REACTIONS OF ELECTRON-RICH OLEFINS WITH

ELECTRON-POOR OLEFINS

by

Mohamed Abdelkader

A Dissertation Submitted to the Faculty of the

DEPARTMENT OF CHEMISTRY

In Partial Fulfillment of the Requirements
For the Degree of

DOCTOR OF PHILOSOPHY

In the Graduate College

THE UNIVERSITY OF ARIZONA

1 9 8 1

THE UNIVERSITY OF ARIZONA
GRADUATE COLLEGE

As members of the Final Examination Committee, we certify that we have read

the dissertation prepared by ____Mohamed Abdelkader_____

entitled _____Reactions of Electron-rich Olefins with_____

_____Electron-poor Olefins_____

_____

_____

_____

and recommend that it be accepted as fulfilling the dissertation requirement

for the Degree of _____Doctor of Philosophy_____.

M. Bal	5-8-81
	Date
A. Kubohn	5-8-81
	Date
John V. Rund	5-8-81
	Date
H.K. Hall, Jr.	5/8/81
	Date
J. Mulvaney	
	Date

Final approval and acceptance of this dissertation is contingent upon the
candidate's submission of the final copy of the dissertation to the Graduate
College.

I hereby certify that I have read this dissertation prepared under my
direction and recommend that it be accepted as fulfilling the dissertation
requirement.

H.K. Hall, Jr.   5/8/81

Dissertation Director   Date

STATEMENT BY AUTHOR

This dissertation has been submitted in partial fulfillment of requirements for an advanced degree at The University of Arizona and is deposited in the University Library to be made available to borrowers under rules of the Library.

Brief quotations from this dissertation are allowable without special permission, provided that accurate acknowledgment of source is made. Requests for permission for extended quotation from or reproduction of this manuscript in whole or in part may be granted by the head of the major department or the Dean of the Graduate College when in his judgment the proposed use of the material is in the interests of scholarship. In all other instances, however, permission must be obtained from the author.

SIGNED: _____

ACKNOWLEDGMENTS

TABLE OF CONTENTS

TABLE OF CONTENTS--Continued

LIST OF TABLES

ABSTRACT

Reactions of the electron-poor olefins trimethyl ethylenetri-
carboxilate 2, dimethyl cyanofumarate 10, and tetramethyl ethylenetetra-
carboxylate 14 with the electron-rich olefins p-methoxystyrene 1,
N-ethyl-3-vinylcarbazole 16 and dimethylvinylamine 22, gave small
molecules, such as dihydropyrans 3 and 12, cyclobutanes 9, 15, 17, 20
and 21, and 1-butenes 4 and 23, and polymers 5, 8, 11, and 18. These
reactions can be explained as proceeding via tetramethylene intermediates
exhibiting biradical and/or zwitterionic character. The biradical nature
of the tetramethylenes in the case of p-methoxystyrene 1 was supported
by the formation of alternating copolymers 5 and 11, identical to those
formed by deliberate free radical initiated copolymerization, and in-
hibition by free radical inhibitors. The rates of the reactions were
insensitive to solvent polarity when biradical tetramethylenes were the
intermediates.

The zwitterionic nature of the tetramethylenes in the case of
N-ethyl-3-vinylcarbazole 16 and dimethylvinylamine 22, best explained
the mechanism. This character was supported by the formation of the
homopolymer 18, identical to those initiated cationically; this polymeri-
zation was inhibited by triethylamine. The reactions of 16 were favored
in polar solvents and this is consistent with a dipolar intermediate.

An ion-radical mechanism was excluded for these reactions because
a deliberate generation of cation-radicals of 1 and 16 in the presence

of trimethyl ethylenetricarboxylate 2 gave cyclodimer 7 and copolymer 5

in the former case and only homopolymer 18 in the latter.

The reactivity sequence 10 ⟩ 2 ⟩14 is dictated largely by reso-

nance stabilization of, and steric hindrance to, tetramethylene formation.

CHAPTER 1

INTRODUCTION

Thermal reactions of electron-rich olefins with electron-poor

olefins are known to produce a variety of products, both small molecules

and polymers. Small molecules include cyclobutanes, 1-butenes, and

cyclohexanes; polymers include homopolymer of either or both olefins,

and 1:1 alternating copolymers.

