic sulfur generation. These methods are gathered in Table I along with the requisite sulfur species. A short critique of each method follows.

Method (1) would involve the irradiation of $^3\text{S}_2$, which is itself not yet available in solution.



Method (2a) would require thiozone. This compound has been



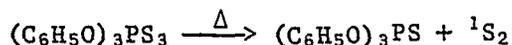
identified in sulfur vapor³³ and produced by irradiation of S_3Cl_2 ³⁴. Photolysis would undoubtedly produce several reactive species in addition to $^1\text{S}_2$.

TABLE I

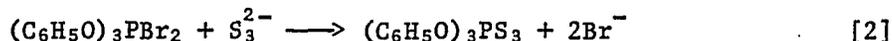
METHODS OF $^1\text{O}_2$ GENERATION TO BE CONSIDERED FOR $^1\text{S}_2$ GENERATION	
Method of $^1\text{O}_2$ Generation	Sulfur Species Needed for $^1\text{S}_2$ Generation
(1) $^3\text{O}_2 \xrightarrow{h\nu} ^1\text{O}_2$ (a) dye sensitized irradiation ^a (b) I_2 sensitized irradiation ^b (c) direct irradiation with laser beam at high pressure in vapor phase ^c (d) formation in incandescent tungsten filament ^d (e) passage through radiofrequency or microwave discharge ^e	$^3\text{S}_2$
(2) (a) photolysis of ozone ^f (b) thermal decomposition of phosphite ozonides ^g	S_3 phosphite thiozonides
(3) thermal decomposition of phthaloyl peroxide ^h	phthaloyl disulfide
(4) $\text{O}_2^- \longrightarrow \text{O}_2 + \text{e}^-$ (both singlet and triplet O_2) (a) in dimethylsulfoxide ⁱ (b) electrogenerated radical ion electron transfer ^j	S_2^-
(5) $4\text{K}_3\text{CrO}_8 + 2\text{H}_2\text{O} \longrightarrow 4\text{K}_2\text{CrO}_4 + 4\text{KOH} + 7 ^1\text{O}_2^{\text{k}}$	CrS_8^{3-}
(6) (a) $\text{H}_2\text{O}_2 + \text{OCl}^- + \text{OH}^- \longrightarrow \text{H}_2\text{O} + \text{OH}^- + \text{Cl}^- + ^1\text{O}_2^{\text{l}}$ (b) $\text{H}_2\text{O}_2 + \text{Br}_{2\text{m}} + 2\text{OH}^- \longrightarrow 2\text{H}_2\text{O} + 2\text{Br}^- + ^1\text{O}_2$ (c) alkaline decomposition of nitriles in presence of $\text{H}_2\text{O}_2^{\text{n}}$ (d) alkaline decomposition of peroxy-carboxylic acids ^o	H_2S_2 perthiocarboxylic acids
(7) thermal decomposition of an endo peroxide of an aromatic system such as anthracene, rubrene, etc. ^p	an endo disulfide of some aromatic system

^aRef. 3,5,6. ^bRef. 7. ^cRef. 8,9. ^dRef. 10. ^eRef. 11-13. ^fRef. 14.
^gRef. 15-21. ^hRef. 22. ⁱRef. 23. ^jRef. 24. ^kRef. 25,26. ^lRef. 27,28.
^mRef. 29. ⁿRef. 29. ^oRef. 29,30. ^pRef. 31,32.

The phosphite thiozonides needed for Method (2b) are not known compounds. However, they could presumably be prepared from phosphite

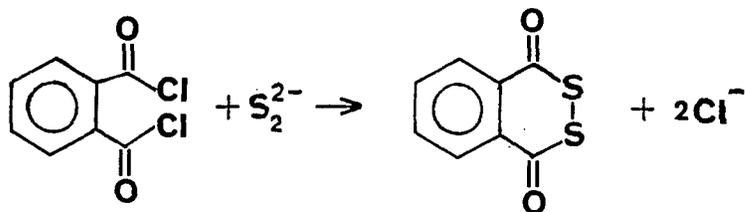


dihalides, as in Equation [2]. Unfortunately, although S_3^{2-} is a well



known substance, it tends to disproportionate to S_4^{2-} and S_5^{2-} , at least in aqueous solution³⁵, thus making this approach less attractive.

Method (3) would require the thermal decomposition of phthaloyl disulfide, which is unknown, but which presumably could be made from phthaloyl chloride as shown. However, the potentiality of generating ${}^1\text{S}_2$ by the use of this disulfide is unassessable because the mechanism of



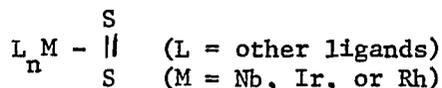
${}^1\text{O}_2$ generation from phthaloyl peroxide has not been established. A comparison of the two methods is not possible under these circumstances.

Method (4) would involve the supersulfide anion S_2^- . Claims exist

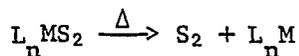


that in dipolar aprotic solvents, ethanol, and water this species is in equilibrium with S_4^{2-} from Na_2S_4 ³⁶⁻³⁸. However, these findings have been questioned³⁹, the species present being identified as S_3^- .

Method (5) does show some promise. Although the chromium salt indicated in Table I is not known, niobium⁴⁰, iridium⁴¹, and rhodium^{41,42} complexes containing non-bridging S-S as a ligand have been prepared. These complexes present the additional feature that their S₂ ligands are bonded to the metal in a π fashion. Although these complexes do not



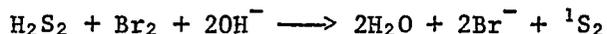
give up S₂ on hydrolysis, they may do so upon thermolysis. In fact, one



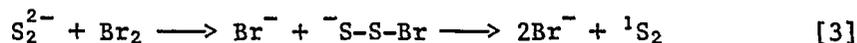
rhodium complex⁴² does lose S₂ very easily in the mass spectrometer.

Of course, the cost of generating S₂ through a complex containing rhodium or iridium would be a deterrent to practical usage.

Method (6) requires H₂S₂ in alkaline solution, and is illustrated by analogy to Method (6b). Unfortunately, under such conditions H₂S₂

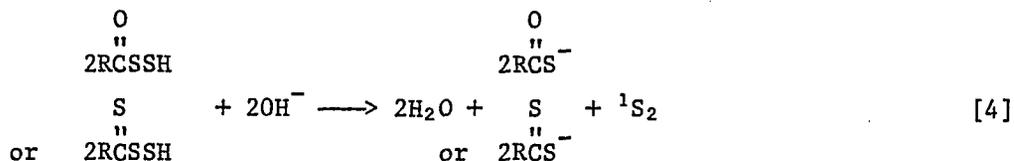


disproportionates⁴³. However, an alteration of conditions may allow the achievement of the same results. This is outlined in Equation [3].



The possibility would also exist for the intermediate ⁻S-S-Br to react with trapping reagent in competition with its decomposition to yield ¹S₂. Such a process might give the same or different products from those of reaction of the trapping reagent with ¹S₂ directly.

On the other hand, Method (6d) does not seem as promising. Peroxy-carboxylic acids decompose to give $^1\text{O}_2$ at a pH equal to their pK_a . Consequently, both the acid and its salt are required. The analogous reaction producing $^1\text{S}_2$ is shown in Equation [4]. Although metal com-



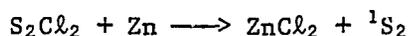
plexes of perthiocarboxylates are known⁴⁴, the corresponding acids are not reported.

By far the most attractive method for $^1\text{S}_2$ generation is Method (7). However, before this method is more fully discussed, a few other alternatives will be briefly mentioned. Most of these do not have analogs in $^1\text{O}_2$ chemistry.

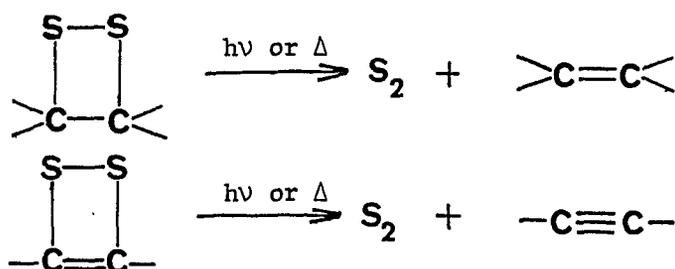
First, photolysis or thermolysis of S_8 in solution gives radical chains of various lengths⁴⁵. S_2 may be among the many reactive species produced, but is probably present as $^3\text{S}_2$.

Photolysis of H_2S ³³, S_2Cl_2 ⁴⁶, COS ^{33,47}, and CS_2 ⁴⁸ all produce S_2 . However, several other reactive species are produced at the same time.

Reduction of S_2Cl_2 , for example by Zn, does not seem to have been explored.

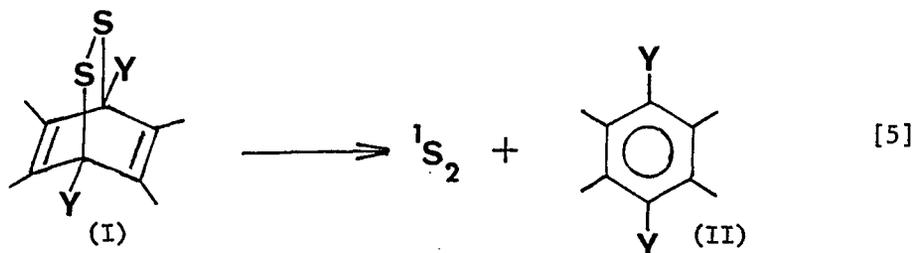


Lastly, an elimination of S_2 from either 1,2-dithietanes or 1,2-dithietenes may seem to be a possibility. The former compounds have



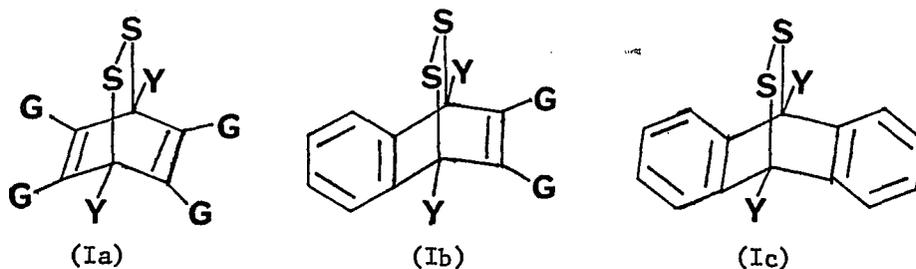
not been characterized (but see Ref. 4) while a few examples of the latter exist⁴⁹⁻⁵³. If dithietanes are assumed to react like the corresponding dioxetanes^{54,55}, then they will undergo thermolysis with cleavage of the S-S bond (although see Ref.4). Dithietenes do react with olefins and acetylenes and dimerize by cleavage of the S-S bond⁴⁹⁻⁵². Likewise, under photolytic conditions, for which concerted loss of 1S_2 would be symmetry allowed by the Woodward-Hoffmann rules⁵⁶, cleavage of the S-S bond is also observed⁵³.

Method (7) will now be considered in detail. A disulfide of the general structure (I) may decompose in a concerted fashion or stepwise to yield an aromatic system (II) and S_2 . If the process is concerted



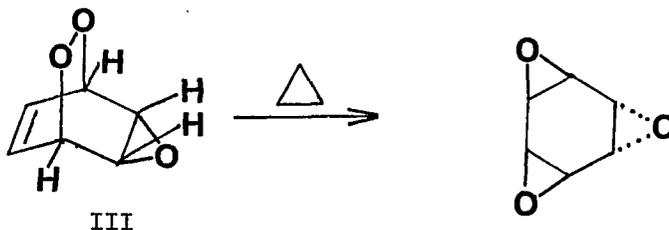
1S_2 will be produced. An additional possibility is the interception of an intermediate (diradical or zwitterionic) by trapping reagent if the process is not concerted. In that case, the products may or may not be the same as would be formed from the same trapping reagent and 1S_2 .

Systems such as (I) are unknown, but several conceivable ones of this general structure can be envisioned. Three of these are indicated below. As a first consideration, the nature of the substituents (G-)



should have little effect on the success or failure of the procedure, but may be chosen for synthetic convenience.

The possible effect of the substituents (Y-) is less clear. In the realm of $^1\text{O}_2$ chemistry no system analogous to (Ia) has been studied. However, (III) undergoes thermolysis with cleavage of the O-O bond⁵⁷.



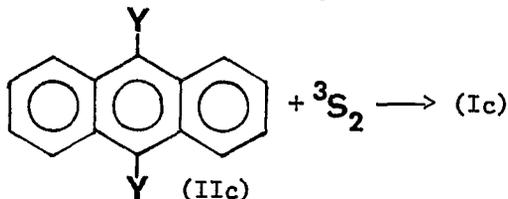
Only one system analogous to (Ib) has been studied⁵⁸, while several systems analogous to (Ic), i.e., anthracene derivatives, have been investigated. Of these only the 9,10-diphenylanthracene system (analogous to Ic, Y- = C₆H₅-) liberates $^1\text{O}_2$ readily. Those systems with other aryl groups in the 9,10 positions are somewhat less effective, while those systems containing even one hydrogen atom or alkyl residue at those positions give up no oxygen. Indeed, 9,10-dihydroanthracene-9,10-endoperoxide (the analog of Ic, Y- = H-) undergoes thermolysis with exclusive cleavage of the O-O bond⁵⁹.

Thermolytic cleavage of the S-S bond should be a less likely possibility for Ia - Ic than it is for the analogous oxygen containing

systems. The S-S bond is much stronger than the O-O bond (70 kcal/mole vs. 32 kcal/mole)⁶⁰, while the C-S bond strength is slightly less than that of a C-O bond (73 kcal/mole vs. 77 kcal/mole)⁶⁰. Thus, the thermal loss of S₂ from Ia - Ic via C-S bond cleavage is a viable possibility.

Many varied synthetic approaches exist for developing the structures (I). These methods are listed in Table II. However, the feasibility of each method is determined not only by the potential for reasonable reaction conditions, reasonable yields, etc., but also by the potential to establish the two sulfur atoms with the necessary *cis* stereochemistry relative to one another. In addition, the disulfide bridge can only be closed if the sulfurs are arranged not only *cis*, but diquasiaxially as well. In many 1,4-cyclohexadiene systems, ring flipping is easily accomplished and readily interconverts the quasia-equatorial and quasiaxial positions⁶¹, so only *cis* stereochemistry may be a necessity. Of course, the less attractive possibility exists of attempting to isomerize the *trans* isomer, if that were the product formed.

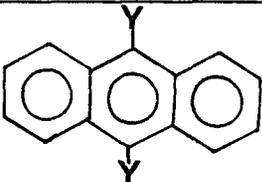
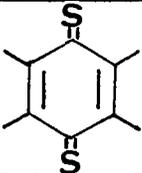
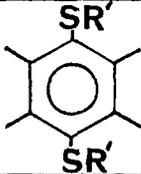
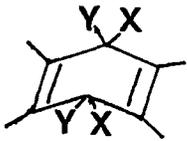
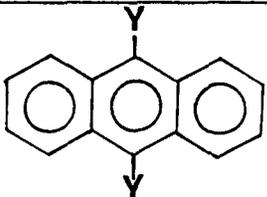
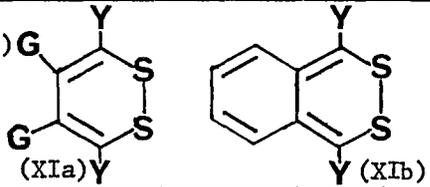
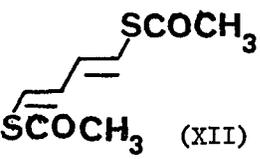
Perhaps Method (7a) is the most direct approach to (Ic). This method involves radical addition of ³S₂ to a system of structure (IIc).



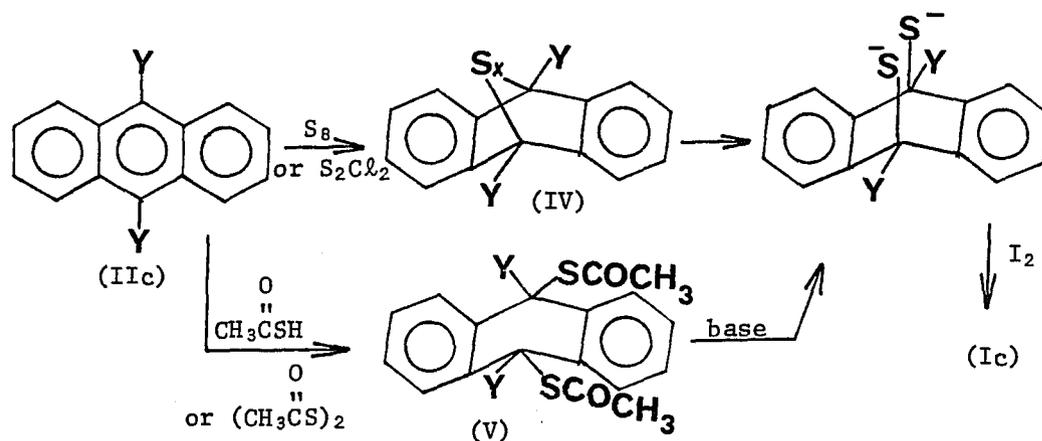
However, the aforementioned problem of obtaining ³S₂ in solution negates this approach. On the other hand, thermal or photolytic addition of other sulfur containing species is more feasible. Stereochemistry is only assured if the reactant consists of a short chain of sulfur atoms.

TABLE II

POSSIBLE SYNTHETIC APPROACHES TO COMPOUNDS
OF THE GENERAL STRUCTURE (I)

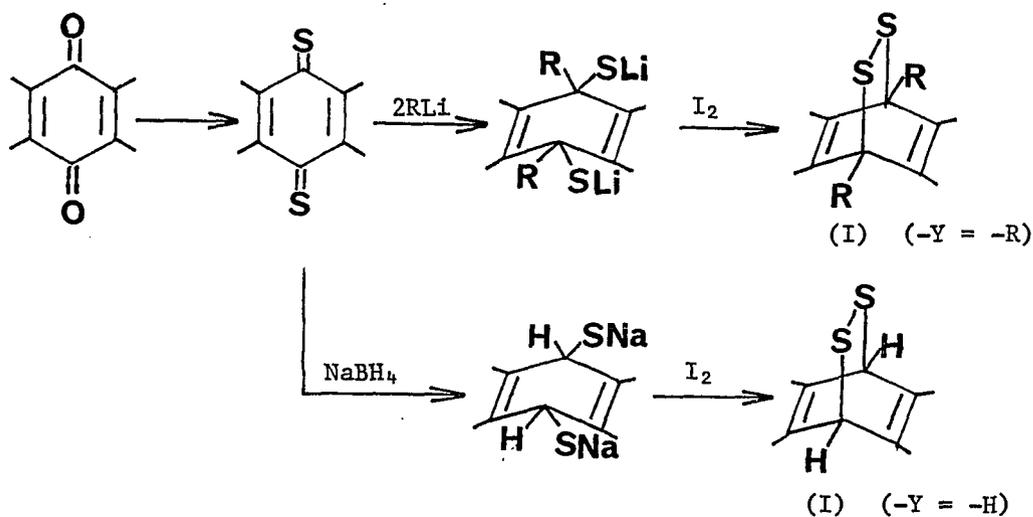
Method	Organic Precursor	General Approach
(7a)		(IIc) Radical addition of 3S_2 across the 9,10 positions
(7b)		Nucleophilic addition to the C=S, followed by oxidation of the resulting bis thiolate
(7c)		(VI) Birch reduction of the aromatic system to a 1,4-cyclohexadiene, followed by elaboration of the sulfur substituents to the disulfide bridge.
(7d)		(IX) Displacement of the leaving group X- by sulfur nucleophiles, such as S_2 .
(7e)		(IIc) Oxidation to the cation radical or dication, followed by treatment with sulfur nucleophiles; reduction to the anion radical or dianion, followed by treatment with sulfur electrophiles.
(7f)		Diels-Alder cycloaddition of an acetylene with a 1,2-dithiin.
(7g)		Diels-Alder cycloaddition of an acetylene with (XII).

Some possible reagents are S_8 and S_2Cl_2 . The resulting polysulfide (IV) is easily reduced and then re-oxidized to the disulfide⁶²⁻⁶⁴. Further



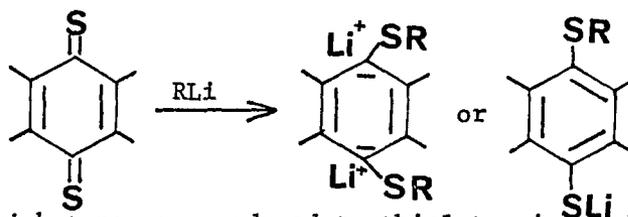
possible reagents which cannot assure the stereochemistry are various thiols or disulfides which would give products (V), easily elaborated to the disulfide. Obvious examples of this latter case are thiolacetic acid and acetyl disulfide.

In conjunction with Method (7b) the following sequence can be considered:



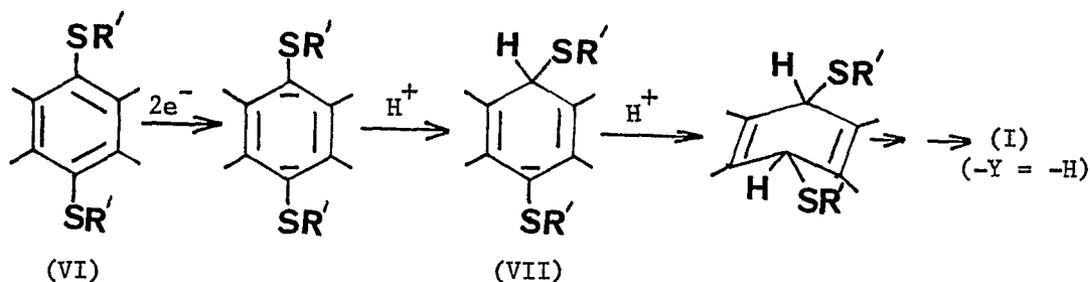
Obviously, stereochemistry is not assured. More importantly, even though certain ketones can be readily converted to the corresponding thioketones, no reported cases exist of a similar reaction involving *p*-quinones. In fact, in one case, anthraquinone failed to give this reaction under conditions which worked quite well for other ketones⁶⁵.

An additional problem arises in that organolithiums and Grignard reagents react with thioketones via attack on sulfur rather than on carbon⁶⁶. Thus, two possible unwanted modes of reaction are:



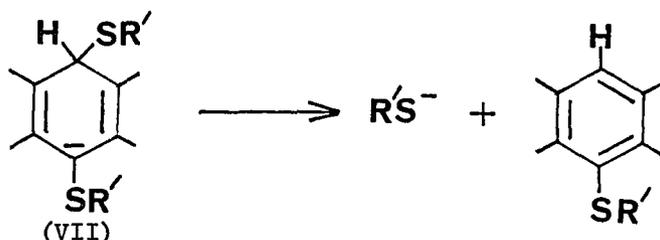
However, thioketones are reduced to thiolates in good yield by hydride reducing agents⁶⁷.

Method (7c) constitutes a third approach to the synthesis of (I), and involves the Birch reduction of an aromatic system (VI) containing sulfur substituents appropriately placed para to one another. Once

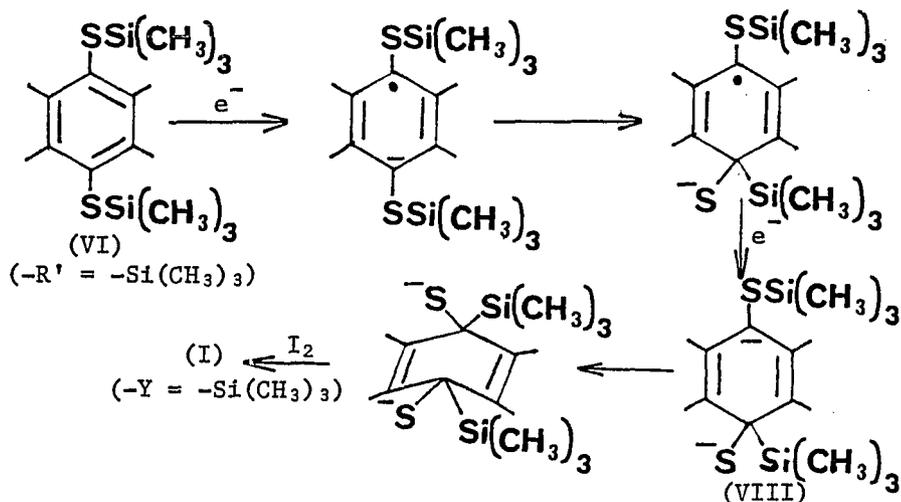


again the stereochemistry is not assured unless the sulfurs are connected in some way.

Several additional problems exist with this scheme. For one, no reports exist of Birch reductions on sulfur substituted aromatic rings. Initial reduction may proceed as indicated, but an intermediate such as (VII) could aromatize by elimination of thiolate.