Background

According to Bartlett (1968), the fluorinated olefins, tretra-

fluoroethylene and 1,1-dichloro-2,2-difluoroethylene, have been reacted

with dienes to give predominantly cyclobutanes:
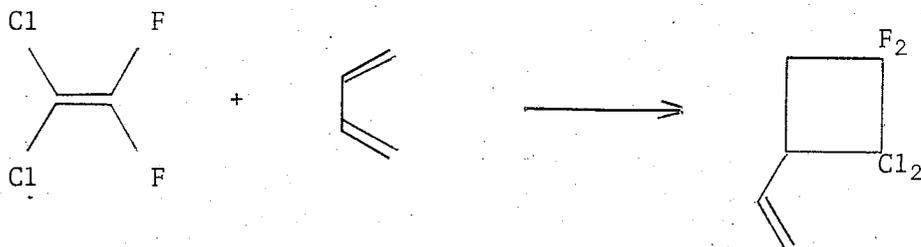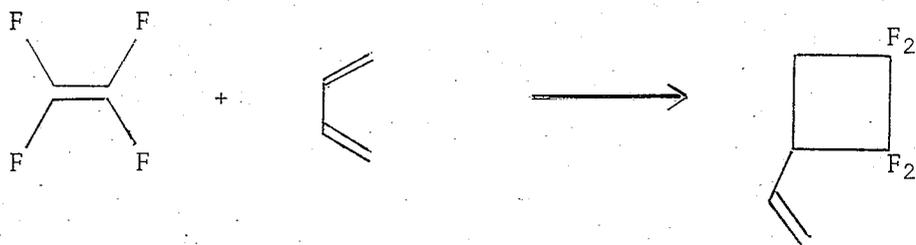
Little (1965), in his attempt to do a Diels-Alder reaction between α-acetoxyacrylonitrile and butadiene, got 14% of cyclobutane adduct.

+ others
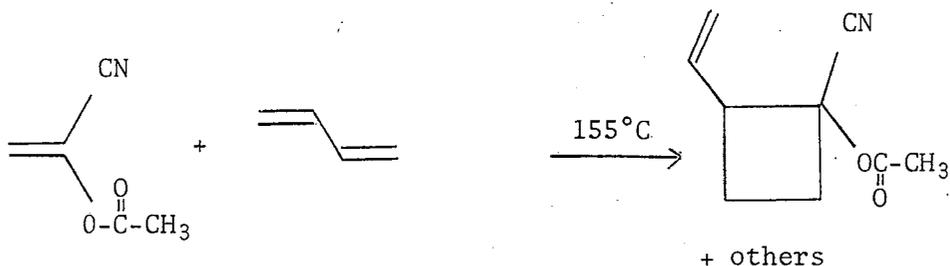
Stille et al. (1975) reacted vinylidene cyanide with vinyl ether to yield cyclobutane adduct and homopolymer of both vinyl ether and vinylidene cyanide:
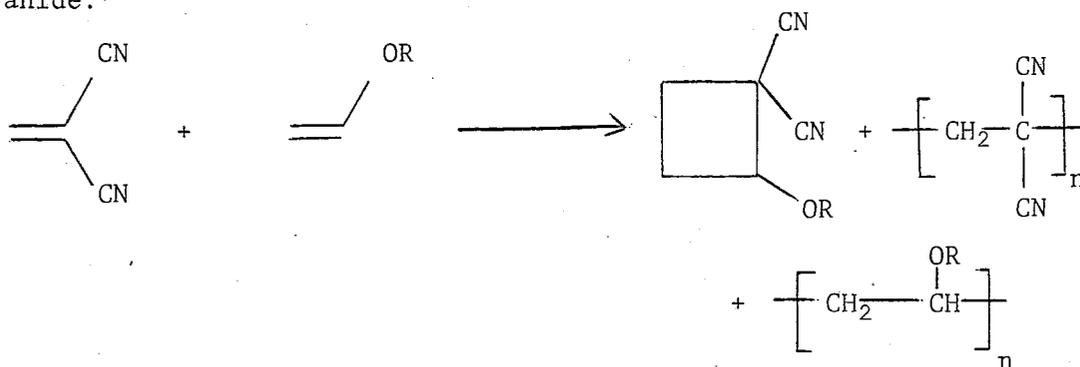
With ketene diethylacetal and dihydropyran they got cyclohexanes from one molecule of olefin and two of vinylidene cyanide, and cyclobutane adduct respectively, accompanied by homopolymers of both donor and acceptor olefins:
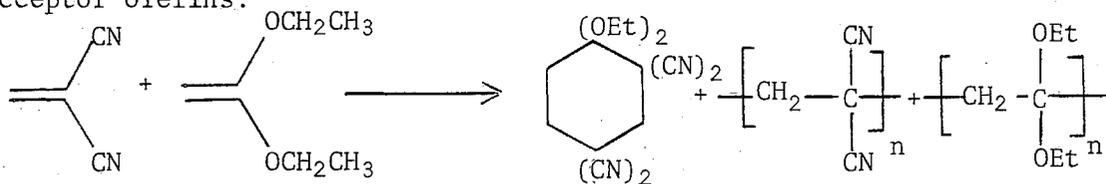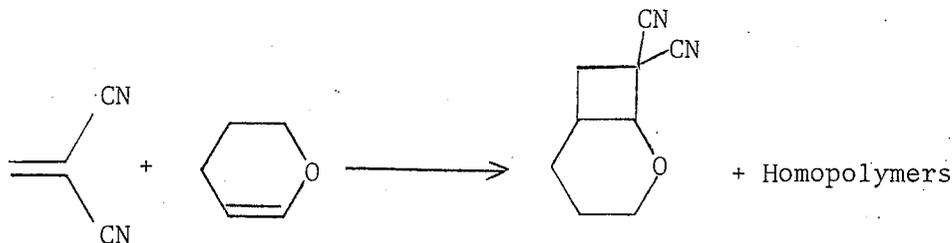
With styrene, they obtained cyclohexanes and copolymer:
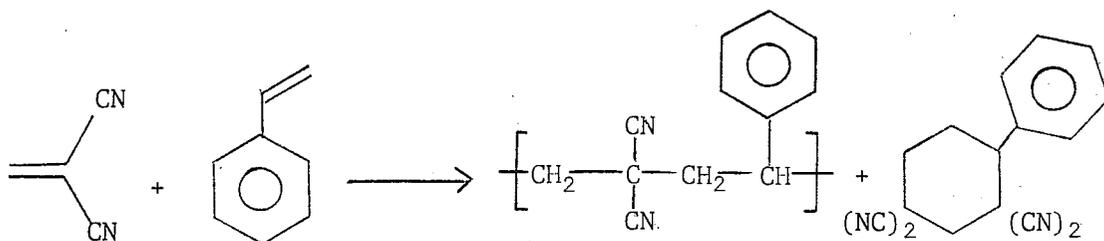
Huisgen and Steiner (1973) reacted vinyl ethers with tetra-cyanoethylene to yield only cyclobutanes:
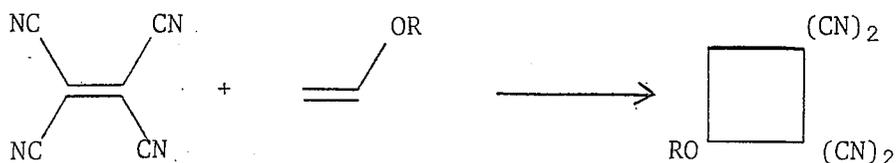
Hall and Ykman (1975) obtained a variety of small molecules such as cyclobutanes, cyclohexanes, and 1-butene, when they reacted vinyl-amines, vinyl sulfide, and ketene acetal with dimethyl ethylenedicarboxy-late, trimethyl ethylenetricarboxylate and maleic anhydride, respectively:
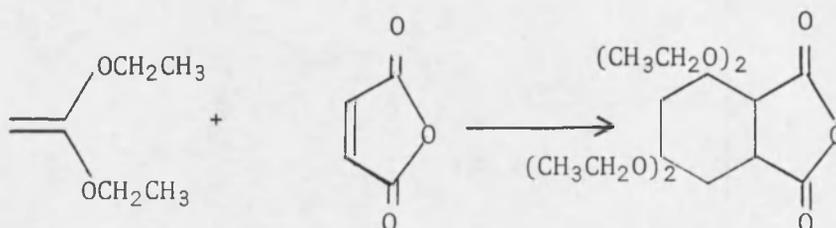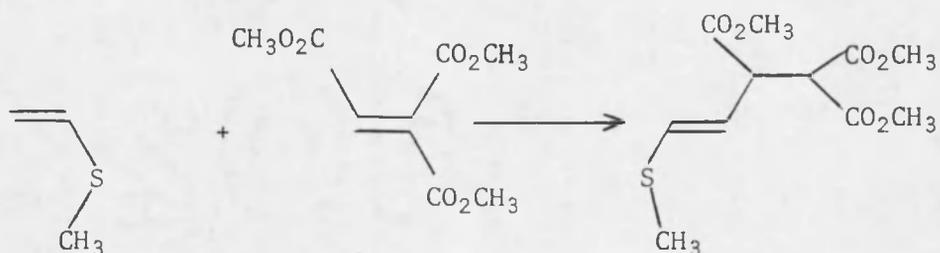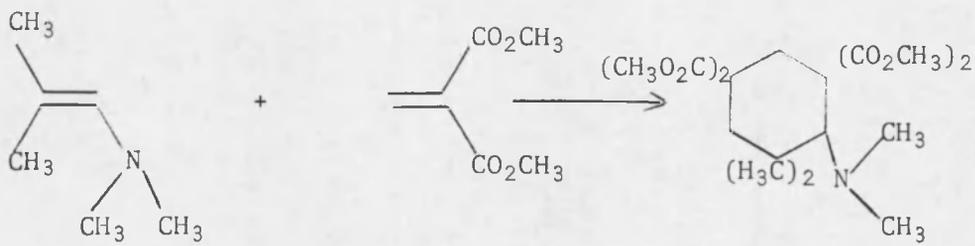
Lately, Glogowski and Hall (1979) obtained cyclobutanes, 1-butenes, homopolymers, and copolymers, depending on the solvent and additives, from the reactions of N-vinylcarbazole and trimethyl ethylene-tricarboxylate:
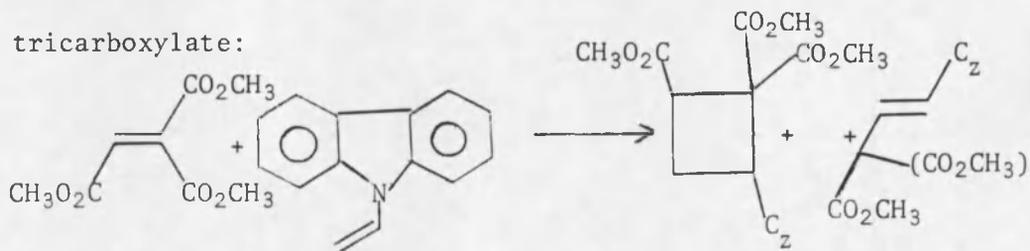
+ Copolymer + Poly(vinylcarbazole)