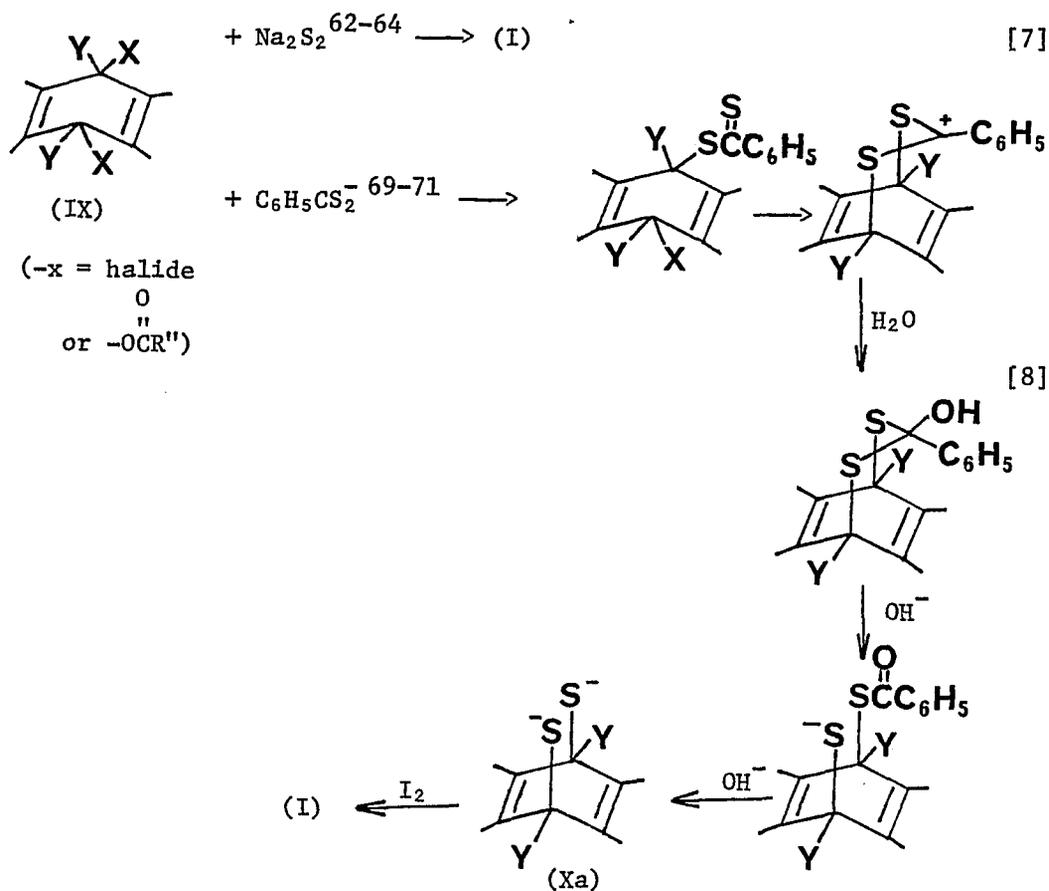
Another problem arises in the choice of the groups (R'-). These need to be easily removable in the elaboration to the disulfide, and yet unaffected under the reduction conditions. Perhaps both of the above mentioned problems may be solved by choosing R'- = (CH₃)₃Si-. Anions of trimethylsilyl thioethers are known to rearrange to carbon silylated products⁶⁸. Thus, a similar rearrangement might take place during the course of the Birch reduction. Not only can the disulfide bridge now be

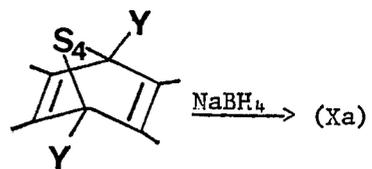
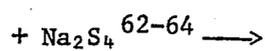


[6]

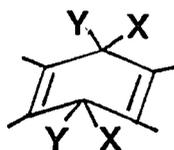
closed by oxidation if the stereochemistry is correct, but the possibility of aromatization is minimized, since (VIII) would have to eliminate S^{2-} , which is a poorer leaving group than the $R'S^-$ which can be eliminated from (VII) (Equation [6]).

Another possible synthetic scheme leading to (I) is Method (7d). This involves the nucleophilic displacement of some leaving group (X^-) in a molecule (IX) by sulfur containing nucleophiles. Possibilities are indicated and include dianions that can lead to the proper stereochemical situation.

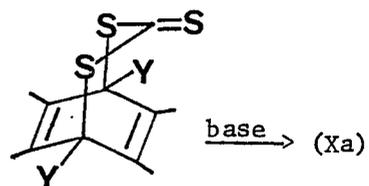
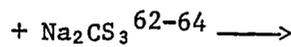




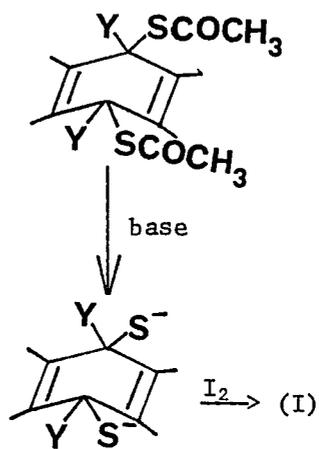
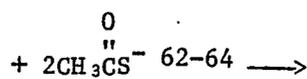
[9]



(IX)

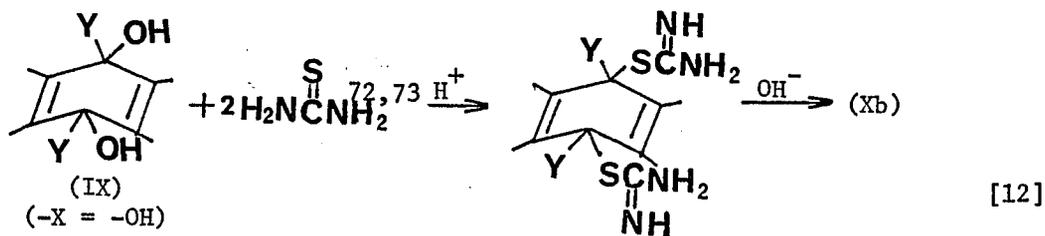


[10]



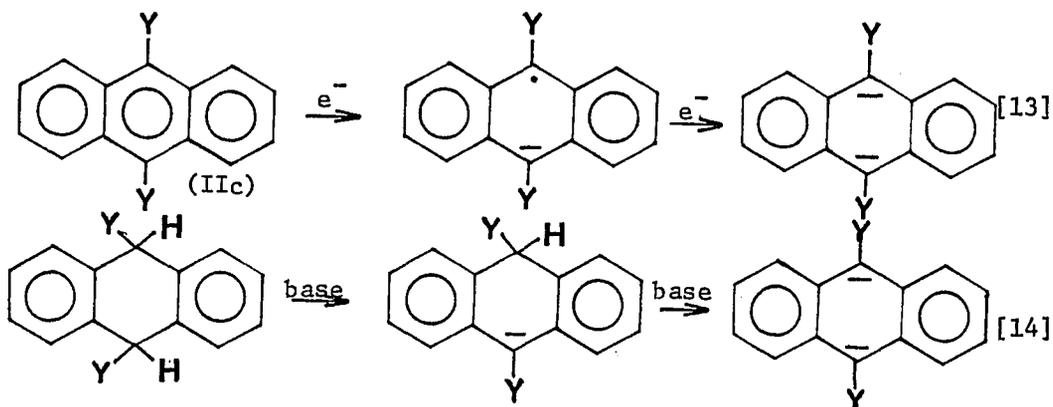
[11]

(Xb)

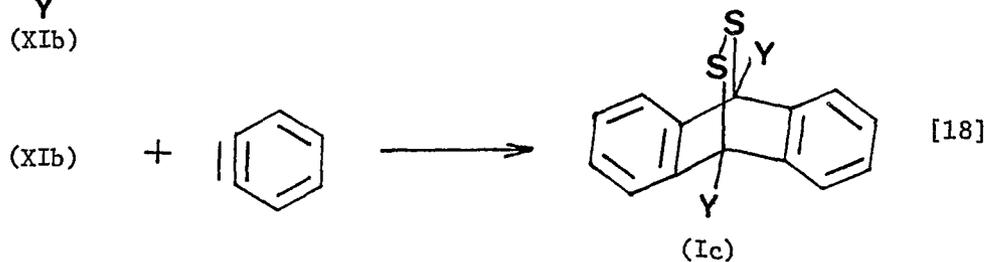
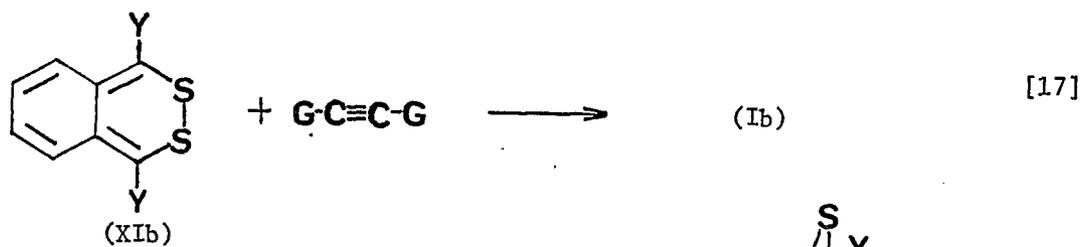
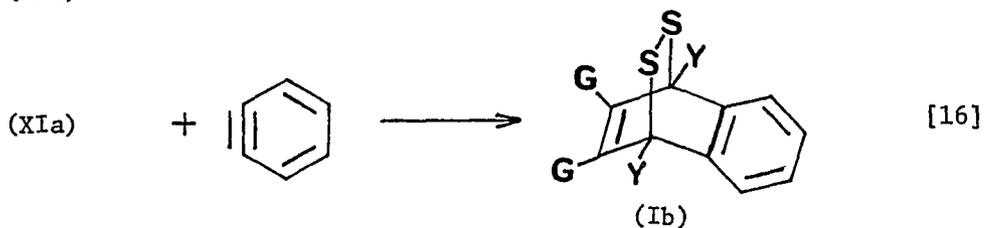
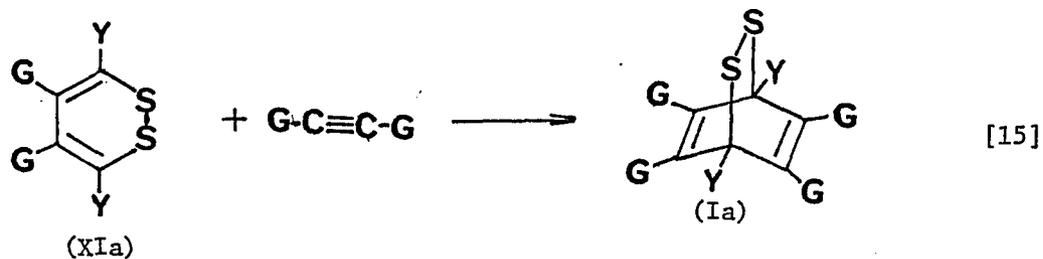


This is an attractive approach since many varied systems of the structure (IX) are known and do give nucleophilic displacement with certain nucleophiles⁷⁴. In addition, the sulfur containing nucleophiles are all easily obtainable.

Method (7e) involves the formation of system (Ic) from the corresponding dication, cation radical, dianion, or anion radical. The cationic species would be expected to react with the sulfur containing nucleophiles of Equations [7] - [12], while the anionic species can react with such sulfur electrophiles as S_8 ⁶⁴, S_2Cl_2 , or acetyl disulfide⁶⁴. The cations can best be prepared by electrochemical oxidation of the parent anthracene system⁷⁵, while the anions can be obtained in several ways^{61,76-78}. A few of these are shown in Equations [13] and [14].

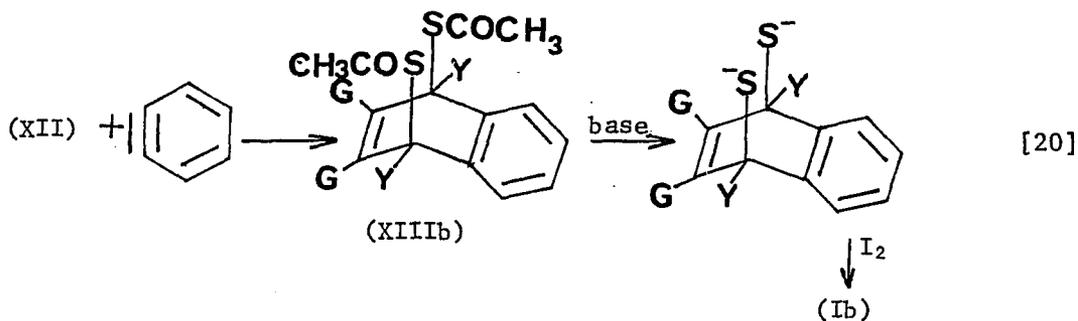
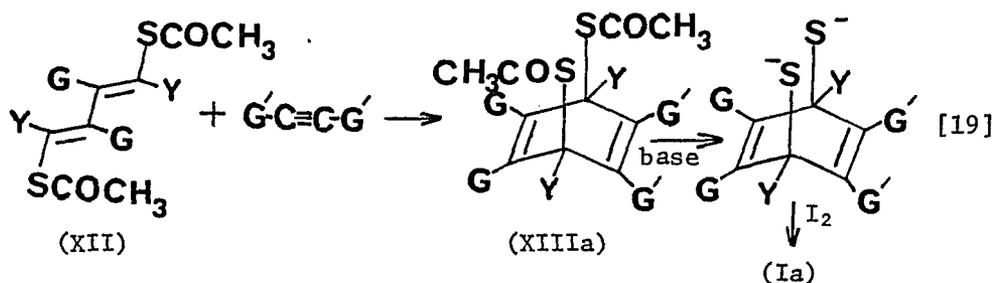


Lastly, Method (7f) involves the construction of systems (I) by means of Diels-Alder cycloaddition reactions. Some possibilities are listed in Equations [15] - [18]. Unfortunately, simple o-dithiins (XIa)



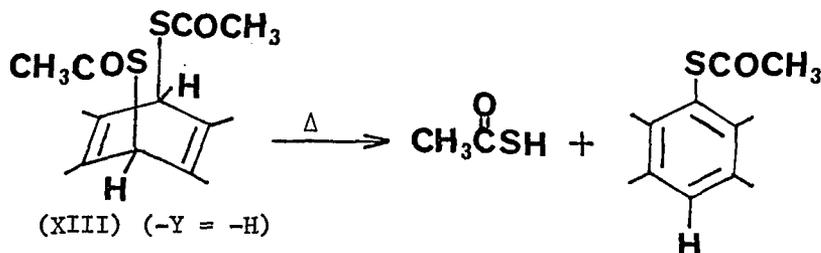
do not undergo Diels-Alder reaction, even with the very reactive dienophiles maleic anhydride and tetracyanoethylene^{79,80}. Instead they extrude a sulfur atom. The *o*-benzodithiins (XIb) are known⁸¹, but have not been used in Diels-Alder reactions.

An alternative method (7g) which can be used to prepare systems (Ia) or (Ib) is illustrated in Equations [19] and [20]. Unsubstituted



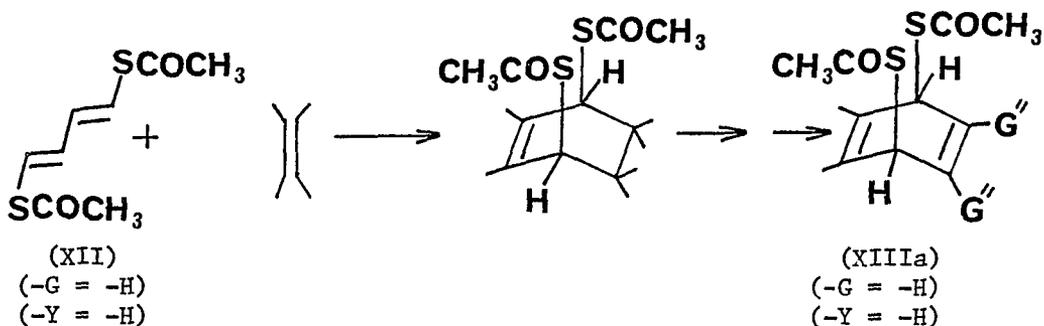
(XII) (i.e., G- = H-, Y- = H-) has been prepared^{79,82}, and apparently does enter into Diels-Alder reactions. In addition, the *trans, trans* isomer of (XII) is the isomer which will give Diels-Alder reaction most easily, and will also lead to a product (XIII) which must have the sulfur atoms in a *cis* arrangement⁵⁶.

One potential problem with this approach is that the intermediate product (XIII) (Y = H-) can easily aromatize by loss of thiolacetic acid. This problem is apt to arise under those circumstances which re-



quire an acetylenic dienophile and somewhat vigorous reaction conditions. The obvious resolution to such a problem is to use an acetylenic dienophile which will undergo reaction with (XII) under conditions mild enough to insure that subsequent elimination of thiolacetic acid from (XIII) does not occur. The most reactive acetylenic dienophiles are those which make up a part of a strained cyclic system⁸³ or those with powerful electron withdrawing substituents⁸⁴.

The problem of elimination leading to aromatization may be circumvented entirely by the use of an olefinic dienophile. However, this

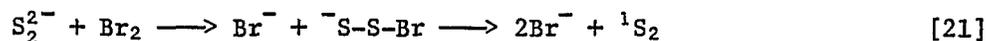


approach will involve the need for a longer reaction sequence in order to introduce the second double bond in (XIIIa).

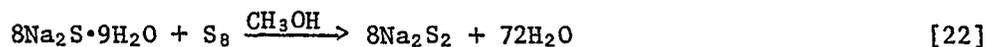
CHAPTER II

RESULTS AND DISCUSSION

The first approach studied for the generation of $^1\text{S}_2$ was that outlined in Method (6) of Table I and shown again in Equation [21]. The



solution of sodium disulfide initially used in this approach was prepared from hydrated sodium sulfide and elemental sulfur in methanol⁸⁵. A



control experiment indicated that bromine in benzene rapidly oxidized this methanolic sodium disulfide to elemental sulfur as expected.

Further experiments were conducted to determine suitable trapping reagents for $^1\text{S}_2$ if it were indeed being formed in the bromine oxidation of sodium disulfide. These experiments consisted of simultaneous addition of methanolic sodium disulfide solution and of a benzene solution of bromine to a well-stirred solution of the potential trapping reagent in benzene at room temperature. The progress of the reaction (if any) was followed by tlc. The potential trapping reagents screened in this manner were mainly olefins, acetylenes, cyclic dienes, and aromatic systems and are listed in Table III along with the results of the experiments. In particular, the olefins were chosen so as to be representative of both electron rich and electron poor compounds. In only two cases were products other than starting material and sulfur observed,

TABLE III
CONTROL EXPERIMENTS FOR OXIDATION OF Na_2S_2 BY Br_2

Trapping Reagent ^a	Reagents Added ^b				
	Br_2 ^c	Br_2 , then Na_2S_2	Na_2S_2 ^d	Na_2S_2 , then Br_2	Br_2 and Na_2S_2 ^e
1,3-cyclohexadiene	+	-	-	sulfur	sulfur
furan	+	-	-	sulfur	sulfur
1,3-diphenylisobenzofuran	+	-	-	sulfur	sulfur
tetraphenylcyclopentadienone	+	-	-	sulfur	sulfur
anthracene	+	-	-	sulfur	sulfur
9,10-dimethylantracene	+	++	-	sulfur	+,sulfur
9,10-diphenylantracene	+	-	-	sulfur	sulfur
cyclohexene	+	-	-	sulfur	sulfur
tetramethylethylene	+	-	-	sulfur	sulfur
vinylene carbonate	+	-	-	sulfur	sulfur
tetrachloroethylene	+	-	-	sulfur	sulfur
fumaronitrile	+	-	-	sulfur	sulfur
diphenylacetylene	+	-	-	sulfur	sulfur
dimethyl acetylenedicarboxylate	+	-	-	sulfur	+,sulfur
diphenylmethane	-	sulfur	-	sulfur	sulfur
blank	-	sulfur	-	sulfur	sulfur

^a0.25 mmol in 0.5 ml benzene.

^bReaction as observed by tlc is indicated by +. If addition of one reagent caused reaction, and then addition of the next reagent caused another reaction, the symbol used is ++.

^cA 0.5 ml aliquot of a solution of 800 mg Br_2 in 10 ml benzene.

^dA 1.0 ml aliquot of a solution of 3.7g $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ and 0.50g S_8 in 62.5 ml methanol.

^eReagents added simultaneously from two syringes.

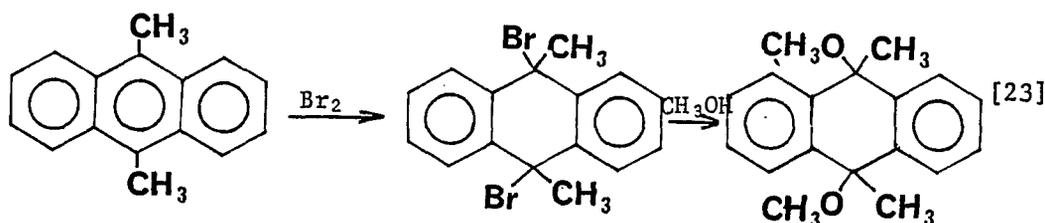
i.e., in the reactions with 9,10-dimethylanthracene and with dimethyl acetylenedicarboxylate.

Furthermore, additional control experiments were conducted and the results are also included in Table III. These were

- (i) trapping reagent in benzene + Br₂ in benzene
- (ii) the mixture from (i) + methanolic Na₂S₂
- (iii) trapping reagent in benzene + methanolic Na₂S₂
- (iv) the mixture from (iii) + Br₂ in benzene.

These experiments indicated that in no screening experiment above had brominated trapping reagent been formed, and sodium disulfide had not reacted with any of the trapping reagents. An immediate conclusion from the first result is that bromine generally reacted much more rapidly with sodium disulfide than with trapping reagent. This fact was also borne out by the results of (iv), which in all cases showed the formation of sulfur, but no brominated products.

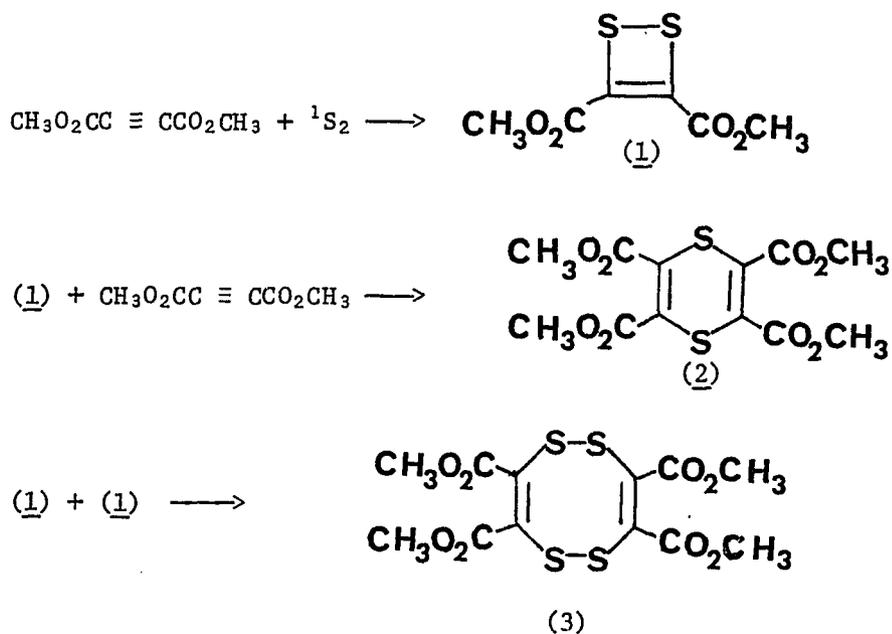
However, the additional control experiments did indicate that the new product which had been formed in the reaction of 9,10-dimethylanthracene was the same as that formed by treating brominated 9,10-dimethylanthracene with methanolic sodium disulfide. Further investigation revealed that the reaction had been with the solvent rather than with sodium disulfide, and had already been observed under somewhat similar circumstances²⁹. The reaction was conducted preparatively



using ethanol instead of methanol. No other brominated trapping reagent reacted under these conditions with methanolic sodium disulfide.

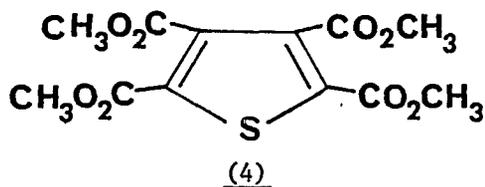
Thus, the only interesting reaction was that with dimethyl acetylenedicarboxylate. This reaction was scaled up and the new product isolated. The anticipated products and their conceivable modes of formation are shown in Scheme I⁴⁹⁻⁵².

Scheme I:

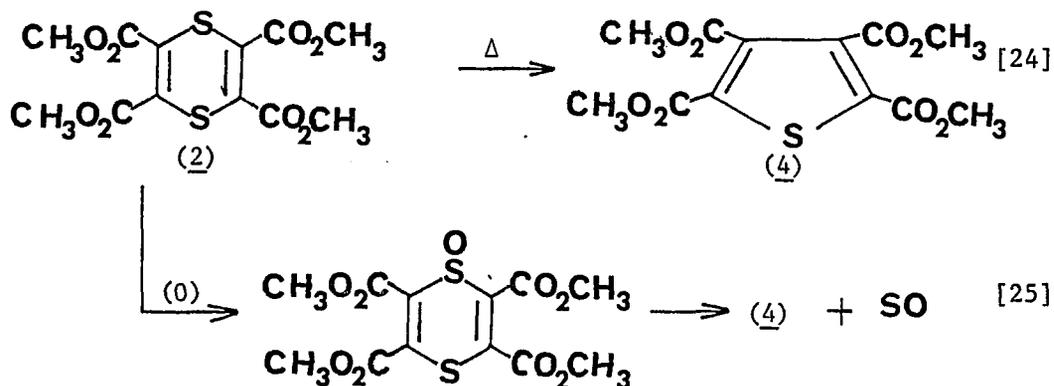


Here ${}^1\text{S}_2$ is used as the source of sulfur atoms, but other possibilities (${}^3\text{S}_2$, ${}^-\text{S-S-Br}$) exist.