And finally, Hall, Dunn and Padias (1980) obtained cyclobutane adduct by reacting p-dimethylaminostyrene with tri- and tetra-ester ethylenes:
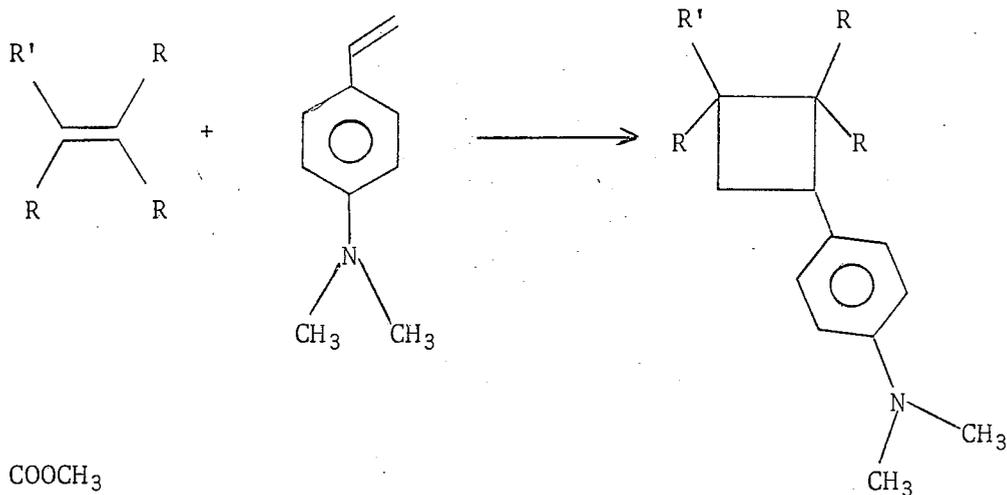
R = COOCH$_3$

R' = H or COOCH$_3$

Mechanism

Most of the previous reactions formed [$\pi^2 + \pi^2$] cycloaddition products. It is known that [2 + 2] thermal cycloadditions are orbital symmetry forbidden to go through a concerted supra-supra mechanism, but a supra-antara process is allowed. The latter is geometrically diffi-cult, and needs a considerable energy of distortion, which will not permit it to occur. Bartlett, Huisgen, Stille, and Hall ended with a stepwise mechanism.

The interpretation of their results implicated a tetramethylene, with diradical character, or purely zwitterionic character, or an hypo-thetical tetramethylene with both characters which is a resonance hybrid of zwitterion and biradical proposed by Salem and Rowland (1972):
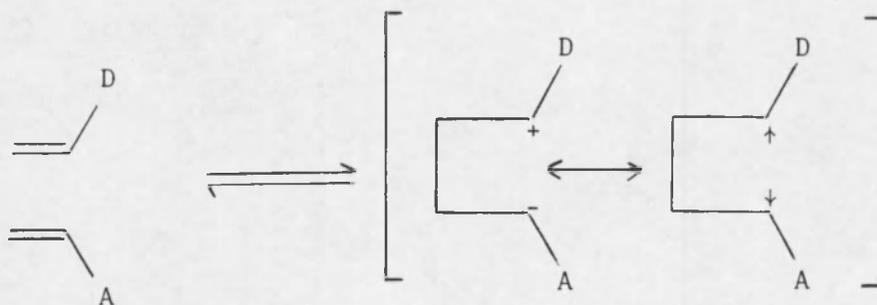
The biradical intermediate explained well the results of Bartlett (1968, 1970), where cyclobutanes formed from the reaction of fluoro-ethylenes or α-acetoxyacrylonitrile with butadienes. Huisgen (1977) used the dipolar tetramethylene to explain his results. The latter has been used by Hall and Ykman (1975) and Hall et al. (1980) to satis-factorily explain their results, too.

The zwitterionic character has been supported by polar substi-tuents and solvent effect. Huisgen and coworkers (1977) trapped the tetramethylene from vinyl ethers and tetracyanoethylene with polar re-agents such as alcohols or unsaturated compounds such as acetone, aceto-nitrile, and N-benzylidenemethylamine:
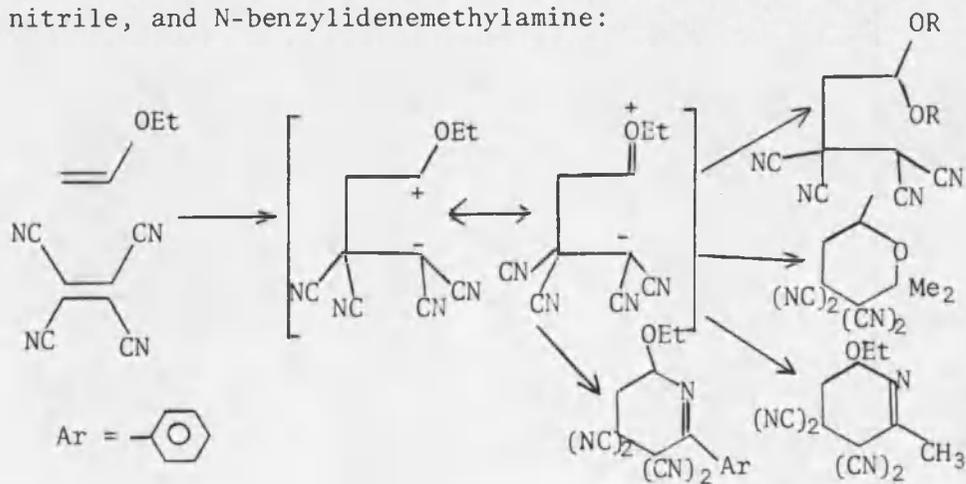
The formation of cyclohexanes and their assigned structures are consistent with the dipolar intermediate. One of the olefins is playing the role of a trapping agent. In the case of Hall and Ykman (1975) the electron-rich olefin trapped the tetramethylene from ketene diethylacetal and maleic anhydride:
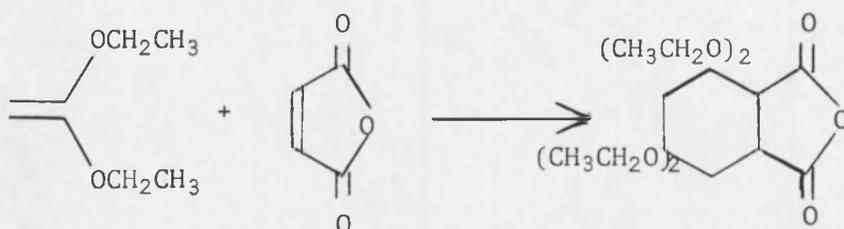
Other cases are known where the electron-rich olefins, diethyl 1,1-ethylenedicarboxylate and vinylidene cyanide, intercepted the intermediates, in the case of Hall and Ykman (1975) and Stille et al. (1975), respectively.