Unfortunately, only an unidentifiable viscous oil was produced. This oil stored at 0° for several months eventually deposited a few crystals which were isolated and purified and shown to have the structure (4) by independent synthesis⁸⁶. The yield was less than 1% based on dimethyl acetylenedicarboxylate.

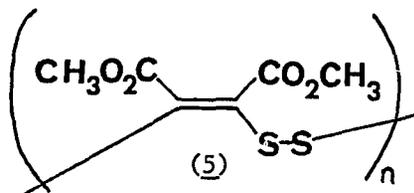


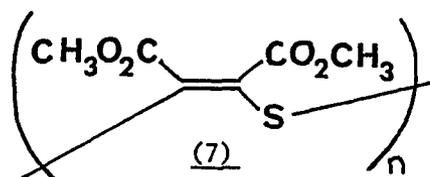
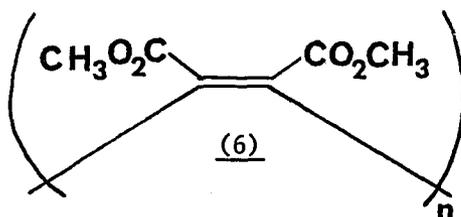
The thiophene (4) was a somewhat unexpected product. It could have reasonably arisen by either thermal extrusion of a sulfur atom from p-dithiin (2) or by oxidation of (2) followed by extrusion of SO^{87} .



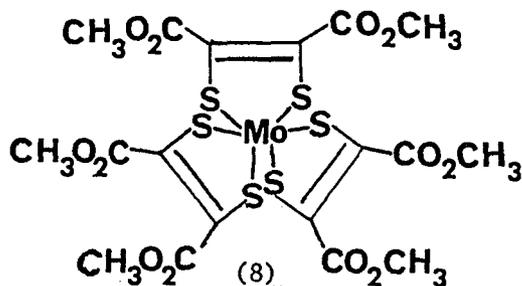
Neither of these conditions seem to have been met under the reaction conditions used unless bromine somehow served as an oxidant. Furthermore, although (4) can be formed from dimethyl acetylenedicarboxylate and sulfur, this requires a temperature of 160° ⁸⁶.

The oil remaining after removal of (4) was deemed to be a polymer with any one of the following possible structures:



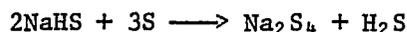


Attempts to convert this polymer to a monomeric material, both for the purpose of structure determination and in order to salvage useful products, failed. Treatment of the oil with sodium borohydride, which would have reduced the disulfide linkages in (5), gave no noticeable change. Likewise, treatment with $\text{Mo}(\text{CO})_6$ in an attempt to produce a compound such as (8)⁵³ proved fruitless.



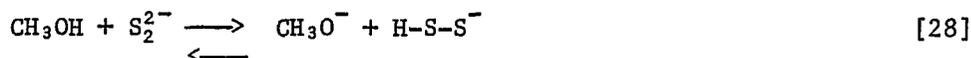
On other occasions, sodium disulfide was prepared in alternative ways. These preparations led to even more dissatisfying results. Solid sodium disulfide prepared from sodium tetrasulfide and sodium in

ethanol⁸⁸ (Equation [26]) or by fusion of anhydrous sodium sulfide and sulfur at 500°⁸⁹ (Equation [27]) was soluble in three solvents tested - methanol, formamide, and N,N-dimethylformamide. The methanolic solution



reacted exothermically with dimethyl acetylenedicarboxylate to produce a distillable oligomer containing methoxyl groups. This reaction was reproducible and also occurred when bromine was present. This result is contrary to the results mentioned previously and casts doubts on the nature of the methanolic sodium disulfide solution described previously⁹⁰. The sodium disulfide produced by the methods of Equations [26] and [27] was analyzed by ESCA before use, and was found to be pure⁹¹.

The oligomer is possibly formed due to anionic polymerization of dimethyl acetylenedicarboxylate catalyzed by methoxide, which in turn is present due to the equilibrium [28]. The pK_2 of H_2S_2 is 9.7³⁵; thus, a solution of disulfide dianion should be quite basic.



The formamide solution of sodium disulfide also reacted exothermically with dimethyl acetylenedicarboxylate, and the reaction was not pursued further. The solution of sodium disulfide in N,N-dimethylformamide turned very dark and probably contained many species in addition

to S_2^{2-} ³⁶. It also was studied no further. Mention should also be made of the fact that reaction of hexafluoro-2-butyne with bromine and this sodium disulfide in methanol produced a solid oligomer which contained methoxyl substituents.

Obviously, a nonacidic solvent was needed which would dissolve sodium disulfide (without reaction) as well as bromine and dimethyl acetylenedicarboxylate. To this end the solubility of sodium disulfide as well as its supposed complexes with 18-crown-6 and 15-crown-5 was tested in several solvents and the results are presented in Table IV. As can be seen the only encouraging result was that involving the 15-crown-5 complex in acetonitrile. However, further experiments were not conducted.

The next approach taken was the general one of Method (7) of Table I directed toward the preparation of dihydroaromatics bridged in a 1,4-sense with an endo disulfide. These compounds were to serve as precursors for 1S_2 generation. More detail is given in Table II, and indeed each of these methods was tried to some extent except for Method (7b).

First, the preparation of dihydrobenzene systems was attempted as in Method (7g) utilizing a Diels-Alder reaction between compound (9), prepared in 21% overall yield by the route shown in Scheme II^{79,82}, and various acetylenes.

The results of six such experiments are gathered in Table V.

TABLE IV

SOLUBILITY OF Na_2S_2 AND ITS COMPLEXES IN VARIOUS SOLVENTS

Solvent ^a	Na_2S_2 ^b	18-crown-6 complex ^c	15-crown-5 complex ^c
pentane	-	-	-
benzene	-	-	-
carbon tetrachloride	-	-	-
diethyl ether	-	-	-
tetrahydrofuran	-	-	-
dimethoxyethane	-	-	-
ethyl acetate	-	-	-
ethanol	+ ^d	+	+
acetonitrile	-	-	+ ^d
dimethylformamide	+	+	+
nitromethane	-	-	-

^a2.0 ml of solvent used.

^b10 mg used.

^cPrepared from 1.0 mmol Na_2S_2 and 2.0 mmol crown ether in 11.0 ml methanol. The solution was partitioned into 11 1.0 ml fractions, the methanol evaporated, and the test solvent added.

^dPartial solubility.

Scheme II:

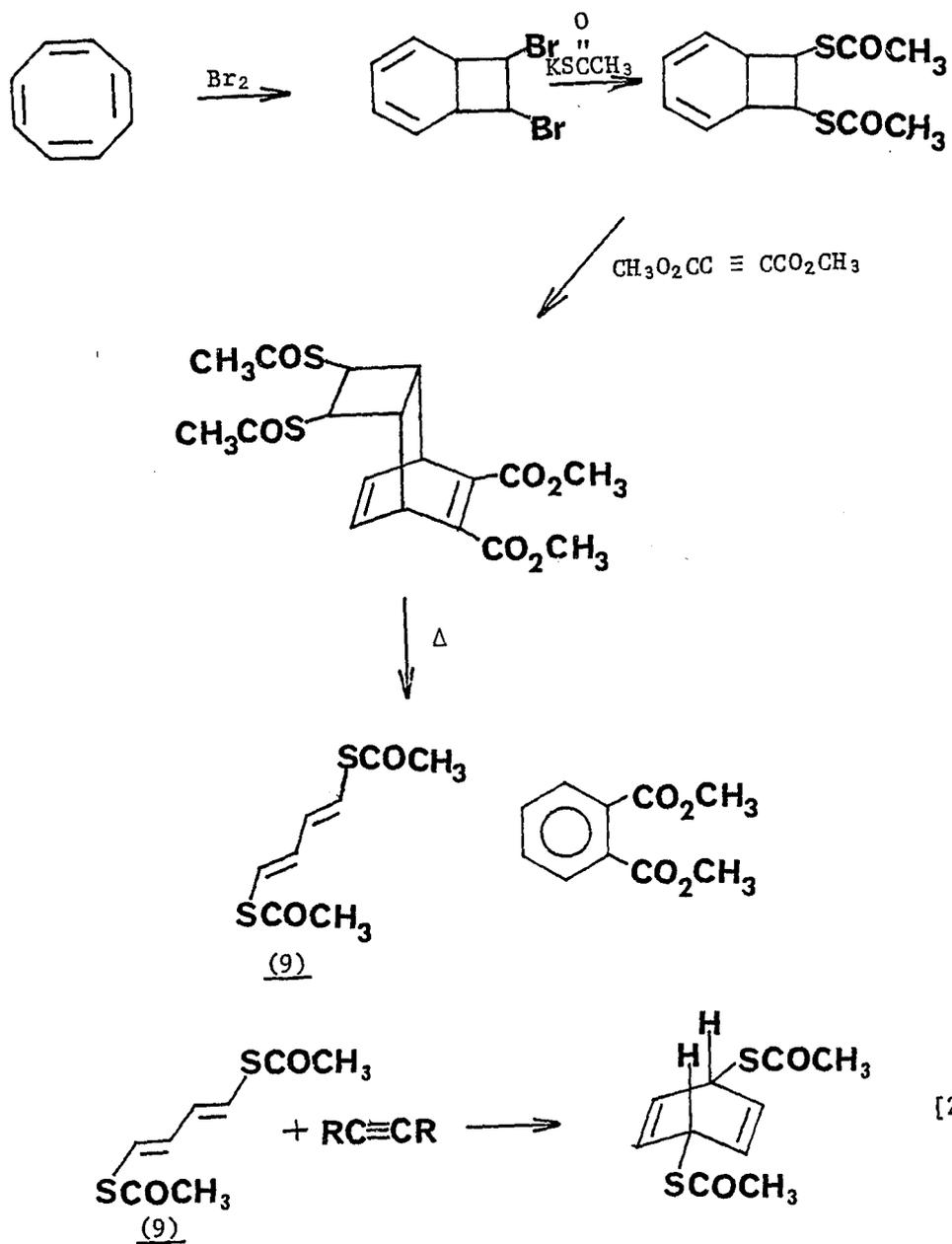


TABLE V
REACTION OF (9) WITH ACETYLENES

Acetylene	Solvent	Conc. of Diene ^a (mol l. ⁻¹)	Temp(°C)	Time(hr)	% Yield
methyl cyanopropiolate	chloroform	0.8	60	72	20.0
dimethyl acetylene- dicarboxylate	benzene	1.0	80	168	0 ^b
	xylene	1.0	140	168	0 ^b
	c	c	60	240	d
hexafluoro-2-butyne	e	0.1 ^f	25	168	0
	e	0.1 ^f	60	168	0
cyclooctyne	chloroform	0.2	25	24	0
benzyne	7:5 tetrahydrofuran- dichloromethane	0.4 ^g	25	2	0
acetylene dicarboxylic acid bis-trimethylsilyl ester (14) c	c	c	85	240	0

^aThe concentrations of the acetylene and the diene used were identical unless otherwise noted.

^bAromatized product formed.

^cNo solvent, only a 30-fold excess of the acetylene.

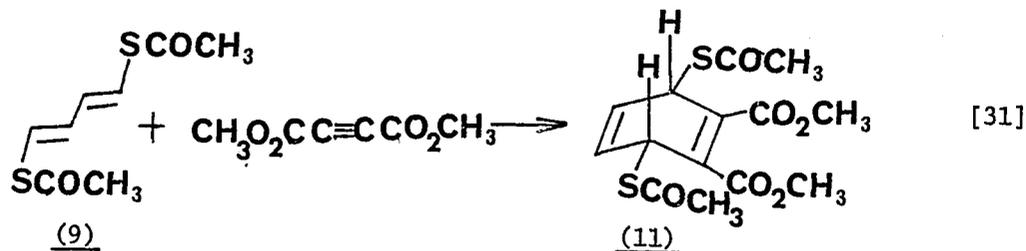
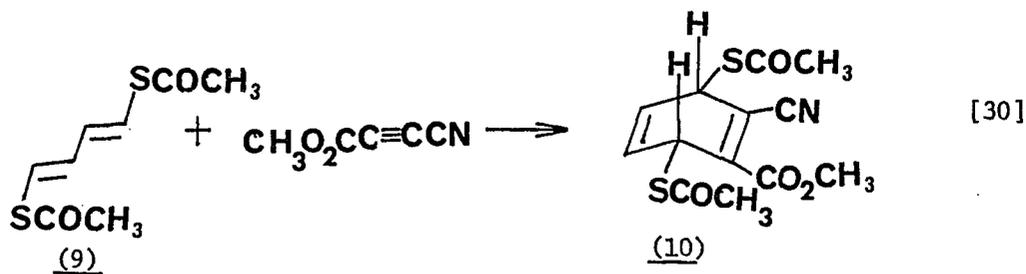
^dNo yield taken; product formation observed by nmr.

^eTetrahydrofuran used in one experiment and chloroform in another.

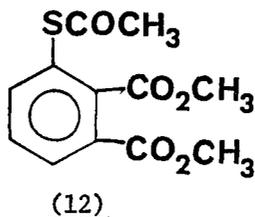
^fA 10-fold excess of the acetylene used at a pressure of 4 atm.

^gA 20-fold excess of the acetylene used.

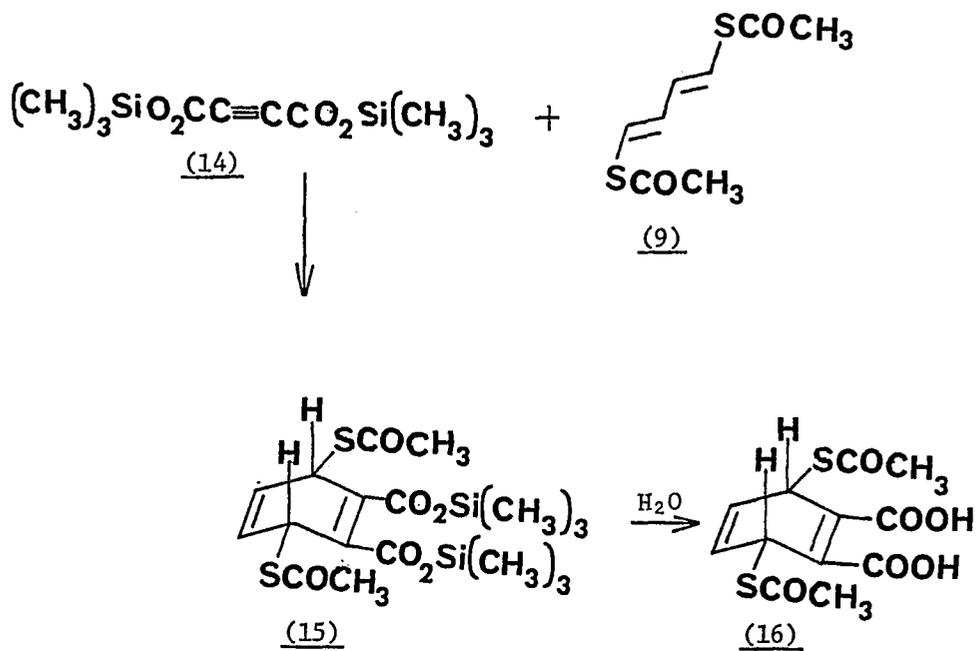
The only successful reactions were those with methyl cyanopropionate to produce (10) and with dimethyl acetylenedicarboxylate to produce (11). The former reaction was carried out with a very small amount of



acetylene^{92,93}, and yielded a small amount of product in equilibrium with starting material. The product was never isolated but was observed in the nmr spectrum of the reaction mixture. The latter reaction would not proceed when one equivalent of dimethyl acetylenedicarboxylate was refluxed in benzene with (9); the reaction gave the aromatized product (12) when conducted at reflux in xylene. The formation of the desired



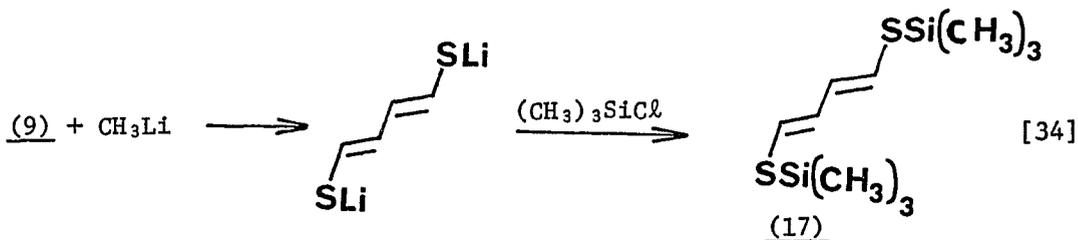
product (11) could be observed by nmr when dimethyl acetylenedicarboxylate was used as the solvent at a temperature of 60°. However,



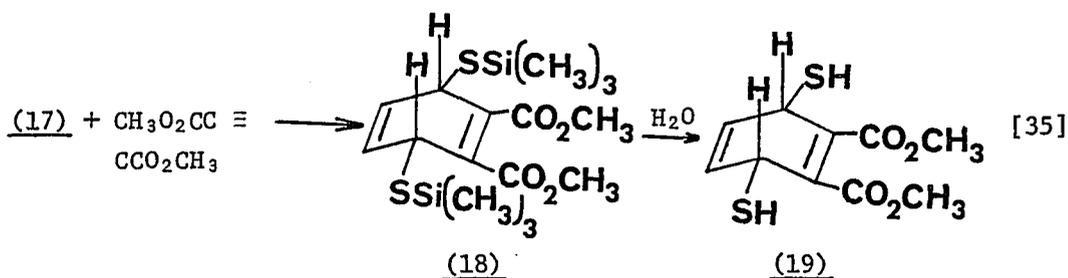
[33]

hope was that the product (15) could be readily hydrolyzed to the corresponding diacid (16). Unfortunately, (14) did not react with (9) under the conditions previously established for reaction with dimethyl acetylenedicarboxylate. The reason could be the steric hindrance in the transition state provided by the large trimethylsilyl groups.

Another variation on this theme was to convert (9) into the bis-trimethylsilyl derivative (17) as in Equation [34]. This was accomplished in 90% yield (by nmr, not isolated). This compound was then to be reacted with dimethyl acetylenedicarboxylate to produce (18), which could be

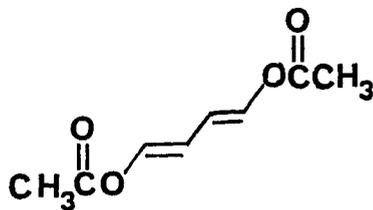


hydrolyzed to the bis-thiol (19). Once again no reaction was observed



under the previously established conditions.

The diene (20), analogous to (9), reacts with dimethyl acetylenedicarboxylate with difficulty⁹⁵. The differences between (9) and (20)



(20)

lie in the facts that (i) sulfur is bulkier than oxygen and can provide

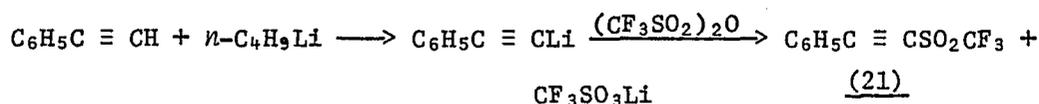
greater hindrance to the attack by a dienophile at the C-1 and C-4 positions of the diene, as well as also restrict the diene from attaining the *s-cis* conformation required for successful Diels-Alder reaction, and (ii) the thioacetoxy groups of (9) are less electron donating to the π system of the diene than are the acetoxy groups of (20). Since Diels-Alder reactions of normal electron demand require electron-rich dienes⁸⁴, both the steric factor and the electronic factor should be expected to diminish the reactivity of (9) relative to (20). Adding bulky trimethylsilyl groups as in (17) just increases the steric prohibition that much more, and this effect overrides the electron donation of the trimethylsilyl groups. Perhaps a distinction could be made between the effect on reactivity of (9) by steric factors vs. electronic factors by construction of a compound with small electron donating groups on sulfur, e.g., methyl groups, and then observation of the reactivity of this compound with dimethyl acetylenedicarboxylate vs. that of (9). This was not tried, however.

The only other way in which the rate of reaction of (9) with an acetylene could be increased is by use of a more reactive acetylene. The only other reported non-gaseous acetylene of significantly higher dienophilicity than dimethyl acetylenedicarboxylate is dicyanoacetylene. However, this compound could not be prepared by the reported procedure⁹⁶ despite several attempts.

Consequently, a study was undertaken to find a substituent which could render an acetylene a potent dienophile yet would allow for simple synthesis of the acetylene and moderate stability on storage. Since the trifluoromethanesulfonyl group is an unusually potent electron-withdrawing

group, as evidenced by its extraordinarily large σ constant⁹⁷, acetylenic dienophiles with such a substituent might undergo especially facile Diels-Alder reactions. Thus, the model system phenyl(trifluoromethanesulfonyl)acetylene (21) was investigated by kinetic comparison with other substituted phenylacetylenes.

Phenyl(trifluoromethanesulfonyl)acetylene was prepared from phenylacetylene as shown in Equation [36]. The ir, nmr, and mass spectra



[36]

support this structural assignment. In addition, controlled catalytic hydrogenation of this acetylene produced *cis*-2-phenyl(1-trifluoromethanesulfonyl)ethylene, and reaction of this acetylene with benzenethiol in the presence of sodium thiophenoxide yielded a crystalline monoadduct.

As illustrated in Tables VI and VII, (21) reacted faster with tetraphenylcyclopentadienone and 1,3-diphenylisobenzofuran than any other phenylacetylene investigated. Note should be made that the rate-determining step in the reaction of tetraphenylcyclopentadienone with phenylacetylene derivatives is believed to be the Diels-Alder addition and not the subsequent decarbonylation step⁹⁸⁻¹⁰¹. Phenyl(trifluoromethanesulfonyl)acetylene reacted 235 and 5.4 times faster than phenylpropioloyl chloride, the next most reactive acetylene studied, with 1,3-diphenylisobenzofuran at 108° and tetraphenylcyclopentadienone at 174°, respectively. Furthermore, (21) reacted readily with cyclopentadiene in

TABLE VI
 SECOND-ORDER RATE CONSTANTS FOR THE REACTIONS^a
 $C_6H_5C \equiv CX$ WITH TETRAPHENYLCYCLOPENTADIENONE

Compound	X	$k_2 \times 10^3 (\text{l. mol}^{-1} \text{sec}^{-1})$
(21)	SO ₂ CF ₃	38.7
(22)	COCl	15.0
(23)	CN	11.0
(24)	CHO	2.70 ^b
(25)	CO ₂ CH ₃	1.56 ^c
(26)	Si(CH ₃) ₃	d

^aAll reactions were run in *p*-cymene as solvent at a temperature of 174.0-174.5° and with an initial concentration of acetylene of $8.1 \times 10^{-2} \text{ mol l}^{-1}$ except for the reaction of (21) in which the initial concentration of acetylene was $3.85 \times 10^{-2} \text{ mol l}^{-1}$.

^bReported¹⁰¹ rate constant $1.69 \times 10^{-3} \text{ l. mol}^{-1} \text{sec}^{-1}$ for this reaction.

^cReported¹⁰¹ rate constant $1.27 \times 10^{-3} \text{ l. mol}^{-1} \text{sec}^{-1}$ for this reaction.

^dThere was no appreciable reaction after 48 hr.

TABLE VII
 SECOND-ORDER RATE CONSTANTS FOR THE REACTIONS^a OF
 $C_6H_5C \equiv CX$ WITH 1,3-DIPHENYLISOBENZOFURAN

Compound	X	$k_2 \times 10^3 (\text{l.mol}^{-1}\text{sec}^{-1})$
(21)	SO_2CF_3	$6.01^b, 13.6^c, 27.1^d, 2940^e$
(22)	$COCl$	12.5
(23)	CN	7.04
(24)	CHO	1.67
(25)	CO_2CH_3	0.690
(26)	$Si(CH_3)_3$	f

^aAll reactions were run in toluene as solvent at a temperature of 107.5-108.0° except where indicated otherwise. The initial concentration of acetylene was $8.10 \times 10^{-2} \text{ mol l}^{-1}$ for (21) and (22) and $2.31 \times 10^{-1} \text{ mol l}^{-1}$ for (23) - (26).

^bTemperature of 23.5°.

^cTemperature of 31.0°.

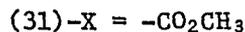
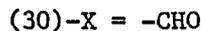
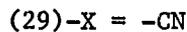
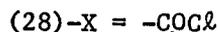
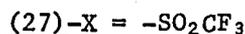
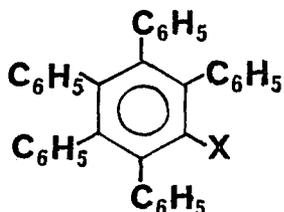
^dTemperature of 41.0°.

^eValue at 108.0° extrapolated from the data obtained at lower temperatures: $E_a = 16.2 \text{ kcal mol}^{-1}$ and $A = 4.42 \times 10^9$.

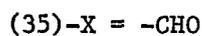
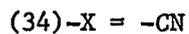
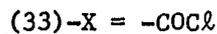
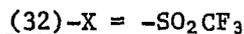
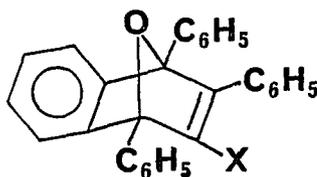
^fThere was no appreciable reaction after 48 hr.

toluene at 24.0 - 24.1° with a second-order rate constant of $2.41 \times 10^{-3} \text{ l.mol}^{-1}\text{sec}^{-1}$, whereas phenylpropioloyl chloride showed no appreciable reaction with cyclopentadiene at room temperature even after 24 hrs. Phenyl(trifluoromethanesulfonyl)acetylene reacted 65 times faster than phenylpropioloyl chloride with 1,3-cyclohexadiene at 81.0 - 81.5° in benzene (the second order rate constants were 1.68×10^{-3} and $2.58 \times 10^{-5} \text{ l.mol}^{-1}\text{sec}^{-1}$, respectively). Surprisingly, (21) even reacted faster with cyclopentadiene than did dimethyl acetylenedicarboxylate. In a competition experiment at room temperature (21) proved 1.7 times more reactive than dimethyl acetylenedicarboxylate^{102,103}.

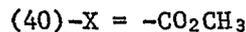
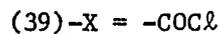
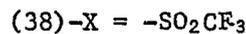
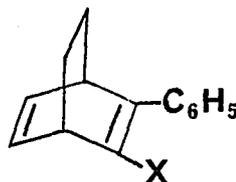
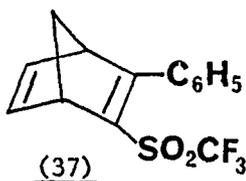
Each of the reactions studied kinetically was run on a preparative scale and the product was isolated and characterized. For the reactions with tetraphenylcyclopentadienone, compounds (27) - (31) were isolated in good yields.



The reactions with 1,3-diphenylisobenzofuran afforded good yields of adducts (32) - (36). Reaction of (21) with cyclopentadiene and



1,3-cyclohexadiene produced adducts (37) and (38), respectively. Phenylpropionyl chloride and 1,3-cyclohexadiene afforded adduct (39), isolated as (40).



The remarkable facility with which (21) undergoes Diels-Alder reactions is ascribable to the electron-withdrawing electronic effect of the trifluoromethanesulfonyl group. The electronic effect is due to an inductive effect and, perhaps, a resonance interaction as well. Studies on the substituent effects of the trifluoromethanesulfonyl group on benzoic acid, aniline, and phenol derivatives suggest that the electron

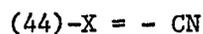
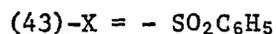
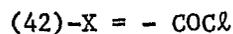
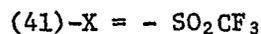
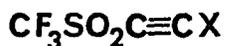
withdrawing effect of this group is due to a significant resonance interaction as well as an inductive effect. The electronic effect of the sulfonyl group is responsible as well for the enhanced dienophilicity of double bonds appended with chlorosulfonyl¹⁰⁴, or alkyl or aryl sulfonyl groups¹⁰⁴⁻¹⁰⁶, the marked dienophilicity of aryl sulfonyl cyanides¹⁰⁷⁻¹¹⁰, at least in part for the potent dienophilicity of thiophene 1,1-dioxide¹¹¹, and the high reactivity of chlorosulfonyl isocyanate¹¹²⁻¹¹⁶ in cycloaddition reactions.

Note should be made that the sulfonyl group enhances dienophilicity despite its unfavorable steric and field effects. Nucleophilic substitution at the carbon of α -substituted sulfones is usually extraordinarily difficult¹¹⁷⁻¹¹⁹ (except if the displacement is intramolecular, as in the Ramberg-Bäcklund¹²⁰, or if an exceptionally good leaving group is attached to the α carbon, such as in an α -diazonium ion¹²¹ or α -trifluoromethanesulfonate¹²²). This difficulty has been attributed to the steric and field effect of the sulfone group. Nevertheless, in the Diels-Alder reaction these unfavorable effects are overwhelmed by the favorable electronic effect. The reason¹²³ for this may be that the steric effect of the sulfonyl group is small and the field effect of the negatively charged oxygen atoms accounts for the difficulty in effecting nucleophilic displacement at the carbon of α -substituted sulfones. Such a field effect would be expected to strongly disfavor the approach of nucleophiles but the effect on the approach of 1,3-dienes would be relatively modest.

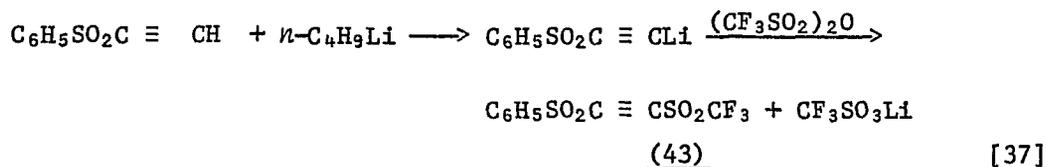
Alternatively, for the Diels-Alder reactions of (21) an unsymmetrical transition state could maximize the rate enhancing electronic

effect and minimize the steric and field effects of the trifluoromethanesulfonyl group. In such a transition state the distance between C-1 of the diene and the carbon bearing the phenyl group in the acetylene would be less than the distance between C-4 of the diene and the acetylenic carbon bearing the trifluoromethanesulfonyl group. Furthermore, the carbon bearing the trifluoromethanesulfonyl group would have a partial negative charge which the trifluoromethanesulfonyl group could stabilize by induction and resonance. However, for Diels-Alder reactions of $\text{ArSO}_2\text{CH}=\text{CHSO}_2\text{Ar}$ an unsymmetrical transition state would minimize the steric and field effect of one but not both arylsulfonyl groups. Nevertheless, these compounds are potent dienophiles¹⁰⁶. Thus, the electronic effect of the sulfonyl group overwhelms the steric and field effects even in these cases. Note, however, that the transition state for the reaction of tetraphenylcyclopentadienone with methyl esters of substituted propiolates has been proposed^{99,100} to be unsymmetrical, but in the opposite sense to that proposed here¹²⁴.

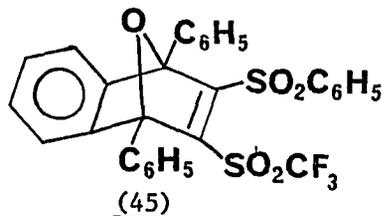
With the knowledge that the trifluoromethanesulfonyl group markedly enhances the dienophilicity of acetylenes, studies were begun to try to prepare an acetylene of high reactivity with one of the following structures:



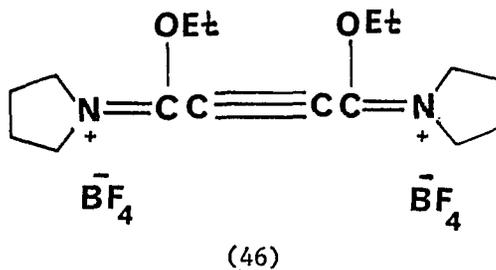
These studies were never completed and only one acetylene, (43), was apparently prepared. This compound was made as shown in Equation [37], but the product was evidently quite unstable and could not be isolated from the dark reaction mixture. Instead it was trapped as the adduct

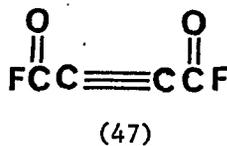


(45) with 1,3-diphenylisobenzofuran. However, once more the same reaction mixture failed to react with (9).



Further studies involving acetylenic dienophiles should concentrate on the compounds (41) - (44), dicyanoacetylene, the unknown but potentially highly reactive (46)¹²⁵, and acetylene bis-carbonyl fluoride (47).





This latter compound is well characterized¹²⁶⁻¹²⁹ (as opposed to the corresponding bis-acid chloride^{130,131}), but apparently has never been tested in Diels-Alder reactions.

Next, Method (7g) of Table II was modified by the use of olefinic and azo dienophiles rather than acetylenes for Diels-Alder reaction with (9). As can be seen from the results listed in Table VIII all reactions which yielded products did so in low yield, with the exception of that with diethyl azodicarboxylate. The reaction with maleic anhydride established an equilibrium which could be driven toward product by the use of a large excess of maleic anhydride. However, under these conditions, isolation of the product from the excess dienophile could not be accomplished reproducibly. Apparently the reactivity of compounds such as bromomaleic anhydride and chloranil is retarded due to steric factors imposed by the halogen atoms. The halogens are electron-donating electronically, a factor which should enhance the reactivity of the dienophile.

Further conversion of the adducts (48) - (51) was not attempted. However, the most appealing elaboration may be that for the adduct (51) shown below.

TABLE VIII
REACTION OF (9) WITH DOUBLE BOND DIENOPHILES

Dienophile	Solvent	Conc. of Diene ^a (mol l. ⁻¹)	Temp(°C)	Time(hr)	% Yield	Adduct
maleic anhydride	toluene	0.5 ^b	110	168	49.0 ^c	(48)
bromomaleic anhydride	chloroform	0.5 ^d	60	120	0	
diethyl azodicarboxylate	toluene	0.5	110	240	70.2	(50)
tetracyanoethylene	1:1 chloroform- benzene	0.5	60	240	26.1	(49)
fumaryl chloride	e	e	65	168	42.0	(51)
<i>p</i> -benzoquinone	benzene	0.5	80	48	0	
chloranil	benzene	0.5	80	48	0	

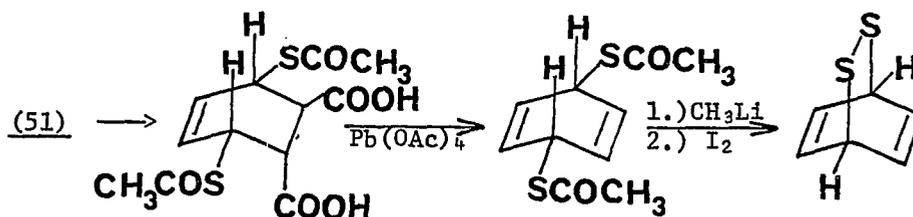
^aThe concentrations of the diene and dienophile were the same unless noted otherwise.

^bA 3-fold excess of maleic anhydride was used.

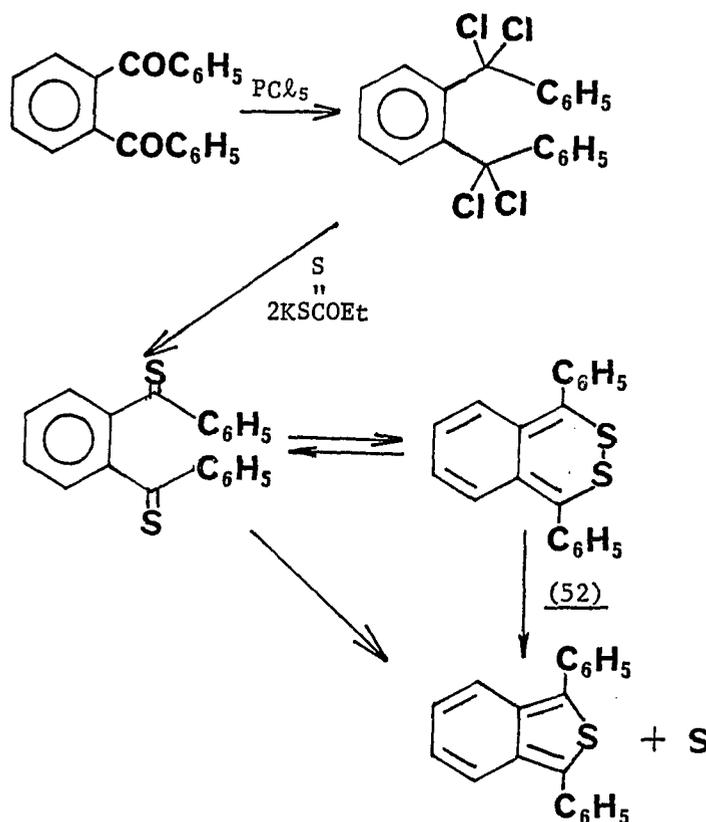
^cIsolation was not reproducible.

^dA 2-fold excess of the dienophile was used.

^eNo solvent, only a 15-fold excess of the dienophile.



One attempt was made to prepare a dihydronaphthalene endo disulfide by Method (7f) of Table II. The *o*-dithiin (52) was to have been prepared by the reported method⁸¹ (Equation [38]) and reacted with dimethyl acetylenedicarboxylate, but the literature preparation yielded no (52), only a 72% yield of 1,3-diphenylisobenzothiophene.

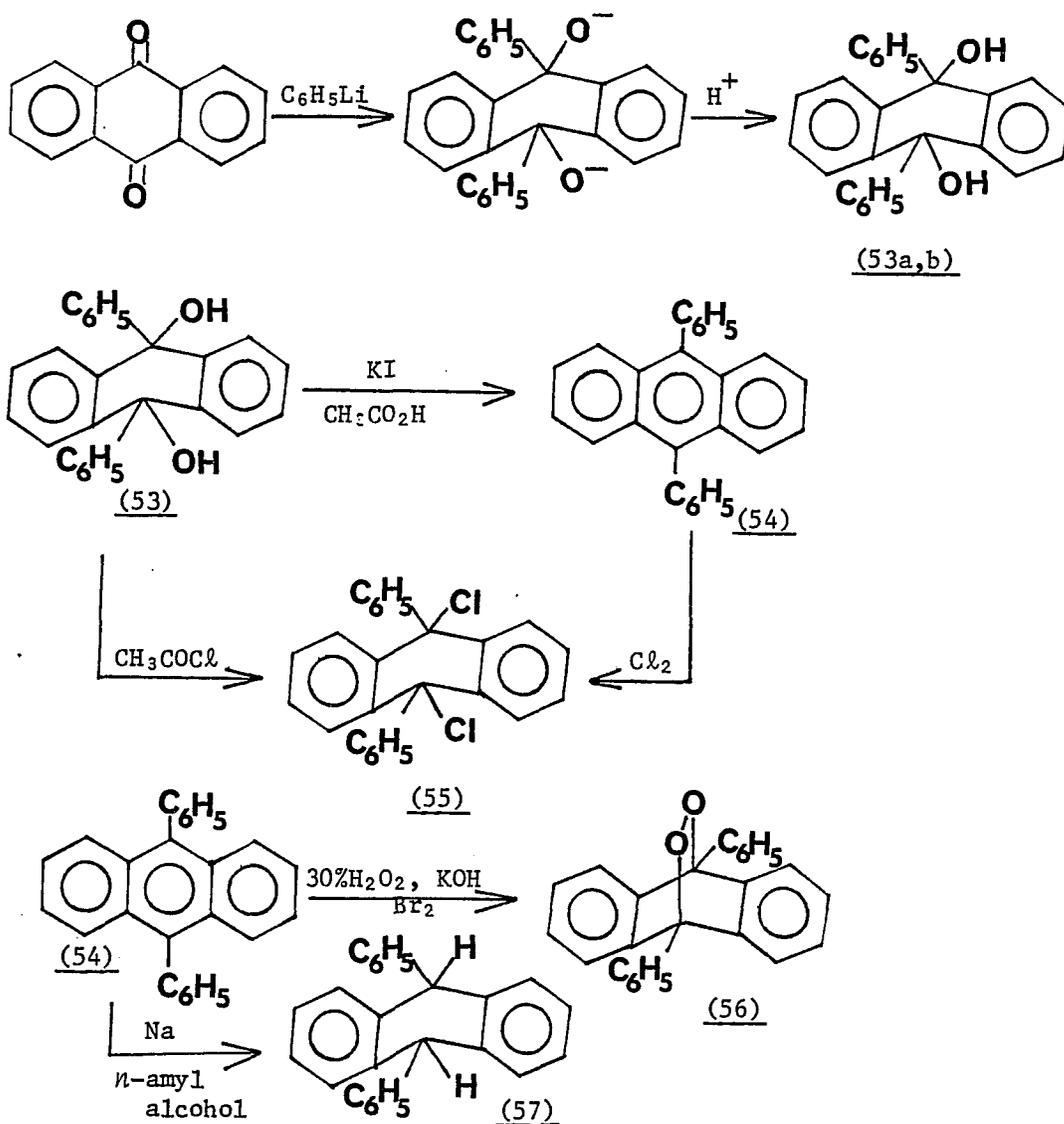


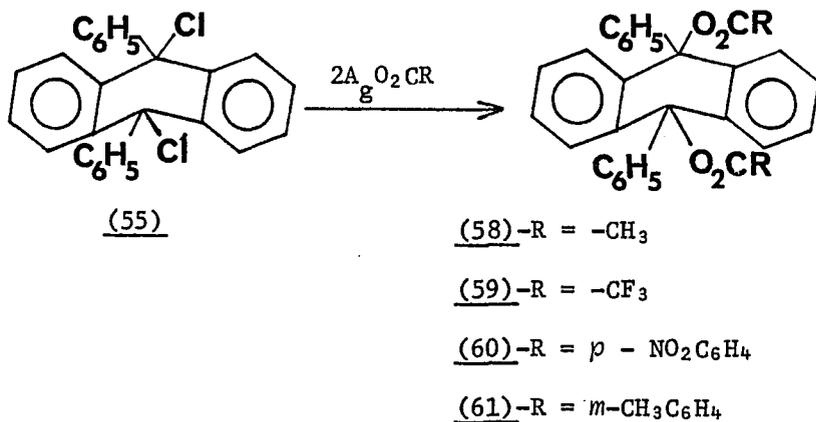
[38]

Lastly, dihydroanthracene systems were investigated, their preparations being attempted by the remaining methods of Table II, i.e., Methods

(7a) and (7c)-(7e). First, 9,10-diphenylanthracene systems were studied, and the syntheses of starting compounds are outlined in Scheme III. Most of these are known substances, but the esters (59) - (61) are new. They were prepared by methods proven reliable for the model triphenylmethyl systems, and their structures were confirmed by ir and nmr.

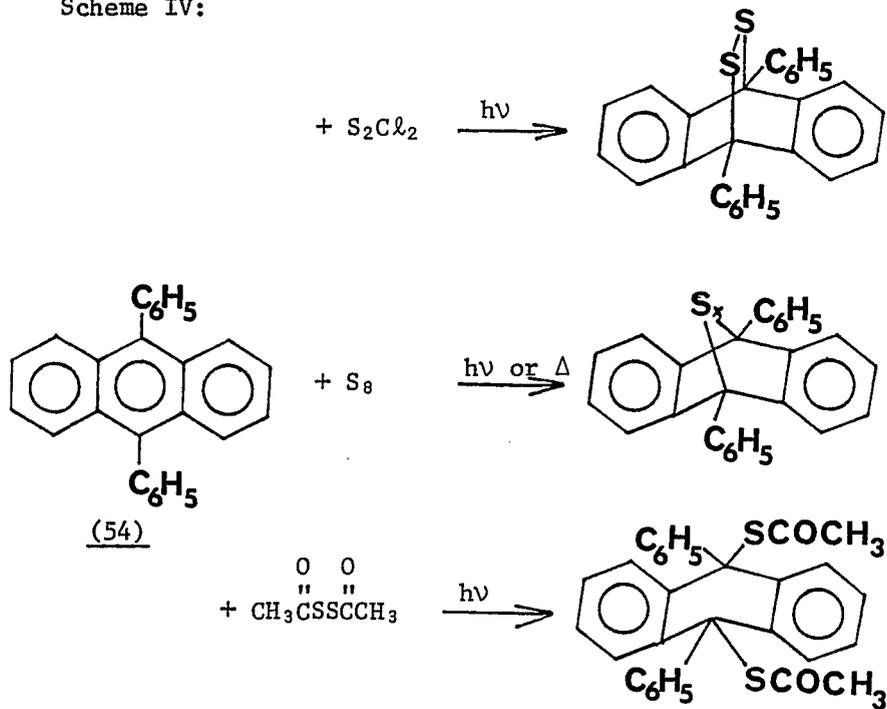
Scheme III:



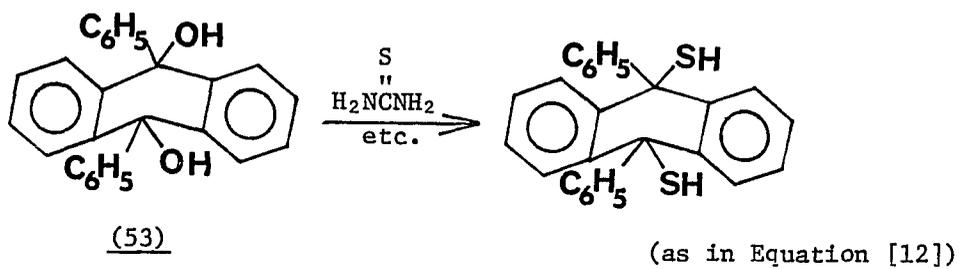
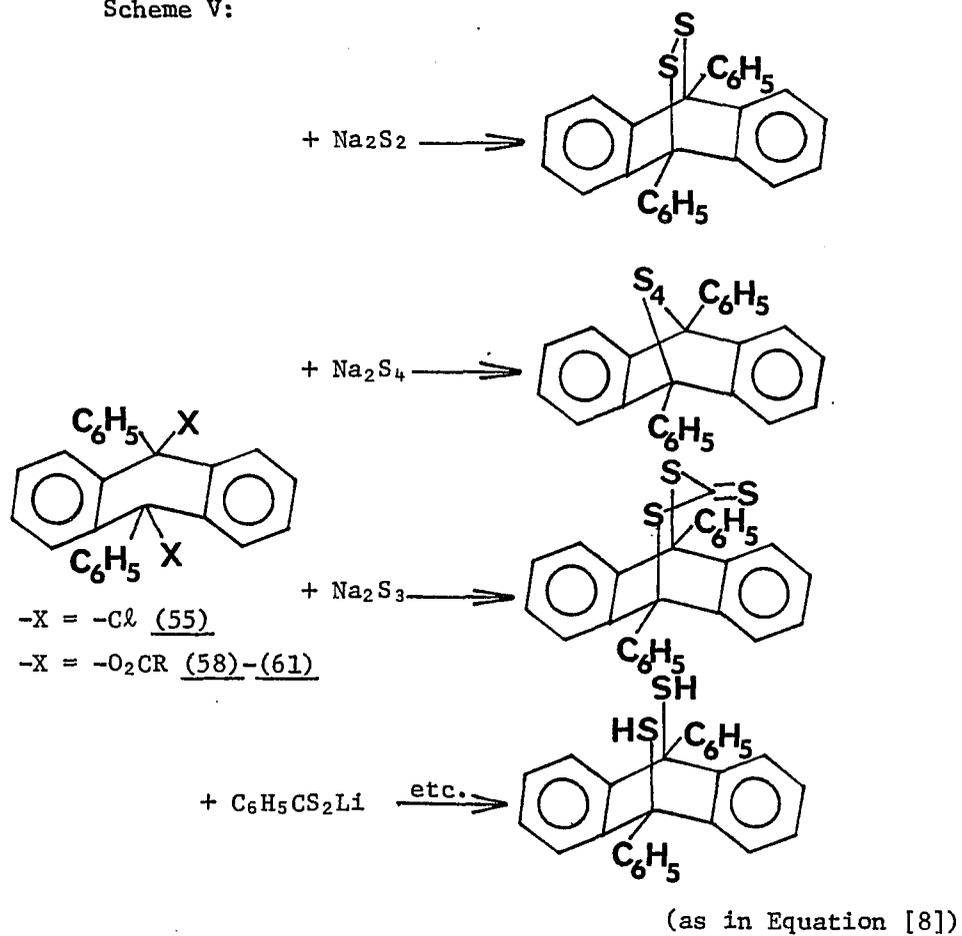


The reactions attempted with these compounds are all outlined in Schemes IV - VI.