An attempt to trap the tetramethylenes formed from the p-dimethyl-aminostyrene with ethylenic tri- or tetraesters and p-methoxystyrene - tetracyanoethylene, by Hall and Dunn (1980), and Huisgen (1977), respectively, did not succeed as mentioned.

Salem and Rowland (1972) combined biradical character with zwitterionic character to end up with a tetramethylene which is a resonance hybrid of zwitterion and singlet biradical:
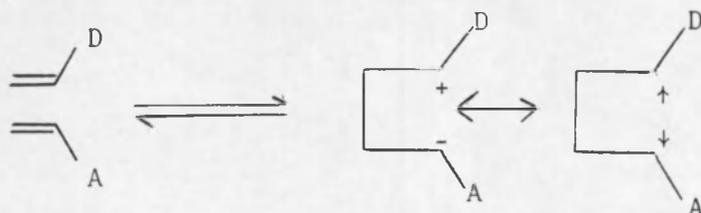
D = electron-rich substituent
A = electron-poor substituent

A study of the related trimethylene was done by Chmurny and Cram (1973). They concluded that in ring opening reactions of cyclopropanes, a spin-paired biradical (a) best represented the trimethylene from methyl 1,3-diphenylcyclopropanecarboxylate whereas a zwitterion (b) best described that from methyl 1-cyano-2-phenylcyclopropanecarboxylate.

(a)   (b)
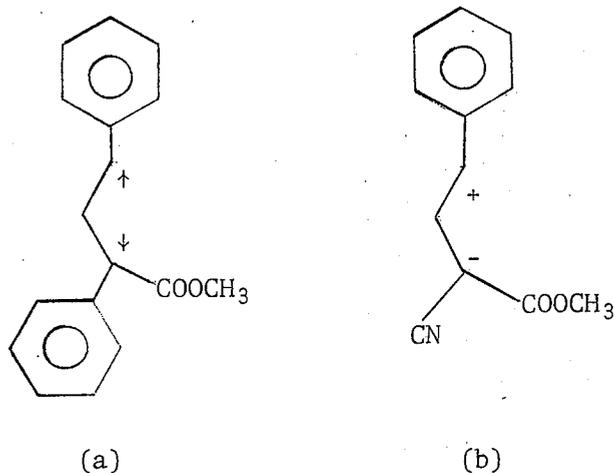
Another interpretation had been suggested by Shirota and Mikawa (1977-1978) to explain the photochemical reaction of N-vinylcarbazole with acceptors. They believed a cation-radical anion-radical pair formed, which induced a cationic polymerization, cyclodimerization and radical polymerication, depending on solvent:

Cationic
polymerization

cyclodime-
rization

less basic solvent

moderately basic solvent

NVCZ + A   ⇌   NVCZ^{+} + A^{-}

less basic solvent

extremely basic solvent

strongly basic solvent

cyclodime-
rization
+ Radical
polymeri-
zation

Radical
polymerication

NVCZ
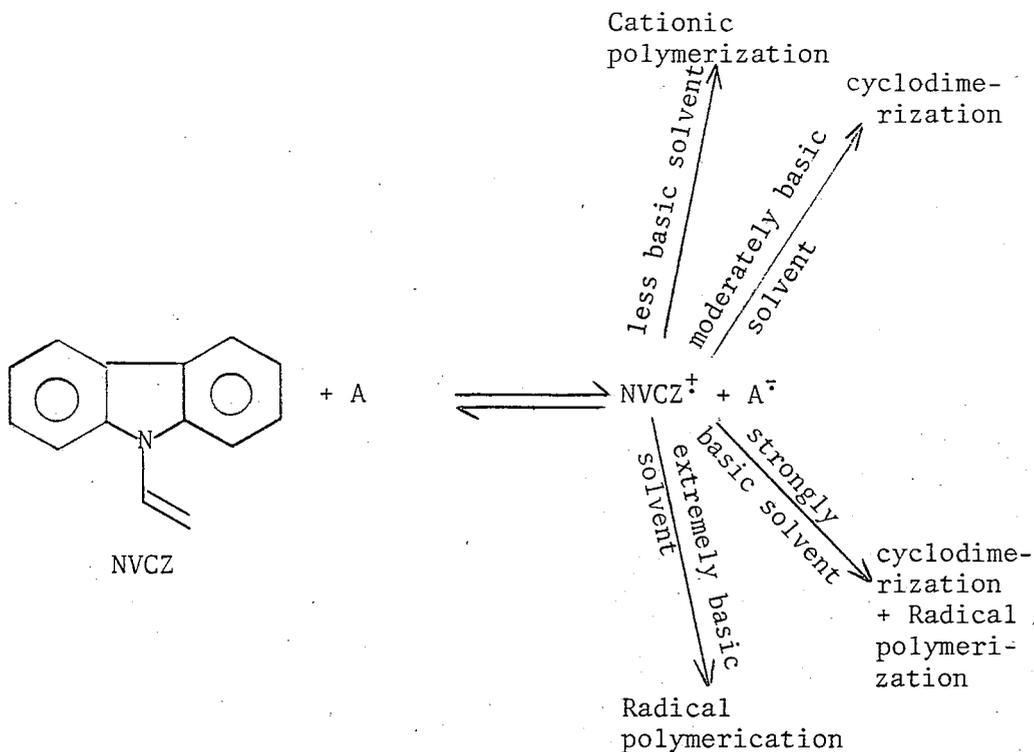
The same type of mechanism has been postulated by Glogowski and
Hall (1979) in the reactions of N-vinylcarbazole with trimethyl ethylene-
tricarboxylate.