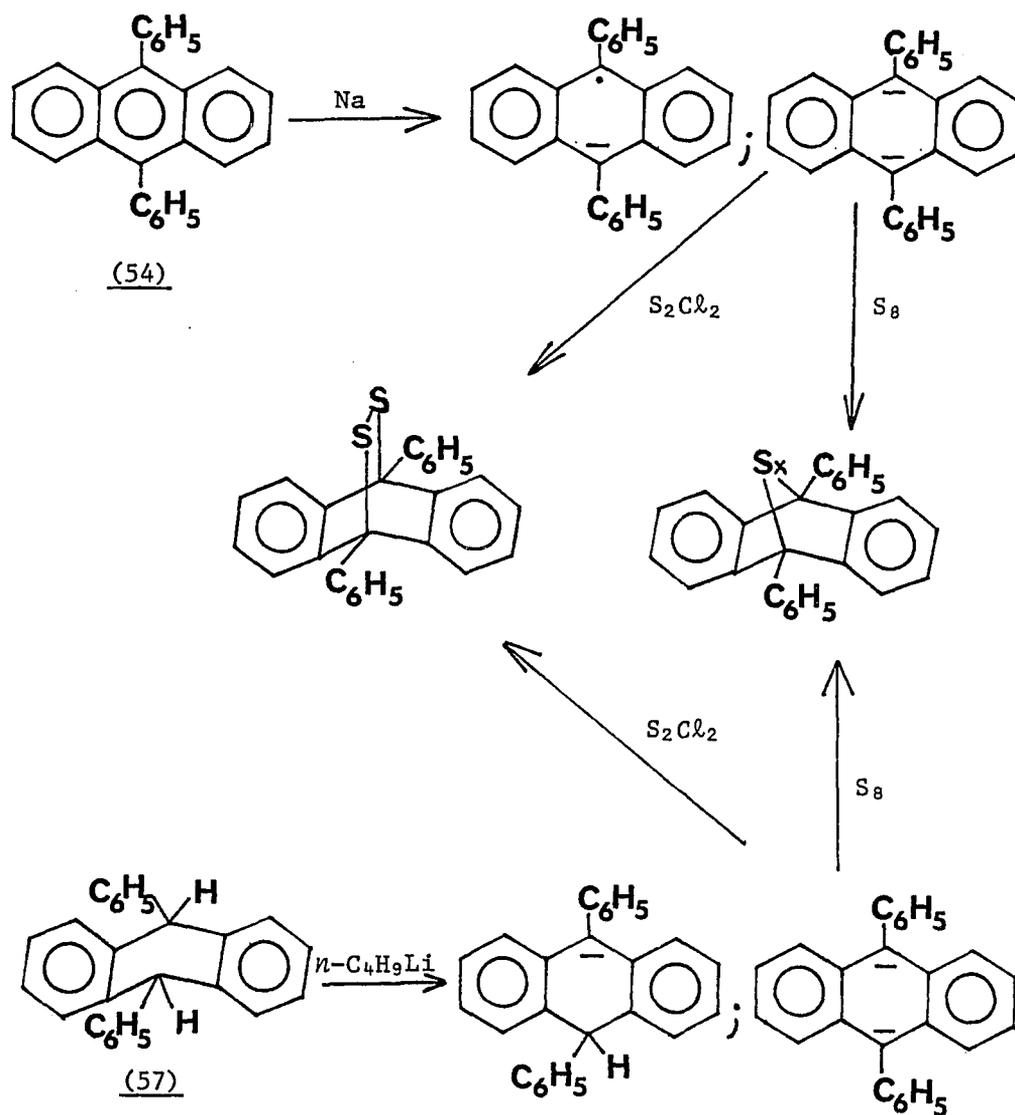
Scheme IV:



Scheme V:

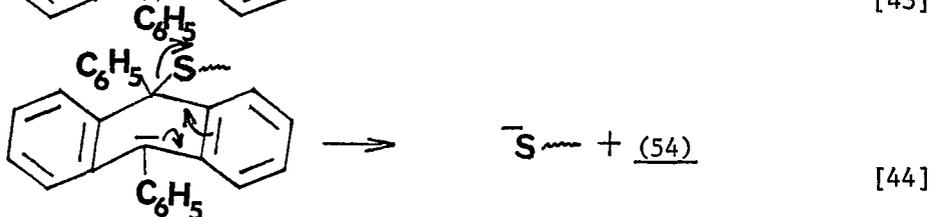
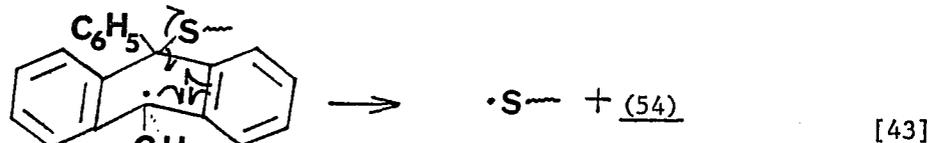
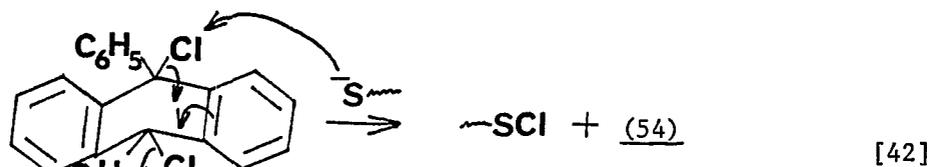
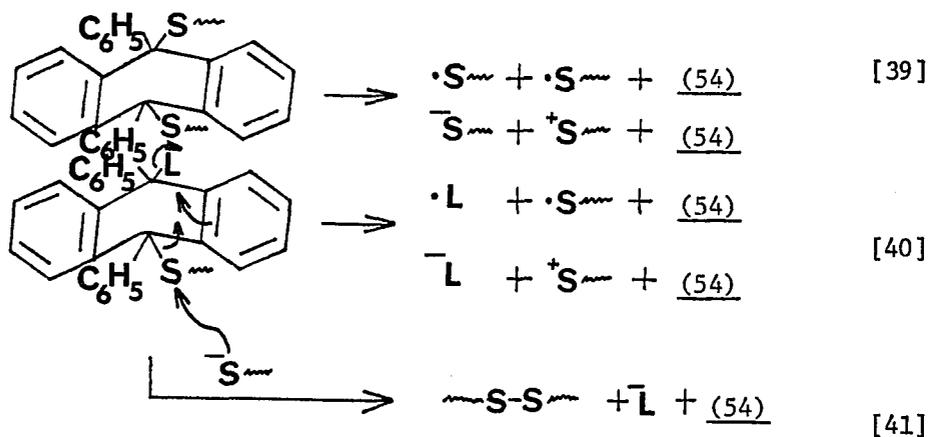


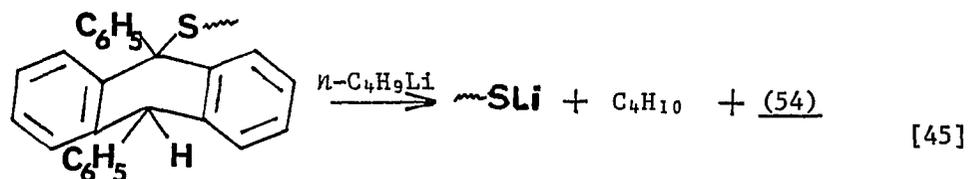
Scheme VI:



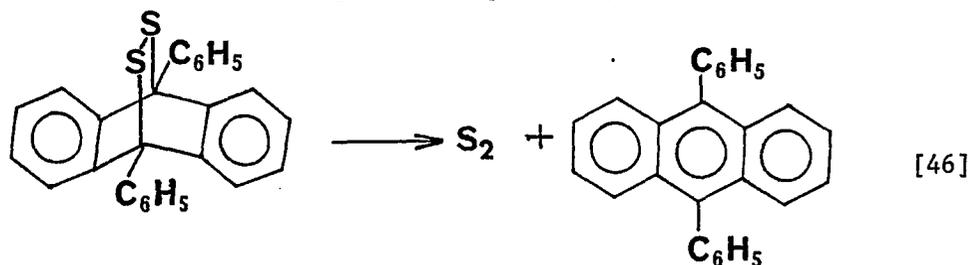
Without fail, every reaction led to quantitative recovery of 9,10-diphenylanthracene. Although the determining factors can be different

in the several cases shown in Schemes IV - VI, this fact reflects the great tendency of the 9,10-dihydro-9,10-diphenylanthracene system to aromatize by 1,4-elimination, if possible, and even perhaps by electron transfer. Representative (albeit descriptive) samples of possible pertinent modes of aromatization of these systems are sketched in a very general way below. Equation [39] schematically represents two ways in



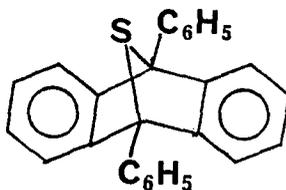


which two sulfur substituents can depart from the 9- and 10-positions. A special case is of course the reaction of Equation [46] which was the whole purpose of this investigation. Equation [40] illustrates the same



principle, but with a sulfur leaving group and another leaving group. Equations [41] and [42] are variations which require attack by a soft base to induce elimination. Radical attack is not excluded, however. Of course, any of these reactions could be stepwise processes rather than the concerted ones shown. Equations [43] and [44] show elimination of a sulfur leaving group from a radical and an anion, respectively, either of which may have been formed as an intermediate in the reactions of Scheme VI. Finally, Equation [45] represents a base induced elimination from an intermediate of Scheme VI.

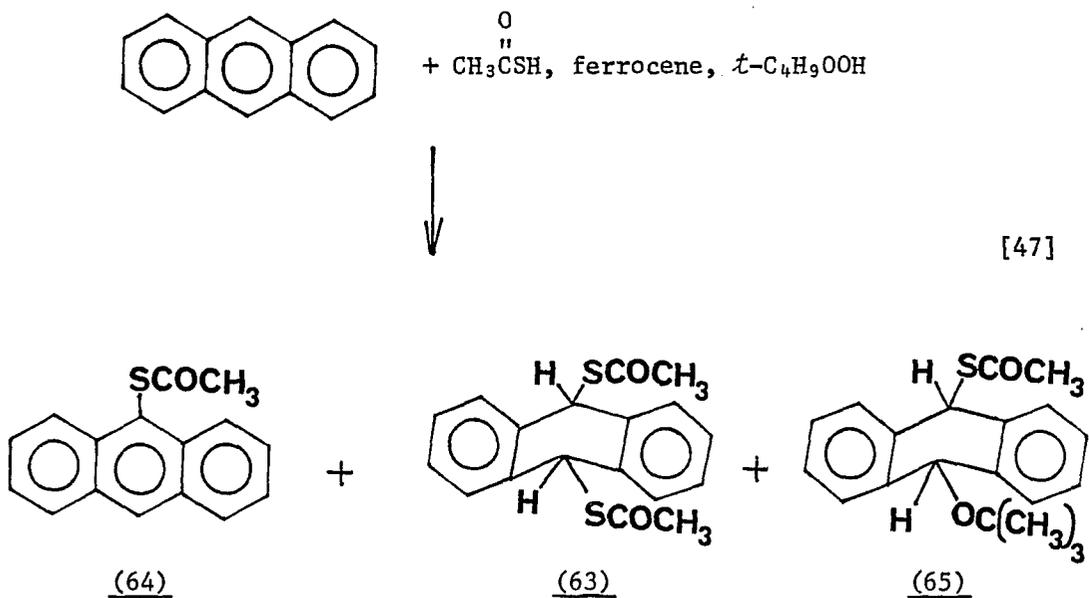
Note should be made of the fact that (53) is reported⁷⁴ to aromatize upon treatment with either H₂S or mercaptoacetic acid. Also, relevant is the fact that the literature holds only one example¹³² of a 9,10-dihydro-9,10-diphenylanthracene system which has sulfur substituents at the 9- and/or 10-positions, that being (62). Because of the great



(62)

driving force for aromatization and the many possible avenues for such aromatization, a system with sulfur atoms in these positions will be extremely difficult to synthesize.

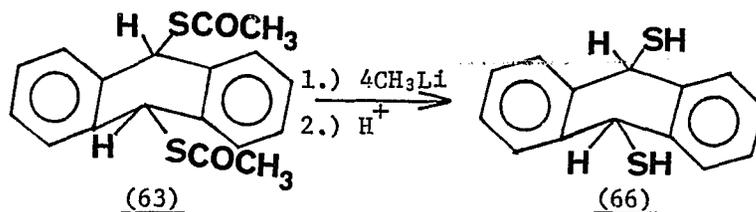
A system which has less driving force for aromatization (by a resonance energy of 78.9 kcal/mole¹³³⁻¹³⁵) than the 9,10-dihydro-9,10-diphenylanthracene one is that of 9,10-dihydroanthracene. Here several 9,10-disulfur substituted derivatives are known^{136,137}. One of these, (63), was prepared in 30% yield by the radical process shown in Equation [47]. This bis-thioacetate was then converted in 77% yield to the cor-



(64)

(63)

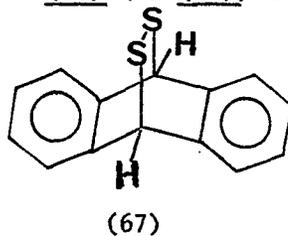
(65)



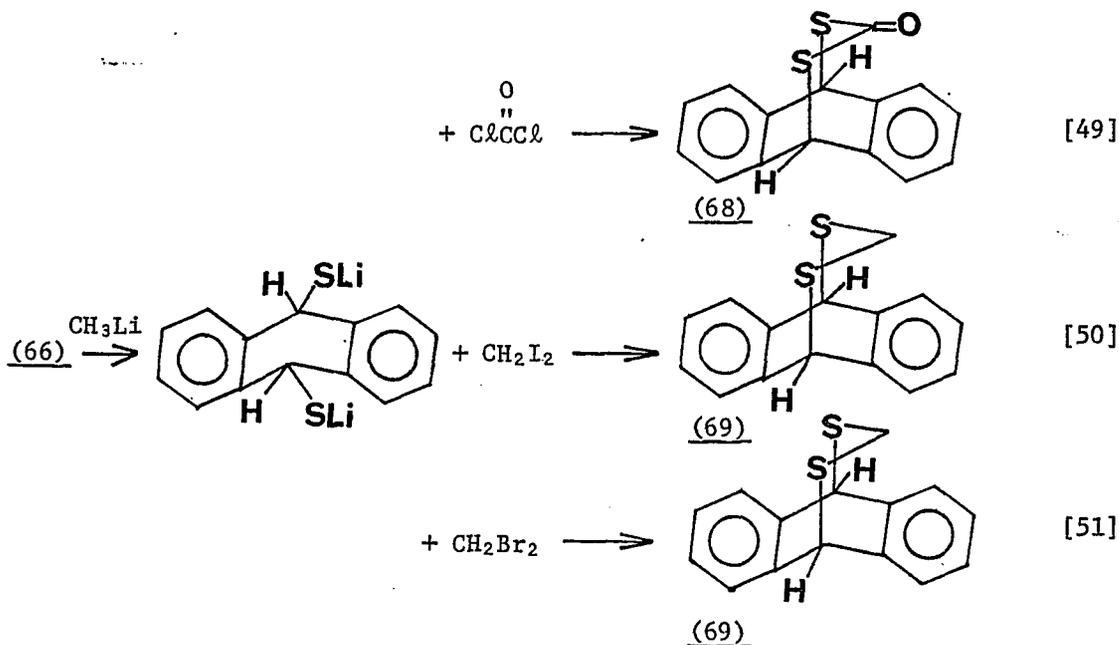
[48].

responding bis-thiol (66) with methyl lithium. Two isomers of (63) have reportedly been isolated from a reaction mixture such as that in Equation [47]¹³⁷, but the only products observed in the present work were anthracene, acetyl disulfide, 9-anthrylthioacetate (64), and one isomer of (63) - that of melting point 146°. At times compound (65) was also found in the reaction mixture, but its production was not reproducible. The conditions governing the formation of only (63), only (65), or a mixture of the two were not established.

Before (66) could be oxidized to a bridged disulfide of structure (67) the stereochemistry of (66) (or (63)) needed to be established.



Several reactions were attempted which had as their purpose the formation of a stable, cyclic, monomeric derivative, such as (68) or (69). Strangely, each reaction produced anthracene as the sole isolated product. The mechanism of anthracene formation should not have been decomposition of (67) produced by oxidation of the bis-thiolate by traces of oxygen since the same techniques were used in the production of this bis-thiolate

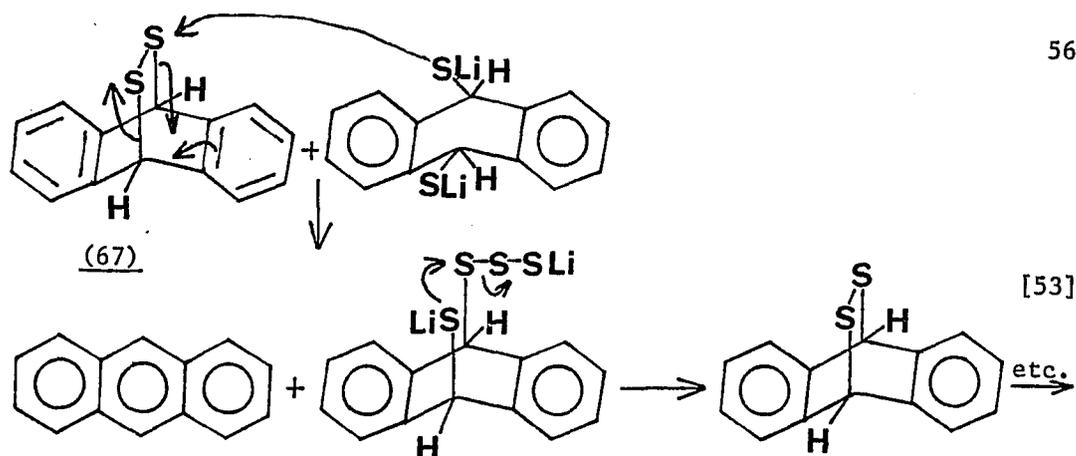


as were used in converting (63) to (66), and anthracene was not observed in that case.

A rationalization is presented in Equation [52] for the reaction



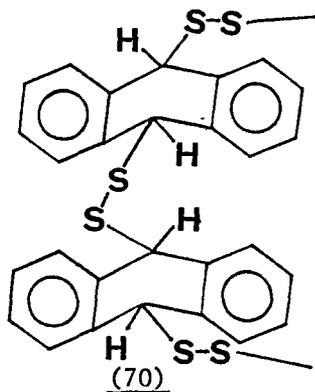
involving phosgene, but no convincing explanation could be thought of for the reactions involving dibromomethane or diiodomethane. A possibility in the case of diiodomethane is that the diiodomethane used contained a trace amount of iodine, which could have served as an oxidant for the formation of a small amount of (67). This in turn could have reacted as shown in Equation [53]. Indeed, the diiodomethane used was still dark



after distillation and was not washed with aqueous sodium thiosulfate solution. However, this precaution was taken with the dibromomethane reagent, and, in fact, this reagent gave a cyclic monomeric product from 1,2-ethanedithiol in 45% yield.

Since the stereochemistry could not be proven by formation of a derivative, an x-ray crystallographic analysis of the structure of (63) will be performed.

Finally, mention should be made of the fact that treatment of (66) with methyllithium in tetrahydrofuran at -78° , followed by one equivalent of iodine, quantitatively produces anthracene and sulfur. Since so many other reactions have also produced anthracene as their product, care must be taken not to assume that (67) was an intermediate under these conditions. The formation of anthracene was so rapid that the intermediate could not be observed by nmr when the reaction was run in an nmr tube at -78° , immediately transferred to the instrument, and the spectrum run at ambient temperature. Undoubtedly, a low temperature spectrum would be most useful. However, it is not clear that the nmr spectrum alone would distinguish between (67) and polymeric disulfide such as (70).



The final approach to a precursor for $^1\text{S}_2$ was that of Method (7c) of Table II. The feasibility of selective reduction of the aromatic portion of a sulfur substituted aromatic system and the subsequent rearrangement of Equation [6] was studied by subjecting phenyl trimethylsilyl sulfide to the conditions shown in Table IX. Reduction by either lithium or sodium alone was very slow, but the addition of a catalytic amount of naphthalene led to rapid and exclusive formation of benzenethiol.

In an effort to find a system in which the aromatic ring would be a more efficient electron acceptor compound (64) was converted in 82% yield to the trimethylsilyl thioether (72) by the route shown in Equation [54]. Upon reduction under a variety of conditions, the major product

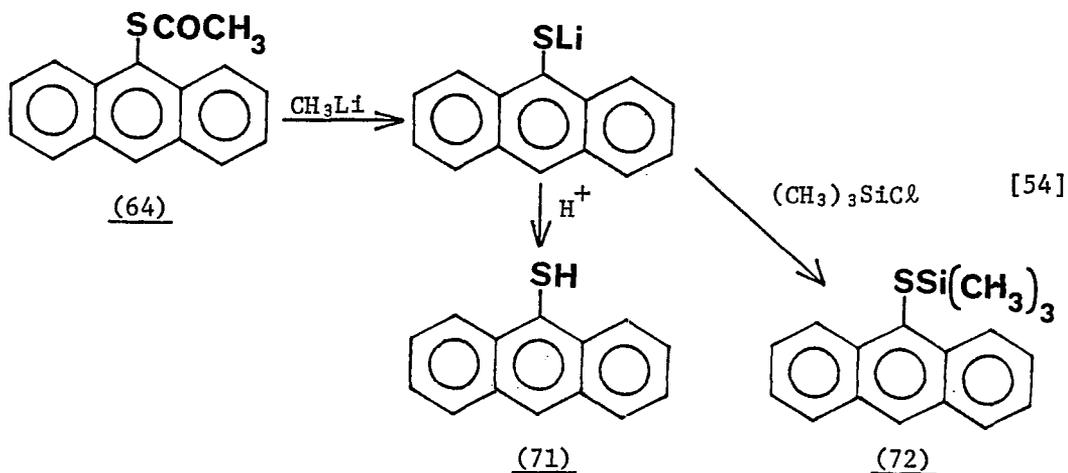


TABLE IX

RESULTS OF REDUCTION OF ARYL TRIMETHYLSILYL SULFIDES

Sulfide ^a	Conditions	Product	Amount(mg)
C ₆ H ₅ SSi(CH ₃) ₃	Li(70 mg), liq.NH ₃ , reflux, 20 hr.	C ₆ H ₅ SH	trace ^b
C ₆ H ₅ SSi(CH ₃) ₃	Na(230 mg), liq.NH ₃ , reflux, 20 hr.	C ₆ H ₅ SH	trace ^b
C ₆ H ₅ SSi(CH ₃) ₃	Na(230 mg), liq.NH ₃ , naphthalene (10 mg), reflux, 0.45 hr.	C ₆ H ₅ SH	509 (4.6mmol)
C ₆ H ₅ SSi(CH ₃) ₃	Li(70 mg), THF ^c , 65°, 48 hr.	C ₆ H ₅ SH	trace ^b
(72)	Na(46 mg), liq.NH ₃ , reflux, 1 hr.	anthracene	160 (0.9mmol)
(72)	Na(46 mg), <i>t</i> -C ₄ H ₉ OH (148 mg), liq.NH ₃ , reflux, 1 hr.	anthracene	160
(72)	Li(14 mg), THF ^d , 25°, 1 hr.	anthracene	160
(72)	Li(14 mg), THF ^d , <i>t</i> -C ₄ H ₉ OH (148 mg), 25°, 1 hr.	anthracene	160

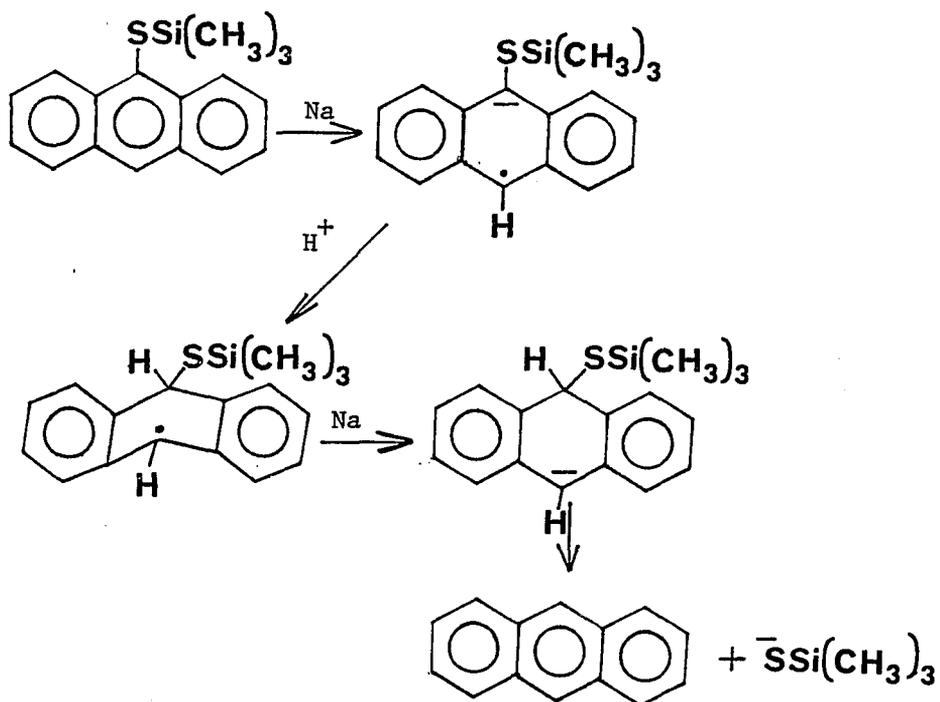
^a5.0 mmol of C₆H₅SSi(CH₃)₃ used and 1.0 mmol of (72) used.

^bDetected by tlc. Starting material was the major component at the end of this time.

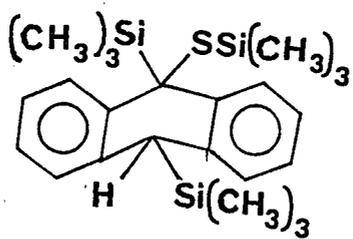
^c10 ml.

^d2 ml.

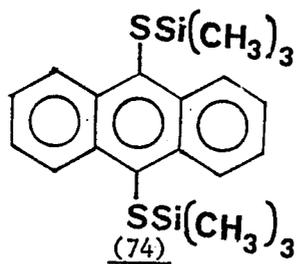
which resulted was anthracene, along with a small amount of 9,10-dihydroanthracene. Evidently, the former was the source of the latter under the reaction conditions. This behavior can be rationalized by assuming the anion radical formed in the first step of the reduction is trapped rapidly by some proton source, and that the anion formed in the second step eliminates more rapidly than it is trapped. This mechanism could



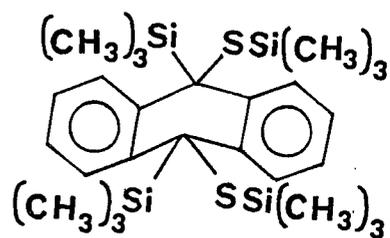
be tested by the inclusion of a large concentration of phenyl trimethylsilyl sulfide in the reaction mixture. Presumably, this silylating agent would trap the initial anion radical and lead to the formation of 9-trimethylsilylanthracene. If luck would allow, perhaps such a large concentration of silylating agent would even trap the second anion to form (73), in which case immediate extension to compound (74) would give (75), a desired product.



(73)



(74)



(75)

CHAPTER III

EXPERIMENTAL SECTION

All reactions were run under anhydrous conditions, and those run under nitrogen atmosphere utilized BTS purified nitrogen. Elemental microanalyses were performed by analysts at Spang Microanalytical Laboratory, Ann Arbor, Michigan. Molecular weights were determined using a Hewlett-Packard Model 302B vapor pressure osmometer. Infrared spectra were taken on a Perkin-Elmer Model 337 ir spectrophotometer. Proton nmr spectra were recorded using a Varian Model T-60 nmr spectrometer and employing tetramethylsilane as an internal standard. Mass spectra were determined employing a Hitachi Perkin-Elmer Model RMU-6E double focusing mass spectrometer. All melting points are corrected and were determined using a Thomas-Hoover melting point apparatus.

Organic reagents were supplied by Aldrich Chemical Co. while inorganic reagents came from Ventron or Baker Chemical Co. Solvents were dried by refluxing over drying agent for 24 hr, followed by distillation under nitrogen from the drying agent. A center cut was always taken.

3.1 Sodium Disulfide

(a)⁸⁵ Sodium disulfide in methanol was prepared as needed by dissolving sodium sulfide nonahydrate (3.76g, 15.6 mmol) and sulfur (0.50g, 15.6 mmol) in methanol (62.5 ml) in a 100 ml three-necked flask fitted with a reflux condenser and a gas inlet. The system was swept

with nitrogen and kept under nitrogen atmosphere while being stirred and heated at reflux for 1 hr. Upon cooling to room temperature, a small amount of material would settle to the bottom of the orange solution if the stirrer were turned off. Aliquots were withdrawn by syringe from the still solution by opening one neck of the flask under a stream of nitrogen.

(b)⁸⁸ In a 500 ml three-neck flask fitted with a reflux condenser and gas inlet was placed absolute ethanol (150 ml). This was stirred under a nitrogen atmosphere as small pieces of sodium (4.95g, 0.215 mol) were added through one neck of the flask over a period of 15 min. Once all the sodium had been consumed dry hydrogen sulfide, which had been passed through a calcium chloride drying tube, was bubbled through the solution for 25 min. The mixture was brought to reflux for 10 min. in order to expel any excess hydrogen sulfide. When the solution had cooled to room temperature sulfur (10.35g, 0.323 mol) was added at once. The deep red mixture was brought to reflux for 1 hr. At the end of this time the heating bath was removed and the mixture allowed to cool. While still somewhat warm, the mixture was treated with sodium metal (9.90g, 0.430 mol), which was added rapidly. The mixture immediately turned from red to yellow. The solution was heated one last time at 80° for 0.5 hr, and then allowed to cool to room temperature. The yellow product precipitated from solution and was collected on a glass frit in a glove bag under nitrogen. The material was dried at 80° for 24 hr in a drying oven under high vacuum to yield a powdery solid((19.03g, 80.5%): uncorrected mp 469° (lit.⁸⁸ mp 475°).

(c)⁸⁹ In a glove bag under nitrogen a clean, dry Pyrex tube was filled with an intimate mixture of anhydrous sodium sulfide (2.00g, 25.6 mmol) and sulfur (0.82g, 25.6 mmol). The tube was removed from the glove bag and immediately attached to a vacuum pump. It was sealed under high vacuum with a torch, the contents spread uniformly over the length of the tube, and the mixture heated for 1 hr at 500° in a muffle furnace. After cooling to room temperature, the tube was opened in a glove bag under nitrogen and the contents extracted with dry methanol. The methanol was evaporated on a vacuum pump to yield a yellow solid (2.50g, 88.7%): uncorrected mp 472° (lit.⁸⁸ mp 475°).

3.2 ESCA Studies of Sodium Disulfide

The sodium disulfide prepared in parts (b) and (c) above were analyzed by Mr. Patrick Brand. The results showed only a single peak at 159.7ev relative to carbon 1s (285ev), and no peak at 162.5ev, in complete accord with the literature⁹¹.

3.3 Sodium Disulfide Complex with 18-Crown-6

In a glove bag under nitrogen a 25 ml round bottom flask was charged with solid, dry sodium disulfide (110 mg, 1.0 mmol), 18-crown-6 (528 mg, 2.0 mmol), and dry methanol (11 ml). The flask was stoppered and the mixture stirred for 2 hr in the glove bag.

3.4 Sodium Disulfide Complex with 15-Crown-5

This complex was prepared in exactly the same manner as that above utilizing 15-crown-5 (440 mg, 2.0 mmol).

3.5 Tests of Solubilities of Sodium Disulfide and Its Crown Ether Complexes

Each of the solutions of crown ether complex prepared as above was partitioned by syringe in the glove bag into eleven different flasks. Each flask was removed from the glove bag and the methanol evaporated on a rotary evaporator protected by a drying tower. Then 2 ml of a dry test solvent was added to the dark oil which remained. Solubility was observed as the gradual dissolution of all or part of the dark solid or semi-solid which would coat the flask immediately after addition of the solvent.

In a like manner sodium disulfide (10 mg, 0.09 mmol) was treated with 2 ml of dry test solvent in a flask in a glove bag under nitrogen. The results and solvents tested are reported in Table IV.

3.6 Bromine and/or Sodium Disulfide Reactions with Trapping Reagents

In a glove bag under nitrogen a series of test tubes, each containing a small stir bar, were arranged above a magnetic stirrer. Each test tube contained one of the trapping reagents (0.25 mmol) listed in Table III dissolved or suspended in benzene (0.5 ml), and one tube contained only benzene (0.5 ml). Each solution was stirred in succession as simultaneously from two syringes were added an aliquot (0.5 ml) of a solution of bromine (800 mg, 5.0 mmol) in benzene (10 ml) and an aliquot (1.0 ml) of the sodium disulfide solution in methanol prepared in part (a) above. After all additions were complete, each mixture was checked on tlc vs. a benzene solution of trapping reagent and a benzene suspension of sulfur.

In a like manner, experiments were conducted in which the bromine solution was added first, the mixture spotted on tlc, then the methanolic sodium disulfide solution added, and the mixture spotted on tlc, and the reverse situation in which the sodium disulfide solution was added first, etc.

3.7 9,10-Diethoxy-9,10-dimethyl-9,10-dihydroanthracene

In a 10 mL round bottom flask equipped with a pressure-equilibrating addition funnel were placed 9,10-dimethylanthracene (206 mg, 1.0 mmol) and absolute ethanol (2 mL). The addition funnel contained bromine (160 mg, 1.0 mmol) in benzene (4 mL). This bromine solution was added dropwise to the solution of 9,10-dimethylanthracene. The mixture was then stirred at room temperature for 0.5 hr.

The mixture was filtered and the filtrate treated with water (10 mL). The layers were separated, and the organic layer was dried over anhydrous magnesium sulfate. Evaporation of the solvent left a crude solid which was chromatographed on silica gel. Recrystallization from benzene of the resulting solid yielded white crystals (96 mg, 32.4%): mp 191-192°; nmr (CCl₄) δ 7.07-7.90(m,8), 2.87 (q, $J = 7\text{Hz}$, 4), 1.55 (s,6), 1.07 (t, $J = 7\text{Hz}$, 6).

3.8 Dimethyl Acetylenedicarboxylate Reaction with Bromine and Sodium Disulfide: Isolation of Tetramethyl Thiophenetetracarboxylate (4)

A 50 mL three-necked flask was fitted with two pressure-equilibrating addition funnels and a gas inlet. In the flask was placed dimethyl acetylenedicarboxylate (5g, 35.2 mmol) and benzene (10 mL). In

one addition funnel was placed bromine (800 mg, 5.0 mmol) in benzene (10 ml), and in the other addition funnel was placed an aliquot of the methanolic sodium disulfide solution prepared in part (a) above (20 ml). The mixture was placed under nitrogen atmosphere, and with efficient stirring the solutions of bromine and sodium disulfide were added dropwise and simultaneously to the solution of the acetylene. The rates of addition were adjusted such that the sodium disulfide solution flowed twice as quickly as the bromine solution, and the addition of both were completed at the same time. Once the addition was completed the mixture was allowed to stir under nitrogen 1 hr.

The reaction mixture was filtered and the filtrate washed with water (2 x 80 ml). The organic layer was separated, dried over anhydrous magnesium sulfate, and the solvent evaporated to leave a crude oil (4.96g). Chromatography on silica gel (300g) using benzene as eluant removed sulfur (30 mg) and dimethyl acetylenedicarboxylate (3.13g). The third band to elute was still a dark viscous oil (1.51g): nmr (CCl₄) δ 3.7-4.0 (many peaks).

This oil was stored at 0° for several months, after which time it was observed to have deposited a few fine crystals. The oil was dissolved in cold diethyl ether (3 ml) and the crystals collected by filtration. They were recrystallized from diethyl ether to yield white needles (15mg, 0.95%): mp 126-127°; ir(KBr) 1720(C = O), 1545(C = C) cm⁻¹; nmr(CDCl₃) δ 3.90(s); mass spectrum *m/e* 316 (P), 285 (P-31), 255 (P-61), 227 (P-89), 197 (P-119), 169 (P-147), 138 (P-178), 110 (P-206).

Anal. Calcd for C₁₂H₁₂O₈S: C, 45.47; H, 3.80; S 10.13.

Found: C, 45.62; H, 3.75; S 10.16.

This data is identical to that for tetramethyl thiophenetetra-carboxylate which was synthesized independently⁸⁶. In addition, the mixture melting point of the isolated crystals with this authentic sample was undepressed.

3.9 Reduction of Polymer with Sodium Borohydride

In a 15 ml round bottom flask were placed the oil obtained by chromatography above (100 mg) and isopropanol (5 ml). An excess (500 mg) of sodium borohydride was added and the mixture allowed to stir under nitrogen atmosphere for 2 hr. As nothing appeared to be happening, the mixture was then heated at 80° for 2 hr. At the end of this time, acetone (10 ml) was added in portions to the solution at room temperature until the sodium borohydride had been killed. The mixture was poured into water (50 ml) and partitioned with diethyl ether (2 x 20 ml). The organic layer was separated, dried over anhydrous magnesium sulfate, and the solvent evaporated to yield a dark oil (96 mg) which had an nmr spectrum (CCl₄) identical to starting material.

3.10 Reaction of Polymer with Molybdenum Hexacarbonyl

In a 50 ml round bottom flask equipped with a reflux condenser were placed the polymer obtained by chromatography above (100 mg), molybdenum hexacarbonyl (110 mg), and chloroform (20 ml). The mixture was heated at reflux under nitrogen for 100 hr. At the end of that time both tlc and nmr (CCl₄) indicated only starting material to be present.

3.11 Hexafluoro-2-butyne Reaction with Bromine and Sodium Disulfide

In a 50 ml three neck flask fitted with two pressure-equilibrating addition funnels and a gas bubbler was placed benzene (10 ml). One addition funnel contained bromine (800 mg, 5.0 mmol) in benzene (10 ml), while the other contained solid sodium disulfide (550 mg, 5.0 mmol) in methanol (20 ml). Hexafluoro-2-butyne was bubbled through the solvent in the flask for 2 min. to give a saturated solution, and then, with the bubbling continuing, the bromine and sodium disulfide solutions were added simultaneously, with the sodium disulfide solution being added at twice the rate of the bromine solution. The bubbling was continued for 2 min. after the addition was completed, and the reaction mixture was allowed to stir for 1 hr more.

The mixture was filtered and the solvent evaporated from the filtrate to leave a yellow oil which was distilled under reduced pressure in a bulb-to-bulb apparatus at 150°. The distillate solidified (130 mg): $\text{ir(KBr)} 1649(\text{C} = \text{C}), 1137(\text{CF}_3)\text{cm}^{-1}$; $\text{nmr(CDCl}_3)\delta 3.87, 3.62, 3.55, 3.40$ (4s, 69), 2.52(s,8); mass spectrum many peaks, even above m/e 500.

3.12 Oligomer Formation from Dimethyl Acetylenedicarboxylate Bromine, and Sodium Disulfide

This experiment was performed in the same manner as that described previously except that the sodium disulfide solution was prepared by dissolving solid sodium disulfide (550 mg, 5.0 mmol) in methanol (20 ml) in a glove bag under nitrogen. Simultaneous addition of the solution of bromine and the solution of sodium disulfide to the solution

of acetylene produced an exothermic reaction with boiling of the solvent. Isolation by evaporation of the solvents, addition of diethyl ether (25 ml), washing with water (2 x 15 ml), separation of the organic layer, and drying of this layer over anhydrous magnesium sulfate produced a clear solution. The solvent was evaporated from this solution to yield a colorless oil (400 mg) which could be distilled under reduced pressure in a bulb-to-bulb apparatus at approximately 170°. The nmr (CCl₄) of this oil showed the following: singlet at 5.07δ, overlapping singlets at 3.77 and 3.73δ, overlapping singlets at 3.63 and 3.60δ, singlet at 3.23δ, and singlet at 2.85δ in the ratio of 3:35:25:32:12. The ir (neat) had intense bands at 1745 and 1630 cm⁻¹.

The same product (74mg) could be obtained by treatment of dimethyl acetylenedicarboxylate (284mg, 2.0 mmol) in benzene (2 ml) with a solution of sodium disulfide (110mg, 1.0 mmol) in methanol (4 ml).

Another exothermic reaction was observed when this smaller scale experiment involving no bromine was repeated using sodium disulfide (110mg, 1.0 mmol) in formamide (4 ml). The product was not isolated.

3.13 1,2-Dibromocyclooctatetraene¹³⁸

In a 250 ml round bottom flask were placed cyclooctatetraene (20.8g, 0.2 mol) and chloroform (100 ml). The flask was fitted with a pressure-equilibrating addition funnel containing bromine (32g, 0.2 mol) in chloroform (100 ml). The flask was cooled in an ice-water bath and covered to prevent light from entering. The bromine solution was then added dropwise with good stirring for 1 hr. Stirring was continued at

this temperature for 2 hr longer and then at room temperature for 2 hr.

The chloroform was evaporated from the reaction mixture to leave a dark oil which was distilled immediately under reduced pressure (bp 80-90° (1 mm)) and was collected as a light yellow oil (48.2g, 91.0%): ir (neat) 1575(C = C), 832, 762, 713, 690 cm^{-1} ; nmr(CDCl_3) δ 5.50-6.27 (m,4), 5.10, 4.98, 4.83, 4.78, 4.65, 4.52(m,2), 3.00-3.90 (m,2).

This product solidified when stored over powdered Dry Ice to give a solid of mp 34-35° which could be recrystallized from pentane.

3.14 7,8-Di(S-thioacetoxyl)bicyclo[4.2.0]octa-2,4-diene

In a 500 ml round bottom flask cooled to 0° were placed 1,2-dibromocyclooctatetraene (32.6g, 123 mmol) which was still cold from storage over powdered Dry Ice, potassium thioacetate (30.8g, 270 mmol), and absolute ethanol (250 ml). The system was placed under nitrogen atmosphere and allowed to stir at room temperature for 64 hr. Then the precipitated potassium bromide (29.5g) was filtered and washed with cold ethanol. The solvent was evaporated from the combined filtrate and washings to leave a lightly colored oil (31.4g, 100%): ir (neat) 1680 (C = O) cm^{-1} ; nmr(CDCl_3) δ 5.33-6.25 (m, 4), 4.02-4.80 (m, 2), 3.03-3.67 (m, 2), 2.27, 2.23 (2s, 6).

This product was generally used crude. However, it could be purified by column chromatography on silica gel (1 kg) using first benzene (3 l.), then 1:1 benzene-chloroform (500 ml), and finally chloroform as solvents. The yield was 24.7g. The product could not be distilled conventionally under high vacuum. However, distillation under

high vacuum on a bulb-to-bulb apparatus was achieved above 200°.

3.15 Adduct from Dimethyl Acetylenedicarboxylate and
7,8-Di(S-thioacetoxy)bicyclo[4.2.0]octa-2,4-diene

In a 250 ml round bottom flask were placed 7,8-di(S-thioacetoxy)bicyclo[4.2.0]octa-2,4-diene (27.0g, 106 mmol), dimethyl acetylenedicarboxylate (15.1g, 106 mmol), and benzene (90 ml). The flask was fitted with a reflux condenser and the mixture heated at a bath temperature of 85-90° for 67 hrs. Evaporation of the solvent then yielded a crude dark oil (38.3g).

The product was purified by chromatography on silica gel (1 kg). Elution with benzene (1 l.), 1:1 benzene-chloroform (500 ml), and chloroform (6 l.) eluted traces of both starting materials. Elution with more chloroform yielded the product as a dark oil (34.9g, 83.2%): ir (neat) 1665-1745 (broad C = O), 1630, 1600 (C = C) cm^{-1} ; nmr(CDCl_3) δ 6.42-6.92 (m, 2), 3.77 (s, 6), 2.32 (s, 6).

3.16 trans,trans-1,4-Di(S-thioacetoxy)-1,3-butadiene (9)^{79,82}

This compound was prepared by pyrolytic decomposition of the adduct from dimethyl acetylenedicarboxylate and 7,8-di(S-thioacetoxy)-bicyclo[4.2.0]octa-2,4-diene. A small amount of the adduct (approximately 250mg) was placed in a 25 ml round bottom flask. The system was set up as in a bulb-to-bulb distillation, placed under high vacuum, and the flask placed in the oven which had been preheated to 250°. After about 5 min., material began collecting in the bulb. The system was

disassembled and the oily product washed out with chloroform. The process was repeated until all of the adduct (34g) had been pyrolyzed. The washings were combined and the solvent evaporated. The product was chromatographed on silica gel (225g) using chloroform as solvent. Recrystallization from toluene yielded beautiful white crystals (6.24g, 35.0%): mp 157-158° (lit.⁸² mp 158°); ir (KBr) 1685 (C = O), 1555 (C = C), 966 (trans-disubstituted ethylene) cm^{-1} ; nmr(CDCl₃) δ 6.15-6.95 (m, 4), 2.35 (s, 6); mass spectrum *m/e* 202 (P), 160 (P-42), 118 (P-84), 85 (P - 117), 58 (P - 144).

3.17 Methyl 2-Cyano-3,6-cis-di(S-thioacetoxycyclohexa-1,4-diene-1-carboxylate (10)

In a 5 ml round bottom flask were placed (9) (81.3mg, 0.4 mmol), methyl cyanopropiolate^{92,93} (43.9mg, 0.4 mmol) and chloroform (0.5 ml). The flask was fitted with a reflux condenser, and the system heated at reflux for 72 hr. At the end of this time the solvent was evaporated, deuteriochloroform (0.5 ml) added, and the nmr spectrum taken. Heating at reflux for an additional 72 hr did not change this spectrum: nmr(CDCl₃) δ 6.15-6.95 (m, 16, starting diene), 3.90 (d, *J* = 2Hz, 2), 4.95 (d, *J* = 2Hz, 2), 3.85 (s, 12, starting acetylene), 3.73 (s, 3), 2.35 (s, 24, starting diene), 2.33 (s, 6).

3.18 Reaction Between (9) and Hexafluoro-2-butyne

This reaction was attempted under four different sets of conditions. A Pyrex tube of volume 6 ml was charged with (9) (20.2mg, 0.1 mmol) and the appropriate solvent (1 ml). The tube was attached to

a vacuum line and chilled in liquid nitrogen. Hexafluoro-2-butyne (160mg, 0.98 mmol) was introduced from the vacuum line. The tube was immediately transferred to a vacuum pump and sealed off under high vacuum while still being cooled in liquid nitrogen. At room temperature, the pressure in the tube should have reached 4 atm. The tube was shaken at room temperature for 1 week in one experiment, and heated at 60° for 1 week in another experiment. Two different solvents, chloroform and tetrahydrofuran, were used for each experiment. In all four cases, no reaction was observed by either tlc or nmr after 1 week.

3.19 Reaction Between (9) and Cyclooctyne

In a 5 ml round bottom flask were placed (9) (20.2mg, 0.1 mmol), cyclooctyne¹³⁹ (10.8mg, 0.1 mmol), and chloroform (0.5 ml). The mixture was stirred under nitrogen at room temperature for 24 hr. At the end of that time the cyclooctyne had disappeared by tlc, but the diene was still present. Isolation by preparative tlc on silica gel using benzene for development yielded unreacted (9) (19.7mg).

3.20 Reaction Between (9) and Benzyne¹⁴⁰

In a 50 ml round bottom flask were placed (9) (101mg, 0.5 mmol), isoamyl nitrite (1.17g, 10 mmol) and dichloromethane (5 ml). The flask was fitted with a pressure-equilibrating addition funnel containing anthranilic acid (1.37g, 10 mmol) and tetrahydrofuran (7 ml). The system was placed under a stream of nitrogen and the flask chilled in an ice-water bath as the solution of anthranilic acid was slowly added to the flask with evolution of gas. The mixture was then allowed to stir

at room temperature for 2 hr. Another experiment was conducted in precisely the same manner except that (9) was not included. Comparison of the reaction mixture with this control by means of tlc showed them both to contain the same array of products. Furthermore, the reaction mixture contained unconsumed diene which was isolated by chromatography on silica gel (150g) using benzene as solvent - yield 98mg.

3.21 Dimethyl 3,6-cis-Di(S-thioacetoxycyclohexa-1,4-diene-1,2-dicarboxylate (11)

(a) In a 5 ml round bottom flask were placed (9) (101mg, 0.5 mmol), dimethyl acetylenedicarboxylate (71mg, 0.5 mmol), and benzene (0.5 ml). The flask was fitted with a reflux condenser and the mixture refluxed under nitrogen for 7 days. At the end of that time, the solvent was evaporated, deuteriochloroform (0.5 ml) added to the residue, and the nmr spectrum taken. This showed only dimethyl acetylenedicarboxylate and (9) to be present.

(b) An identical experiment involving xylene rather than benzene as the solvent was conducted. At the end of 7 days tlc indicated that the diene had been consumed. The nmr spectrum in CDCl_3 of the crude reaction mixture after evaporation of the solvent on a vacuum pump showed the following: δ 7.23-8.13 (m, 3), 3.88 (s, 6), 2.38 (s, 3). This compound was not studied further but was identified as the aromatized product (12).

(c) Lastly, in a 10 ml round bottom flask equipped with a reflux condenser were placed (9) (202mg, 1.0 mmol) and dimethyl acetylenedicarboxylate (3 ml). The mixture was heated at 60° for 10 days under

an atmosphere of nitrogen. At the end of that time, the excess acetylene was evaporated under high vacuum at 100°. Bulb-to-bulb distillation under high vacuum at 230° of a portion of the crude mixture yielded a clear oil: nmr (CDCl_3) δ 4.23 (s, 3), 3.95 (s, 3), 3.87 (s, 3), 3.80 (s, 3). This was identified as the furan (13)⁹⁴. In addition, the residue from distillation contained a product identifiable as (12), which was not present in the crude reaction mixture.

The nmr spectrum of the crude reaction mixture in CDCl_3 contained peaks belonging to dimethyl acetylenedicarboxylate, (13), and a new product identified as the adduct (11): δ 5.92 (d, $J = 4\text{Hz}$, 2), 3.70 (s, 6), 2.33 (s, 6). This product decomposed on attempts to purify it by preparative tlc on silica gel, alumina, or florisil. The other products were not identified.

3.22 Acetylenedicarboxylic Acid Bis-trimethylsilyl Ester (14)

In a 50 mL round bottom flask were placed monopotassium acetylenedicarboxylate (5.7g, 30 mmol), trimethylsilylchloride (9 mL, 8.0g, 73.5 mmol), and tetrahydrofuran (10 mL). The mixture was stirred at room temperature under nitrogen for 7 days. At the end of that time the solvent was evaporated and the residue taken up in diethyl ether (5 mL). This mixture was filtered to remove potassium chloride, and the solvent evaporated again from the filtrate. The oil remaining was distilled under high vacuum (bp 68-70° (0.02 mm)) to yield a colorless oil (6.1g, 78.0%): nmr (neat) δ 0.12 (s).

3.23 Reaction Between (9) and (14)

In a 10 ml round bottom flask were placed (9) (101mg, 0.5 mmol) and (14) (3.9g, 15 mmol). The flask was fitted with a reflux condenser and the mixture heated at 85° under nitrogen for 10 days. At the end of that time tlc indicated no change.

3.24 Phenyl Trifluoromethanesulfonylacetylenyl Sulfone (43)

In a 50 ml three necked flask equipped with a pressure-equilibrating addition funnel were placed phenylsulfonylacetylene¹⁴¹⁻¹⁴³ (166mg, 1.0 mmol) and dry diethyl ether (10 ml). In the addition funnel was placed *n*-butyllithium (64mg, 1.0 mmol) in diethyl ether (5 ml). The system was placed under nitrogen atmosphere and the flask chilled in a Dry Ice-acetone bath. The solution of *n*-butyllithium was then added dropwise to the solution in the flask. The mixture was allowed to stir at this temperature for 0.5 hr. Then a solution of trifluoromethanesulfonic acid anhydride¹⁴⁴ (282mg, 1.0 mmol) in diethyl ether (5 ml) was added very slowly to the salt solution in the flask at -78°.