Scope of the Present Study

It is not easy to diagnose biradicals versus zwitterionic contri-
butions to the tetramethylene intermediate, but it is possible to differ-
entiate a tetramethylene from ion-radicals which usually form cyclodimers.
We planned to utilize vinyl polymerization as a tool to help delineate
the mechanism. Hall and Ykman (1975) and Hall et al. (1980), using free
radical initiation, copolymerized trisubstituted electron-poor olefins
with electron-rich vinyl monomers to form alternating 1:1 copolymers.

On the other hand, electron-rich monomers readily undergo homopolymeriza-
tion under cationic initiation. Accordingly, examination of the polymer
formed in the spontaneous reactions of electron-rich and electron-poor
olefins will give evidence as to the nature of the tetramethylene inter-
mediates:
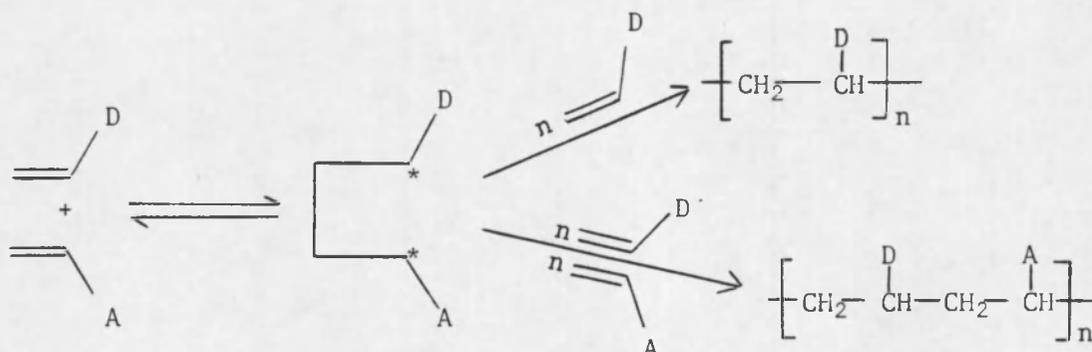
Good evidence for a biradical is the formation of copolymer, and
the homopolymer is the evidence for a zwitterion. Other evidences are
products arising from rotation or from coulombic attractions in the
tetramethylene intermediate. The former implicates biradicals, and the
latter zwitterions. Here we examine the reaction of trimethyl ethylene-
tricarboxylate and dimethyl cyanofumarate with electron-rich monomers:
p-methoxystyrene, N-ethyl-3-vinylcarbazole, and dimethylvinylamine, in
order of decreasing potential of ionization, respectively. Tetramethyl
ethylenetetracarboxylate, which cannot copolymerize, was included for
comparison.