The dark solution was allowed to stir at -78° for 0.5 hr before a solution of 1,3-diphenylisobenzofuran (270mg, 1.0 mmol) in diethyl ether (5 ml) was added all at once. This solution was brought to room temperature and allowed to stir for 72 hr. Chromatography on silica gel (25g) using benzene as solvent produced a white solid which was recrystallized from toluene to yield colorless crystals of (45) (60mg, 10.6%): mp 152-154° dec; ir (KBr) 1599, 1580, 1555, 1498, 1450 (C = C), 1310 (SO₂), 1160 (CF₃), 1100 (SO₂) cm⁻¹; mass spectrum *m/e*, no parent at 568, 435 (P-133), 419 (P-149), 295 (P-273), 270 (P-298).

3.25 Reaction Between (9) and (43)

A solution of (43) in diethyl ether was prepared as described above. After having stirred at -78° for 0.5 hr this solution was treated with a solution of (9) (202mg, 1.0 mmol) in chloroform (3 ml). This mixture was brought to room temperature and allowed to stir under nitrogen for 24 hr. At the end of that time tlc showed many products including (9). Isolation by chromatography on silica gel using benzene as solvent produced unreacted (9) (195mg).

3.26 Dicyanoacetylene⁹⁶

In a Pyrex test tube was placed an intimate mixture of acetylene dicarboxamide (1.68g, 15 mmol), phosphorus pentoxide (3.42g, 25 mmol), and dry sea sand (1.90g). This test tube was fitted with a rubber stopper housing a glass tube which was connected via ground glass fittings to a receiver. The system was placed under high vacuum, the receiver chilled in a liquid nitrogen bath, and the reaction tube plunged into an oven preheated to 230° . The mixture immediately turned black. Heating was continued for 15 min.

At the end of this time the receiver was placed in a Dry Ice-acetone bath and nitrogen admitted to the system. Immediately furan (340mg, 5 mmol) in anhydrous diethyl ether (2 ml) was added to the receiver through a syringe. The mixture was brought to room temperature and allowed to stir under nitrogen for 3 days. At the end of that time, evaporation of the solvent left a white solid (13.5mg). This solid could not be identified as either the monoadduct or bis-adduct from furan and dicyanoacetylene.

3.27 trans,trans-1,4-Bis-trimethylsilylthio-1,3-butadiene (17)

In a 25 mL three necked flask fitted with a pressure-equilibrating addition funnel, a reflux condenser, and a rubber septum were placed (9) (101mg, 0.5 mmol) and dry tetrahydrofuran (1 mL). The addition funnel was charged with methylolithium (44mg, 2.0 mmol) in tetrahydrofuran (1 mL). The system was placed under an atmosphere of nitrogen and the flask chilled in a Dry Ice-acetone bath. The methylolithium was then added dropwise to the cold solution of (9). The mixture was then brought to room temperature and allowed to stir for 0.5 hr. At this time, it was again chilled to -78° and trimethylsilylchloride (4.36g, 20 mmol) added dropwise from a syringe through the septum. Finally, the solution was heated at reflux overnight.

The next day excess trimethylsilylchloride, solvent and by-products were pumped off under high vacuum to leave an oily residue (126mg, 95%): nmr (CCl_4) δ 5.65-6.43 (m, 4), 0.27 (s, 18).

3.28 Reaction Between (17) and Dimethyl Acetylenedicarboxylate

In a 10 mL round bottom flask were placed (17) (126mg, 0.477 mmol) and dimethyl acetylenedicarboxylate (1.5 mL). The flask was fitted with a reflux condenser, and the mixture heated at 65° for 10 days under nitrogen. At the end of this time, an nmr in CDCl_3 showed only the formation of a small amount of (13), but no other product.

3.29 Adduct from (9) and Maleic Anhydride, (48)

In a 10 mL round bottom flask equipped with a reflux condenser were placed (9) (202mg, 1.0 mmol), maleic anhydride (294mg, 3.0 mmol)

and toluene (2 ml). The mixture was refluxed under nitrogen for 7 days, after which time the solvent was removed by evaporation. The product was obtained (one time only) by repeated fractional crystallization from diethyl ether, and was recrystallized from diethyl ether to yield white crystals (147mg, 49.0%): mp 163-164°; ir (KBr) 1840, 1765, 1695 (C = O) cm^{-1} ; nmr (CDCl_3) δ 6.02 (d, $J = 2\text{Hz}$, 2), 4.53 (m, $J = 5\text{Hz}$, 2Hz, 2Hz, 2), 3.73 (d of d, $J = 5\text{Hz}$, 2Hz, 2), 2.40 (s, 6); mass spectrum m/e , no parent at 300, 258 (P - 42), 225 (P - 75), 148 (P - 152), 104 (P - 196).

3.30 1,1,2,2-Tetracyano-3,6-cis-di(S-thioacetoxy)-4-cyclohexene (49)

In a 5 ml round bottom flask fitted with a reflux condenser were placed (9) (101mg, 0.5 mmol), tetracyanoethylene (64mg, 0.5 mmol), and 1:1 chloroform-benzene (1 ml). The solution turned dark immediately. The mixture was heated under nitrogen at 60° for 10 days, after which time the solvent was evaporated. Preparative tlc on silica gel using chloroform for development gave a solid which was recrystallized from chloroform-pentane to yield white crystals (43.1mg, 26.1%): mp 177-182° dec; ir (KBr) 1695 (C = O) cm^{-1} ; nmr (CDCl_3) δ 5.92 (d, $J = 1\text{Hz}$, 2), 5.12 (d, $J = 1\text{Hz}$, 2), 2.52 (s, 6); mass spectrum m/e , no parent at 330, 288 (P - 42), 255 (P - 75), 246 (P - 84), 213 (P - 117).

Anal. calcd for $\text{C}_{14}\text{H}_{10}\text{N}_4\text{O}_2\text{S}_2$: C, 50.91; H, 3.03; N, 16.97; S, 19.39. Found: C, 50.88; H, 2.97; N, 16.79; S, 19.50.

3.31 Diethyl 1,2-Diazo-3,6-cis-di(S-thioacetoxy)-4-cyclohexene-1,2-dicarboxylate (50)

In a 5 ml round bottom flask equipped with a reflux condenser were placed (9) (101mg, 0.5 mmol), diethyl azodicarboxylate (87mg, 0.5

mmol), and toluene (1 mL). The mixture was heated at reflux under nitrogen for 10 days, after which time the solvent was evaporated. The crude oil was chromatographed on silica gel (10g) using 6:1 benzene-ethyl acetate as solvent to yield an orange oil (132mg, 70.2%): ir 1725 (broad C = O) cm^{-1} ; nmr (CCl_4) δ 6.35 (d, $J = 2\text{Hz}$, 2), 5.88 (d, $J = 2\text{Hz}$, 2), 4.20 (q, $J = 7\text{Hz}$, 4), 2.30 (s, 6), 1.28 (t, $J = 7\text{Hz}$, 6); mass spectrum m/e , no parent at 376, 300 (P - 76), 227 (P - 149), 153 (P - 223), 109 (P - 267).

3.32 3,6-cis-Di(S-thioacetoxy)-4-cyclohexene-1,2-trans-dicarboxylic Acid Chloride (51)

In a 10 mL round bottom flask fitted with a reflux condenser were placed (9) (202mg, 1.0 mmol) and fumaryl chloride (2.3g, 15 mmol). The mixture was heated at 65° under nitrogen for 7 days. At that time the excess fumaryl chloride was pumped off under high vacuum at room temperature. The residue was taken up in CCl_4 and the precipitate which formed was filtered. This solid was recrystallized from diethyl ether-pentane to yield white crystals (149mg, 42.0%): mp $149-150^\circ$; ir (KBr) 1795, 1770, 1690 (C = O) cm^{-1} ; nmr (CDCl_3) δ 5.48-6.12 (m, 2), 4.88 (m, 1), 4.53, 4.37 (d of t, $J = 10\text{Hz}$, 2Hz, 1), 4.00 (d of d, $J = 10\text{Hz}$, 4Hz, 1), 3.30 (t, $J = 10\text{Hz}$, 10Hz, 1), 2.38 (s, 6).

3.33 3,6-cis-Di(S-thioacetoxy)-4-cyclohexene-1,2-trans-dicarboxylic Acid

In a 10 mL round bottom flask were placed (51) (89mg, 0.25 mmol), sodium bicarbonate (42mg, 0.5 mmol), and 1:1 tetrahydrofuran:

water (6 mL). Bubbling began immediately upon addition. The mixture was allowed to stir at room temperature overnight, after which time the tetrahydrofuran was evaporated. Water (5 mL) was added, followed by acidification with cold 10% hydrochloric acid solution to pH 3. Diethyl ether (25 mL) was added and the mixture partitioned. The ether layer was then washed with 12 mL of brine, separated, and dried over anhydrous magnesium sulfate. The solvent was evaporated to leave a solid which was recrystallized from ether to yield white crystals (76mg, 95.6%): mp 231-232°; ir (KBr) 2800-3620 (broad, $\overset{\text{O}}{\parallel}\text{C}-\text{H}$), 1695 (broad, C = O) cm^{-1} ; mass spectrum m/e , no parent at 318, 276 (P - 42), 243 (P - 75), 216 (P - 102).

Anal. Calcd for $\text{C}_{12}\text{H}_{14}\text{O}_6\text{S}_2$: C, 45.28; H, 4.40; S, 20.12.
Found: C, 45.25; H, 4.49; S, 20.11.

3.34 Reaction Between (9) and Bromomaleic Anhydride

In a 5 mL round bottom flask equipped with a reflux condenser were placed (9) (101mg, 0.5 mmol), bromomaleic anhydride (177mg, 1 mmol), and chloroform (1 mL). The mixture was heated at reflux under nitrogen for 5 days, after which time tlc indicated no reaction had taken place. Evaporation of the solvent, addition of CDCl_3 , and subsequent observation of the nmr spectrum confirmed this finding.

3.35 Reaction between (9) and *p*-Benzoquinone

In a 5 mL round bottom flask equipped with a reflux condenser were placed (9) (101mg, 0.5 mmol), *p*-benzoquinone (54mg, 0.5 mmol), and benzene (1 mL). The mixture was heated at reflux under nitrogen for

48 hr. At that time tlc of the dark mixture indicated that the benzoquinone had been consumed, but not the diene. Recovery of the diene by preparative tlc on silica gel using chloroform for development yielded 96mg. The other products were not studied.

3.36 Reaction between (9) and Chloranil

In a 5 ml round bottom flask were placed (9) (101mg, 0.5 mmol), tetrachloro-*p*-benzoquinone (123mg, 0.5 mmol), and benzene (1 ml). The flask was fitted with a reflux condenser, and the mixture heated at reflux under nitrogen for 48 hr. At the end of that time both tlc and nmr indicated that no reaction had occurred.

3.37 Phenyl(trifluoromethanesulfonyl)acetylene (21)

In a 250 ml three-necked flask, fitted with a pressure-equilibrating addition funnel, a rubber septum, and a gas inlet, were placed *n*-butyllithium (2.74g, 42.8 mmol) and dry diethyl ether (100 ml). In the addition funnel were placed trifluoromethanesulfonic acid anhydride¹⁴⁴ (12.00g, 42.8 mmol) and diethyl ether (100 ml). To the solution in the flask, chilled in a Dry Ice-acetone bath and under a nitrogen atmosphere, was added freshly distilled phenylacetylene (4.70 ml, 4.36g, 42.8 mmol) dropwise from a syringe. After stirring for 1 hr at -78°, the solution of anhydride was added dropwise and cautiously over a period of 1 hr to the solution of salt at -78°. The mixture was then stirred for an additional 0.5 hr.

The reaction mixture was extracted successively with several 50 ml portions of water and brine. The combined extracts were washed

with diethyl ether and the ether layers were combined and dried over anhydrous magnesium sulfate. Evaporation of the solvent left a dark oil. Two distillations through a short Vigreux column under reduced pressure (bp 57-62° (0.1 mm)) gave a very lightly colored oil (7.25g, 72.5%): ir (neat) 2165 (C \equiv C), 1370 (SO₂), 1195-1230 (CF₃), 1110 (SO₂) cm⁻¹; nmr (CDCl₃) δ 7.18-7.72 (m); mass spectrum *m/e* 234 (P), 165 (P - 69), 101 (P - 133).

The product crystallized with difficulty to give a solid of mp 31°. This material darkened on standing at room temperature under nitrogen but could be stored indefinitely when packed in powdered Dry Ice.

3.38 Catalytic Hydrogenation of (21)

In a 50 ml three-necked flask were placed glacial acetic acid (10 ml) and 5% palladium-on-charcoal (200mg). The flask was attached to a catalytic hydrogenator and the catalyst was saturated with hydrogen. Then (21) (234mg, 1.0 mmol) in acetic acid (2 ml) was added by syringe. The system was allowed to take up hydrogen until such uptake ceased. The volume of hydrogen consumed was 37.6 ml (1.68 mmol), corrected to STP.

The catalyst was filtered and the filtrate was taken up in diethyl ether (50 ml). This solution was extracted successively with several 30 ml portions of saturated aqueous sodium bicarbonate solution, water, and brine. The ether layer was then dried over anhydrous magnesium sulfate. Evaporation of the solvent left a dark oil which was purified by preparative glpc on a 5 ft x 0.25 in. 3% SE-30 on Chromosorb

W (80-100 mesh) column: ir (neat) 1370 (SO_2), 1185-1210 (CF_3), 1110 (SO_2), 680 (cis-disubstituted ethylene) cm^{-1} ; nmr (CCl_4) δ 7.24-7.78 (m, 6, five aromatic H and one vinyl H), 6.40, 6.20 (d, $J = 12\text{Hz}$, vinyl H, collapsed to singlet at δ 6.30 when irradiated at δ 7.50); mass spectrum m/e 236 (P), 167 (P - 69), 103 (P - 133).

Anal. Calcd for $\text{C}_9\text{H}_7\text{F}_3\text{O}_2\text{S}$: C, 45.76; H, 2.97. Found: C, 46.06; H, 2.91.

3.39 Addition of Benzenethiol to (21)

In a 25 ml round bottom flask were placed (21) (468mg, 2.0 mmol) and dry tetrahydrofuran (7 ml). The flask was fitted with a pressure-equilibrating addition funnel containing benzenethiol (220mg, 2.0 mmol), sodium thiophenoxide (10mg), and tetrahydrofuran (7 ml). The solution of benzenethiol was added dropwise over a period of 0.5 hr to the solution of (21), the whole system being maintained under an atmosphere of nitrogen.

The solvent was evaporated and diethyl ether (25 ml) was added to the resulting oil. This solution was extracted successively with several 20 ml portions of water and brine. The ether layer was dried over anhydrous magnesium sulfate, filtered, and evaporated to dryness. The residue was dissolved in benzene (5 ml) and chromatographed on silica gel (35g). Hexane (100 ml), followed by 2:8 benzene-hexane (300 ml), eluted two bands: one containing benzenethiol and the other phenyl disulfide (both identified by tlc). Additional amounts of 2:8 benzene-hexane eluted the adduct of (21) with benzenethiol. Evaporation of the solvents followed by two recrystallizations from CCl_4 -hexane gave

colorless crystals (453mg, 66.0%): mp 114-115°; ir (KBr) 1540 (C = C), 1355 (SO₂), 1180-1200 (CF₃), 1105 (SO₂) cm⁻¹; nmr (CCl₄) δ 7.56 (s, 5), 7.40 (s, 5), 5.40 (s, 1); mass spectrum *m/e* 344 (P), 275 (P - 69), 211 (P - 133), 178 (P - 166), 102 (P - 242).

Anal. Calcd for C₁₅H₁₁F₃O₂S₂: C, 52.33; H, 3.20; S, 18.60.
Found: C, 52.44; H, 3.18; S, 18.56.

3.40 Kinetic Studies

The acetylenes other than (21) used in the kinetic studies were prepared by known procedures. Phenylpropioloyl chloride (22) was made from phenylpropionic acid and PCl₅¹⁴⁵ and was converted into both the corresponding amide¹⁴⁶ and methyl ester (25) (bp 55° (0.22 mm)), the latter by addition of 1 equiv each of methanol and triethylamine. Phenylpropiolamide was dehydrated to the corresponding nitrile (23)¹⁴⁷. Finally, (26) was prepared from phenylacetylene¹⁴⁸. Phenylpropiolaldehyde (24), supplied by Aldrich Chemical Co., was distilled before use.

Tetraphenylcyclopentadienone and 1,3-diphenylisobenzofuran were recrystallized to constant melting point, while cyclopentadiene and 1,3-cyclohexadiene were purified by distillation prior to use.

The solvents (*p*-cymene, toluene, and benzene) were each purified by washing with aqueous potassium permanganate solution, 2 N sulfuric acid solution, and water. This was followed by drying over anhydrous magnesium sulfate, heating at reflux over calcium hydride, and then distilling from calcium hydride.

The reagents were dissolved in the appropriate amount of solvent and were placed in a three-necked flask which was fitted with a

reflux condenser and a thermometer. Each solution contained an equal concentration of acetylene and diene. The flask was flushed with nitrogen and immediately placed in an insulated bath which had been preheated to a constant temperature. Zero time was taken to be that time at which constant internal temperature was reached.

The reactions were followed by measuring the change in ir absorption in the region 2500 to 2000 cm^{-1} of an accurately diluted (with 100 μl of solvent) measured (30-60 μl) aliquot as a function of time. The size of the aliquot removed depended on the initial concentration of reactant, which varied from 3.85×10^{-2} to 0.231 mol l^{-1} .

The competition between (21) and dimethyl acetylenedicarboxylate for cyclopentadiene was conducted by placing (21) (117mg, 0.5 mmol) and dimethyl acetylenedicarboxylate (71mg, 0.5 mmol) together with cyclopentadiene (26.4 mg, 0.4 mmol) in ethyl acetate (6.2 ml) in a stoppered 10 ml round bottom flask under nitrogen. The mixture was stirred for 24 hr at room temperature. The ethyl acetate was evaporated and the residue (224.8mg) taken up in chloroform (25.0 ml). The ir spectrum of this solution was measured and the concentrations of reactants remaining and products formed were calculated by comparing the absorptions at selected wavelengths with spectra of known concentration for the pure compounds. The wavenumbers chosen were: 2170 cm^{-1} for (21), 894 cm^{-1} for dimethyl acetylenedicarboxylate, and 1620 cm^{-1} for dimethyl norborna-2,5-diene-2,3-dicarboxylate. The amounts of the products formed were determined by isolation. The final amounts of material were: 0.25 mmol (21), 0.34 mmol dimethyl acetylenedicarboxylate, 0.24

mmol (37), and 0.16 mmol of dimethyl norborna-2,5-diene-2,3-dicarboxylate.

3.41 Product Studies

All adducts (27) - (40) were prepared in a similar manner. The diene (3 mmol) and the acetylene (3 mmol) were dissolved in the appropriate solvent (13 mL) and were placed in a round bottom flask fitted with a reflux condenser. The solvents used were *p*-cymene for (27) - (31), toluene for (32) - (36), and benzene for (37) and (38) and (39). The solution was then placed under a nitrogen atmosphere and heated at reflux for 48 hr, with the exception of (37) which was maintained at room temperature for 24 hr and (39) which was heated at reflux for 100 hr.

After removal of the solvent the crude product was recrystallized to constant melting point. Toluene was used as recrystallization solvent for (27) - (31), and (32) - (36), while petroleum ether was used for (37). Adducts (38) and (40) were purified by chromatography as described below. Compound (38) was then recrystallized from petroleum ether, while (40) was distilled.

The adduct from dimethyl acetylenedicarboxylate and cyclopentadiene was prepared according to the literature¹⁰².

3.42 Pentaphenylphenyl Trifluoromethanesulfone (27)

1.55g (87.8%); mp 360-362°; ir (KBr) 1360 (SO₂), 1205 (CF₃), 1110 (SO₂) cm⁻¹; nmr (CDCl₃) δ 7.08 (s, 10), 6.78 (s, 15); mass spectrum *m/e* 590 (P), 521 (P - 69), 457 (P - 133).

Anal. Calcd for C₃₇H₂₅F₃O₂S: C, 75.26; H, 4.24; S, 5.42.

Found: C, 75.39; H, 3.99; S, 5.18.

3.43 Pentaphenylbenzoyl Chloride (28)

1.29g (83.0%); mp 285-286°; ir (KBr) 1730 (C = O) cm^{-1} ; nmr (CDCl_3) δ 7.16 (m, 10), 6.82 (m, 15); mass spectrum *m/e*, no parent at 520, 485 (P - 35), 457 (P - 63). This material was converted to (31). The spectra (ir and nmr) of this material are the same as those of authentic (31). Furthermore, the mixture melting point with authentic (31) is undepressed.

3.44 Pentaphenylbenzotrile (29)

1.21g (83.5%); mp 280-281° (lit.¹⁴⁹ mp 271-272°).

3.45 Pentaphenylbenzaldehyde (30)

1.30g (89.4%); mp 263° (lit.¹⁰¹ mp 265°).

3.46 Methyl Pentaphenylbenzoate (31)

1.37g (88.6%); mp 344-345° (lit.¹⁰¹ mp 342°).

3.47 Trifluoromethyl (1,2,4-Triphenyl-1,4-epoxynaphthalene)- 3-sulfone (32)

1.39g (86.2%); mp 192-193°; ir (KBr) 1570 (C = C), 1355 (SO_2), 1185-1200 (CF_3), 1105 (SO_2) cm^{-1} ; nmr (CDCl_3) δ 7.02-7.80 (m); mass spectrum *m/e*, no parent at 504, 371 (P - 133).

Anal. Calcd for $\text{C}_{29}\text{H}_{19}\text{F}_3\text{O}_3\text{S}$: C, 69.05; H, 3.77; S, 6.35; mol wt, 504. Found: C, 69.05; H, 3.91; S, 6.25; mol wt, 510.

3.48 1,2,4-Triphenyl-1,4-epoxynaphthalene-3-carboxylic Acid Chloride (33)

0.97g (74.5%); mp 177-178° dec; ir (KBr) 1710-1765 broad doublet (C = O), 1570 (C = C) cm^{-1} ; nmr (CDCl_3) δ 7.02-7.96 (m); mass spectrum m/e , no parent at 434, 399 (P - 35), 371 (P - 63), 270 (P - 164).

Anal. Calcd for $\text{C}_{29}\text{H}_{19}\text{ClO}_2$: C, 80.18; H, 4.38; Cl, 8.07; mol wt, 434. Found: C, 80.10; H, 4.41; Cl, 8.04; mol wt, 431.

3.49 1,2,4-Triphenyl-1,4-epoxynaphthalene-3-carbonitrile (34)

1.02g (85.5%); mp 189-190° dec; ir (KBr) 2190 (C \equiv N), 1570 (C = C) cm^{-1} ; nmr (CDCl_3) δ 7.02-7.84 (m); mass spectrum m/e 397 (P), 3.9 (P - 78), 270 (P - 127).

Anal. Calcd for $\text{C}_{29}\text{H}_{19}\text{NO}$: C, 87.66; H, 4.79; N, 3.53; mol wt, 397. Found: C, 87.64; H, 4.93; N, 3.29; mol wt, 383.

3.50 1,2,4-Triphenyl-1,4-epoxynaphthalene-3-carboxaldehyde (35)

1.04g (87.0%); mp 161-162°; ir (KBr) 2810 (CH), 1655 (C = O), 1570 (C = C) cm^{-1} ; nmr (CDCl_3) δ 9.70 (s, 1), 7.00-7.98 (m, 19); mass spectrum m/e 400 (P), 372 (P - 28), 270 (P - 130).

Anal. Calcd for $\text{C}_{29}\text{H}_{20}\text{O}_2$: C, 87.00; H, 5.00; mol wt, 400. Found: C, 86.91; H, 5.29; mol wt, 413.

3.51 Methyl 1,2,4-Triphenyl-1,4-epoxynaphthalene-3-carboxylate (36)

1.12g (86.5%); mp 81-82°; ir (KBr) 1700 (C = O), 1570 (C = C) cm^{-1} ; nmr (CCl_4) δ 6.92-7.88 (m, 19), 3.40 (s, 3); mass spectrum m/e , no parent at 430, 399 (P - 31), 371 (P - 59), 270 (P - 160).

Anal. Calcd for $C_{30}H_{22}O_3$: C, 83.72; H, 5.12; mol wt, 430.

Found: C, 83.58; H, 5.32; mol wt, 445.

3.52 Trifluoromethyl 3-Phenylbicyclo[2.2.1]hepta-2,5-dienyl 2-sulfone (37)

0.846g (94.0%); mp 75-76°; ir (KBr) 1590, 1560 (C = C), 1365 (SO₂), 1172-1205 (CF₃), 1110 (SO₂) cm^{-1} ; nmr (CCl₄) δ 7.40 (s, 5), 7.00 (m, 2), 3.99, 4.18 (d, 2, $J = 11Hz$), 2.10, 2.20, 2.41, 2.56 (m, 2); mass spectrum m/e 300 (P), 231 (P - 69), 167 (P - 133), 66 (P - 234).

Anal. Calcd for $C_{14}H_{11}F_3O_2S$: C, 56.00; H, 3.67; S, 10.67; mol wt, 300. Found: C, 56.02; H, 3.82; S, 10.76; mol wt, 300.

3.53 Trifluoromethyl 3-Phenylbicyclo[2.2.2]octa-2,5-dienyl 2-sulfone (38)

Was eluted with 200 ml 8:2 hexane-benzene from a column of 35g of silica gel: 0.674g (71.5%); mp 71-72°; ir (KBr) 1620, 1580 (C = C), 1355 (SO₂), 1175-1200 (CF₃), 1118 (SO₂) cm^{-1} ; nmr (CDCl₃) δ 7.32 (m, 5), 6.50 (m, 2), 4.00, 4.35 (broad d, 2), 1.65 (m, 4); mass spectrum m/e 314 (P), 286 (P - 28), 260 metastable (corresponds to 314 \rightarrow 286), 245 (P - 69), 217 (P - 97), 181 (P - 133), 153 (P - 161).

Anal. Calcd for $C_{15}H_{13}F_3O_2S$: C, 57.32; H, 4.14; S, 10.19. Found: C, 57.37; H, 4.16; S, 10.11.

3.54 Methyl 3-Phenylbicyclo[2.2.2]octa-2,5-diene-2-carboxylate (40)

From 1,3-cyclohexadiene and phenylpropioloyl chloride, followed by methanol and triethylamine; purified by two successive

column chromatographs each on 35g silica gel. The first involved elution with 200 ml of benzene, while the second involved elution with 500 ml of 1:1 hexane-benzene. The product was the second band eluted in the second chromatography: 0.257g (35.7%); ir (neat) 1695 (C = O), 1620, 1605 (C = C) cm^{-1} ; nmr (CCl_4) δ 7.20 (m, 5), 6.35 (m, 2), 3.90, 4.20 (broad d, 2), 3.55 (s, 3), 1.60 (m, 4); mass spectrum m/e 240 (P), 212 (P - 28), 181 (P - 59), 152 (P - 88).

3.55 Derivatives of 9,10-Diphenylanthracene

Isomeric 9,10-dihydroxy-9,10-diphenyl-9,10-dihydroanthracenes (53 a,b) were prepared from 9,10-anthraquinone^{150,151}. The individual isomers (53a) and (53b) were also prepared separately^{152,153}. 9,10-Diphenylanthracene (54) was obtained from (53 a,b) by treatment with potassium iodide in glacial acetic acid¹⁵⁴, and was converted to the 9,10-dichloro compound (55)¹⁵⁵, the 9,10-dihydro compound (57)¹⁵⁶, and the 9,10-endoperoxide (56)²⁹. Finally, (55) was also prepared from (53 a,b)⁷⁴.

3.56 Silver Salts of Carboxylic Acids

Silver trifluoroacetate was prepared according to the literature¹⁵⁷. Silver *p*-nitrobenzoate and silver *m*-toluate were both prepared by the procedure described below. This procedure did not prove effective, however, for the preparation of silver dichloroacetate¹⁵⁸.

p-Nitrobenzoic acid (835mg, 5 mmol) or *m*-toluic acid (680mg, 5 mmol) was dissolved in boiling water (20 ml). While still hot, the acid solution was titrated to the phenolphthalein end point with 1.0 N

sodium hydroxide solution. Meanwhile, a separate solution of silver nitrate (850mg, 5 mmol) in water (2 ml) was prepared. This solution was then added dropwise to the hot solution of the sodium salt of the acid. The silver salt which precipitated was collected by filtration once the solution had cooled, and was washed with large quantities of cold water. The salt was then dried in a vacuum drying oven and stored in the dark.

3.57 Silver *p*-Nitrobenzoate

1.27g (92.6%); mp > 300°; ir (KBr) 1615, 1570, 1370, 1325, 875, 820, 720 cm⁻¹.

3.58 Silver *m*-Toluate

0.93g (76.7%); mp 228-229°; ir (KBr) 1595, 1560, 1510, 1375, 785, 750 cm⁻¹.

3.59 Esters of (53)

9,10-Diacetoxy-9,10-diphenyl-9,10-dihydroanthracene (58) was prepared from (53) by the procedure in the literature⁷⁴. All of the esters (58) - (61) could be obtained from (55) by the procedure which follows: In a 50 ml round bottom flask which was tightly wrapped in aluminum foil were placed (55) (1.0g, 2.5 mmol), the silver salt of the appropriate acid (5.0 mmol), and dry diethyl ether (20 ml). The mixture was stirred in the dark under nitrogen at room temperature for 4 days. The solid material remaining was removed by filtration in a glove bag

under nitrogen, and the solvent evaporated from the filtrate on a rotary evaporator protected by a drying tower.

For (58) the precipitate from the above filtration was washed with boiling benzene (100 ml). The benzene was evaporated and the crude product recrystallized from ethyl acetate. The rest of the esters were obtained from the filtrate from the above filtration. Compound (60) was recrystallized from petroleum ether-benzene, as was (61). However, (59) was very sensitive and decomposed when recrystallization was attempted.

3.60 9,10-Diacetoxy-9,10-diphenyl-9,10-dihydroanthracene (58)

0.69g (61.6%); mp 260-261^o dec (lit.⁷⁴ mp 260^o dec).

3.61 9,10-Bis-trifluoroacetoxy-9,10-diphenyl-9,10-dihydroanthracene (59)

1.03g (74.1%); ir (KBr) 1780 (C = O), 1590 (C = C) cm⁻¹.

3.62 9,10-Bis-(p-nitrobenzoyloxy)-9,10-diphenyl-9,10-dihydroanthracene (60)

1.19g (72.0%; mp 175-176^o; ir (KBr) 1690 (C = O), 1595, 1525, 1480, 1440 cm⁻¹.

3.63 9,10-Bis-(m-methylbenzoyloxy)-9,10-diphenyl-9,10-dihydroanthracene (61)

0.76g (50.5%); ir (KBr) 1680 (C = O), 1580, 1490, 1450 (C = C) cm⁻¹.

3.64 Photolysis of Sulfur and (54)

Solutions saturated in both sulfur and (54) were prepared in the solvents carbon disulfide, benzene, and tetrahydrofuran. A portion of each solution (5 ml) was placed in a quartz photolysis tube, degassed with nitrogen, and placed under a nitrogen atmosphere. Irradiation at 2537 nm¹⁵⁹ for 24 hr followed. During this time, aliquots were withdrawn periodically and the progress of the reaction followed by tlc.

A small spot appeared after the first hour, but did not seem to change in intensity with time. Subsequent preparative tlc revealed this product to be (56). Extended degassing prior to photolysis prevented any formation of this compound in later experiments.

Also, as the reaction progressed, there was deposited a precipitate, the quantity of which increased with time. Additional experiments involving photolysis of sulfur alone in these solvents established that the precipitate was a polymeric form of sulfur - "photosulfur."²

Other than these two products only (54) was found in the reaction mixture at the end of the experiment.

3.65 Photolysis of Sulfur Monochloride and (54)

A portion (5 ml) of a benzene solution saturated in (54) was added to sulfur monochloride (2 ml) in a quartz photolysis tube. The solution was degassed with nitrogen and the system placed under nitrogen atmosphere. Irradiation at 2537 nm¹⁶⁰ for 24 hr followed. No apparent reaction had occurred at the end of this time as observed by tlc.

3.66 Photolysis of Acetyl disulfide and (54)

A portion (5 mL) of a benzene solution saturated in both (54) and acetyl disulfide was placed in a quartz photolysis tube. The system was degassed with nitrogen and placed under nitrogen atmosphere. The mixture was irradiated at 2537 nm for 24 hr. At the end of that time no apparent reaction had occurred as observed by t.l.c.

3.67 Pyrolysis of Sulfur and (54)

In a porcelain crucible were placed (54) (50mg, 0.15 mmol) and sulfur (5mg, 0.15 mmol). On top of the crucible was located a watch glass containing crushed ice. The solids were melted, then fused by heating with a flame. Very little vapor condensed on the underside of the watch glass, indicating little vaporization of either of the reactants. In one experiment, the melt was allowed to cool slowly to room temperature; in another the mixture was rapidly quenched by plunging the crucible into an ice-water bath.

The results of either experiment were the same. The mass was treated with benzene and analyzed by t.l.c. Both (54) and sulfur were observed, as well as a small new spot. Preparative t.l.c yielded (54) (47mg). The new spot was not analyzed further as control experiments showed the same spot to be present after pyrolysis of (54) alone. Pyrolysis of sulfur alone gave no detectable new product.

3.68 Reaction of (55) with Sodium Disulfide

A portion (1 mL) of a solution of sodium disulfide in methanol (200mg/10 mL) was placed in a 10 mL round bottom flask in a

glove bag under nitrogen. To this solution was added (55) (80mg, 0.2 mmol) dissolved in either anhydrous diethyl ether (3 ml), acetone (2 ml), or pyridine (2 ml). The mixture was then stirred at room temperature for 3 hr.

Workup of the ether and acetone solutions involved evaporation of the solvent and partitioning of the residue between water (5 ml) and ether (15 ml). On the other hand, the pyridine solution was treated with 2 N hydrochloric acid solution (10 ml), followed by ether (15 ml). In each case, the organic layer was then washed with brine (10 ml), separated, and dried over anhydrous magnesium sulfate. The solvent was evaporated and the residue taken up in benzene. Preparative tlc of this mixture using hexane for development yielded approximately the same results in each case - (54) (65mg) and sulfur (11mg).

3.69 Reaction of (55) with Sodium Tetrasulfide

A portion (1 ml) of a solution of sodium tetrasulfide in ethanol⁸⁸ (1.21g/10 ml) was taken up by syringe and added to a solution of (55) (280mg, 0.7 mmol) in either dry acetonitrile (30 ml) or pyridine (20 ml) in a 100 ml round bottom flask under nitrogen atmosphere. The mixture was allowed to stir at room temperature for 3 hr.

Workup followed the same procedure as described in the sodium disulfide experiment. Only one half of the crude material was committed to preparative tlc to yield (54) (114mg) and sulfur (44mg).

3.70 Reaction of (55) with Sodium Trithiocarbonate

A portion (1 ml) of a solution of sodium trithiocarbonate¹⁶¹ in ethanol (1.54g/10 ml) was added by syringe to a solution of (55) (401mg, 1.0 mmol) in dry acetonitrile (30 ml) in a 50 ml round bottom flask under nitrogen atmosphere. The mixture was allowed to stir at room temperature for 3 hr.

The reaction mixture was poured into water (100 ml) and extracted with ether (2 x 15 ml). The organic layers were combined and dried over anhydrous magnesium sulfate. Evaporation of the solvent left a crude solid, half of which was subjected to preparative tlc using benzene as developing agent. This yielded (54) (150mg). The sulfur containing material was not analyzed.

3.71 Reaction of (55) with p-Dithiotoluuate Anion

A portion (1 ml) of a solution of p-dithiotoluuate¹⁶² (1.71g p-tolyl bromide, 760mg carbon disulfide, 10 ml water) was added by syringe to a solution of (55) (401mg, 1.0 mmol) in either acetone (10 ml), acetonitrile (30 ml), or N,N-dimethylformamide (20 ml). The mixture was allowed to stir at room temperature under nitrogen for 3 hr.

The reaction mixture was poured into a large quantity of water and extracted numerous times with diethyl ether. The organic layers were combined and washed several times with water. The organic layer was dried over anhydrous magnesium sulfate, and the solvent evaporated. One half of the crude material was subjected to preparative tlc, and in each case this yielded (54) (140-150mg). The sulfur containing material was not analyzed.

3.72 Reactions of Esters (58) - (61)

These experiments were conducted in the same manner as the four just described with the following exception: In those cases in which the inorganic sulfur species was prepared in alcohol solvent, the alcohol was pumped off under high vacuum and replaced with an equal amount of hexamethylphosphoric triamide. Nevertheless, the results were consistently the same; preparative tlc of the crude reaction mixture produced a nearly quantitative yield of (54).

3.73 Reaction Between (53) and Thiourea

In a 200 mL round bottom flask were placed (53) (1.0g, 2.75 mmol), thiourea (420mg, 5.5 mmol), and glacial acetic acid (8 mL). This mixture was chilled in an ice-water bath, and to it were added, with stirring, acetic acid (8 mL) and concentrated sulfuric acid (0.3 mL, 0.55g, 5.6 mmol). The solution immediately turned red, then a very dark green. The mixture was stirred at room temperature for 10 hr. Then the flask was placed in an ice-water bath and 3 N sodium hydroxide solution (100 mL) added. This mixture was then refluxed for 3 hr.

The reaction mixture was extracted with diethyl ether (20 mL) and the layers separated. The organic layer was washed with 0.5 N hydrochloric acid solution (2 x 10 mL), saturated aqueous sodium bicarbonate solution until the aqueous layer was basic to litmus, brine (10 mL), and water (10 mL). The ether layer was then dried over anhydrous magnesium sulfate, and the solvent evaporated to yield (54) (0.90g).

The original aqueous layer was treated with 0.5 N hydrochloric acid solution (20 ml) and extracted with ether (20 ml). This ether layer yielded no additional product.

3.74 Reaction of the Anion Radical of (54) with Sulfur and Sulfur Monochloride

In a 100 ml three-necked flask equipped with a reflux condenser and a high-speed stirrer was placed xylene (40 ml). The system was flushed with nitrogen as sodium metal (23mg, 1.0 mmol) was quickly added. The flask was stoppered and the mixture brought to reflux. When it was certain the sodium had melted, the high-speed stirrer was turned on, thus producing sodium sand dispersed throughout the xylene. The mixture was allowed to cool to room temperature and the sand to settle in the flask.

The xylene was siphoned off and a solution of (54) (330mg, 1.0 mmol) in tetrahydrofuran (15 ml) added. The mixture was brought to reflux under nitrogen and stirred with a conventional magnetic stirrer.

After 24 hr the solution was a deep red-brown. At this time, sulfur (256mg) or sulfur monochloride (135mg, 1.0 mmol) was added to the solution in the flask, and the mixture was stirred for an additional 10 hr.

Analysis by preparative tlc indicated that only (54) and sulfur were present in the reaction mixture at the end of this time. The experiments were repeated using twice as much sodium with the same results.

3.75 Reaction Between the Anion of (57) and Sulfur and Sulfur Monochloride

In a 25 ml three-necked flask equipped with a pressure-equilibrating addition funnel and a reflux condenser were placed (57) (332mg, 1.0 mmol) and dry tetrahydrofuran (10 ml). In the addition funnel were placed *n*-butyllithium (64mg, 1.0 mmol) and tetrahydrofuran (5 ml). The system was placed under nitrogen atmosphere and the flask chilled in a Dry Ice-acetone bath as the *n*-butyllithium was added dropwise to the solution of (57). The mixture stirred at -78° for 0.5 hr, then at room temperature for 0.5 hr. The mixture was then cooled again to -78° and sulfur (256mg) or sulfur monochloride (135mg, 1.0 mmol) added. Finally, the mixture was allowed to stir at -78° for 0.5 hr, then at reflux for 5 hr. At the end of this time, preparative tlc indicated the only products present were (54) and sulfur in each case.

3.76 9,10-Di(S-thioacetoxy)-9,10-dihydroanthracene (63)¹³⁷

In a 500 ml three-necked flask equipped with a pressure-equilibrating addition funnel and a gas inlet were placed anthracene (10g, 56.2 mmol), freshly distilled thioacetic acid (50g, 658 mmol), and benzene (150 ml). In the addition funnel were placed *t*-butylhydroperoxide (15g) which had been freshly prepared¹⁶³ and fractionated, ferrocene (250mg), and benzene (25 ml). Stirring of the mixture in the flask was begun under an atmosphere of nitrogen. A hot solution of *t*-butylhydroperoxide (0.5g), ferrocene (20mg), and benzene (3 ml) was added to the mixture in the flask, and immediately dropwise addition of the mixture in the addition funnel was started. The rate of addition

was apparently critical and the optimum rate appeared to be about 2 drops per sec. Soon the mixture turned various dark colors and began to foam from the heat generated, but the addition was not slowed down nor was a cooling bath provided. Shortly after the addition was complete, the solution turned light yellow and cooled back to room temperature. It was allowed to stir for a total of 2 hr from the start of addition.

The mixture was filtered and the solvent evaporated from the filtrate. At about half the original volume, methanol (50 ml) was added causing any unreacted anthracene to precipitate. This was filtered and the solvents evaporated completely from the filtrate. The crude oil was fractionally crystallized several times with methanol. The major product at this stage was (64). When the oil would yield no more solid, it was chromatographed on silica gel (1 kg) with 2:1 benzene-pentane as solvent. This ultimately produced a band which contained (63) and (64) in a ratio of 3:1. Under less desirable conditions (65) would also be present in this band. Fractional crystallization from hexane produced pure (63) as yellow crystals (5.49g, 29.8%): mp 146-147°; ir (KBr) 1685 (C = O), 1490, 1460, 1430 (C = C) cm^{-1} ; nmr (CDCl_3) δ 7.10-7.65 (m, 8), 6.12 (s, 2), 2.35 (s, 6); mass spectrum *m/e*, no parent at 328, 253 (P - 75), 211 (P - 117), 178 (P - 150).

3.77 9,10-Dihydroanthracene-9,10-bis-thiol (66)

In a 50 ml round bottom flask equipped with a pressure-equilibrating addition funnel were placed (63) (328mg, 1.0 mmol) and dry diethyl ether (10 ml). In the addition funnel were placed methyl-lithium (88mg, 4.0 mmol) and diethyl ether (5 ml). The system was

placed under a nitrogen atmosphere and the flask chilled in a Dry Ice-acetone bath. Then the methyllithium was added dropwise to the solution of (63). After the addition was complete the mixture was brought to room temperature and allowed to stir for 0.5 hr. At this time, it was quenched with saturated aqueous ammonium chloride solution (15 ml).

The mixture was extracted and the ether layer washed with water (10 ml), separated, and dried over anhydrous magnesium sulfate. Evaporation of the solvent left a crude solid which was recrystallized from pentane-benzene to give yellow crystals (188mg, 77.0%): mp 144-205° dec; ir (KBr) 2470 (S-H), 1480, 1455 (C = C) cm^{-1} ; nmr (CDCl_3) δ 7.12-7.60 (m, 8), 5.40, 5.28 (d, $J = 6\text{Hz}$, 2) 3.10, 3.00 (d, $J = 6\text{Hz}$, 2); mass spectrum m/e , no parent at 244, 178 (P - 66).

3.78 Reaction of the Dianion of (66) with Phosgene

In a 10 ml round bottom flask equipped with a pressure equilibrating addition funnel were placed (66) (122mg, 0.5 mmol) and dry toluene (3 ml). In the addition funnel were placed methyllithium (22mg, 1.0 mmol) and toluene (2 ml). The flask was chilled in a Dry Ice-acetone bath and the methyllithium added dropwise under nitrogen to the solution of (66).

In a separate flask, phosgene (1.0g) was condensed through cottonseed oil into toluene (10 ml) at 0°. An aliquot (0.50 ml) was extracted by syringe and added to the dithiolate at -78°. The color immediately disappeared. The system was brought to room temperature and allowed to stir for 1 hr. At that time, the mixture was treated with saturated aqueous ammonium chloride solution (10 ml) and partitioned.

The organic layer was separated, dried over anhydrous magnesium sulfate, and the solvent evaporated. Preparative tlc yielded anthracene (79mg).

3.79 Reaction of the Dianion of (66) with Dibromomethane and Diiodomethane

In a 10 ml round bottom flask equipped with a pressure-equilibrating addition funnel were placed (66) (122mg, 0.5 mmol) and dry dimethoxyethane (3 ml). In the addition funnel were placed methyl-lithium (22mg, 1.0 mmol) and dimethoxyethane (2 ml). The flask was chilled in a Dry Ice-acetone bath and the methyllithium added dropwise under nitrogen. The mixture was then stirred for 0.5 hr.

Next, freshly distilled dibromomethane (87mg, 0.5 mmol) or diiodomethane (134mg, 0.5 mmol) in dimethoxyethane (2 ml) was added to the dithiolate at -78° . The mixture was allowed to come to room temperature and stir overnight. It was then treated with saturated aqueous ammonium chloride solution (10 ml) and poured into water (20 ml). This solution was partitioned into diethyl ether (10 ml). The layers were separated and the organic layer dried over anhydrous magnesium sulfate. Evaporation of the solvent and preparative tlc yielded anthracene nearly quantitatively in each case.

3.80 Reaction of the Dianion of (66) with Iodine

In an nmr tube fitted with a rubber septum were placed (66) (40mg, 0.16 mmol) and tetrahydrofuran (0.2 ml). The system was flushed with nitrogen and the nmr spectrum taken. Then the tube was chilled in a Dry Ice-acetone bath and *n*-butyllithium (20.5mg, 0.32 mmol) added.

After 5 min a solution of iodine (40.6mg, 0.16 mmol) in tetrahydrofuran (0.2 ml) was added. The color remained dark. The tube was immediately transferred to the nmr spectrometer and the spectrum taken. The spectrum was identical with that of anthracene. Work up by preparative tlc yielded anthracene and sulfur quantitatively.

3.81 9-Trimethylsilylthioanthracene (72)

In a 50 ml three-necked flask fitted with a pressure-equilibrating addition funnel, a reflux condenser, and a rubber septum were placed (64) (1.08g, 4 mmol) and dry diethyl ether (15 ml). In the addition funnel were placed methyllithium (176mg, 8 mmol) and diethyl ether (5 ml). The system was placed under a nitrogen atmosphere and the flask chilled in a Dry Ice-acetone bath. The methyllithium was then added dropwise to the solution of (64). After the addition was complete the reaction mixture was treated with trimethylsilylchloride (5 ml) and heated at reflux for 2 hr.

The solvent and excess trimethylsilylchloride were pumped off under high vacuum and the residue taken up in diethyl ether (10 ml). The precipitate of lithium chloride was filtered in a glove bag under nitrogen. The ether was again evaporated with a stream of nitrogen to yield a gummy solid. This was recrystallized from benzene-pentane to yield yellow-orange crystals (926mg, 82.1%): mp 97-98°; ir (KBr) 1600 (C = C), 1258, 835, 730 cm^{-1} ; nmr (CDCl_3) δ 8.77-9.07, 8.40, 7.80-8.15, 7.20-7.70 (m, 9), 0.12 (s, 9).

3.82 Reduction of Phenyl Trimethylsilyl Sulfide

In a 25 ml three-necked flask was placed phenyl trimethylsilyl sulfide¹⁶⁴ (915mg, 5.0 mmol). In one experiment the flask was fitted with a reflux condenser and dry tetrahydrofuran (10 ml) was added. In two other experiments, a Dry Ice condenser was attached and liquid ammonia (approximately 10 ml) condensed into the flask. Both systems were kept under nitrogen atmosphere. In the tetrahydrofuran experiment, lithium metal (70mg, 10.0 mmol) was added, while in one liquid ammonia experiment the same quantity of lithium was introduced and in the other sodium metal (230mg, 10.0 mmol) was used. The tetrahydrofuran solution was heated at reflux for 48 hr and the liquid ammonia solutions were allowed to reflux for 20 hr. At the end of these times, the reaction mixtures were checked by tlc and nmr even though the metals had not been consumed. The tlc showed starting material and a small new spot which could be identified as benzenethiol. The nmr showed only those peaks due to starting material.

When naphthalene (10mg) was added to the refluxing solution of starting material and sodium in liquid ammonia, the blue color of the dissolved sodium disappeared within 15 min. The solution was allowed to reflux an additional 0.5 hr, solid ammonium chloride (300mg) was added, and the ammonia evaporated under a stream of nitrogen. Then diethyl ether (10 ml) was added and the solution filtered in a glove bag under nitrogen, followed by evaporation of the solvent under a stream of nitrogen. An nmr in CDCl_3 of the crude product showed it to be benzenethiol (509mg).

3.83 Reduction of (72)

In a 25 ml three-necked flask was placed (72) (282mg, 1.0 mmol). In one experiment, dry tetrahydrofuran (2 ml) was added and the flask was fitted with a reflux condenser. In the other experiment, the flask was fitted with a Dry Ice condenser and liquid ammonia (approximately 5 ml) was condensed into the flask. In the tetrahydrofuran experiment, lithium metal (14mg, 2.0 mmol) was added, while for the liquid ammonia experiment sodium metal (46mg, 2.0 mmol) was used. Both systems were placed under nitrogen atmosphere. The tetrahydrofuran solution was allowed to stir at room temperature for 1 hr at which time it had turned red. Workup involved evaporation of the solvent under reduced pressure, addition of diethyl ether (10 ml), and extraction with water (10 ml). The liquid ammonia solution was allowed to reflux 1 hr after which time it was dark brown. Addition of solid ammonium chloride (150mg) immediately caused a color change to orange. Diethyl ether (10 ml) was added and the ammonia evaporated under a stream of nitrogen. The ether solution was then extracted with water (10 ml).

Both ether layers were separated and dried over anhydrous magnesium sulfate. Evaporation of the solvent gave a crude product which was subjected to preparative tlc using petroleum ether-benzene (8:1) as developing agent. In both cases, three products were isolated and identified by tlc, nmr, mp, and mixture mp with authentic compounds. These were anthracene (~ 160mg), 9,10-dihydroanthracene (~ 20mg), and 9-anthryldisulfide (~ 10mg).

The two experiments above were modified by the addition of *t*-butyl alcohol (148mg, 2.0 mmol) simultaneously with the addition of

the metal. Again, in both cases, the results were the same as before.

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