RESULTS

Reactions of p-Methoxystyrene with Acceptors

Trimethyl Ethylenetricarboxylate

The reaction of p-methoxystyrene 1 with trimethyl ethylenetri-carboxylate 2 gave a bright yellow transient color and yielded both small molecules 3 and 4 and macromolecule 5.
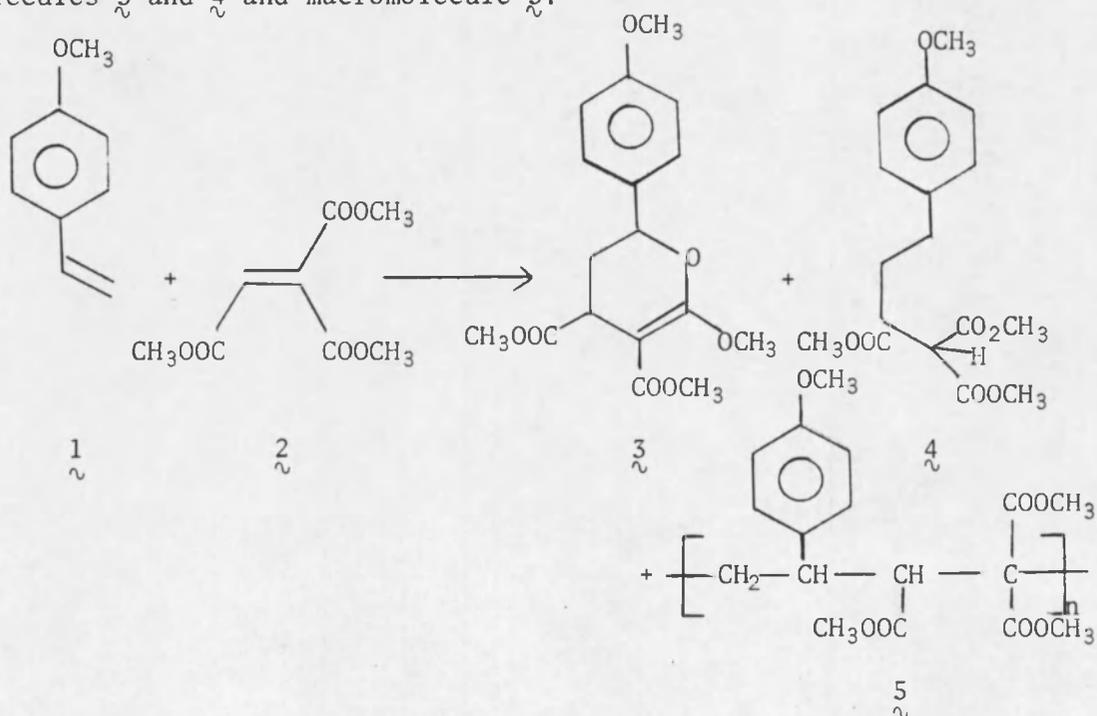
Dihydropyran 3 was isolated in crystalline form, mp 93 - 94° C. The sharp melting point supported one isomeric form with the phenyl group and the non-conjugated carbomethoxy at the equatorial position.

11

The assigned structure was confirmed by infrared and nmr spectra as well as elemental analysis. The ir spectrum showed the presence of a ketene acetal absorption at 1660 cm^{-1} ($C=CO_2$), and the nmr showed a quartet downfield at δ 5.2 for the proton α to the phenyl group, with coupling constants 10 and 4 Hz confirming a six membered ring by analogy to cyclohexanes which have in general coupling constants in the range of 6-14 and 0-5 Hz for axial-axial and equatorial-axial or equatorial-equatorial coupling, respectively. The high shift is probably due to the ring current created by the phenyl group, with the proton held in the deshielding zone of the ring. This effect is favored when the proton is in the axial position. Because of the 1,3-interaction, the carbomethoxy at carbon 4 is favored in the equatorial position.

The 1-butene 4 was also isolated as a white powder, mp 73 - 74° C. It was given the trans structure on the basis of nmr spectrum: the coupling constant between the olefinic protons is 14 Hz. Alternating copolymer 5, a white non-crystalline solid, was characterized by elemental analysis and ir and nmr spectra (see Experimental).

Temperature Effect. Below 70°, little reaction was observed. At 70° only the kinetically favored dihydropyran 3 formed, in low yield (Table 1). At 85° more total product, a mixture of dihydropyran and 1-butene 4, was obtained. At 116° C only the thermodynamically stable 1-butene 4 formed in a good yield. Copolymer 5 formation accompanied these reactions.

Effect of Free Radical Inhibitors and Initiators. The free radical inhibitors diphenylpicrylhydrazyl (DPPH) and

Table 1. Reaction of p-methoxystyrene with trimethyl ethylenetri-carboxylate at 70 and 116° C.[a]

Solvent	Temperature	Additives	Dihydro-pyran 3	1-Butene 4	Copolymer 5
None	70°C	None	5.5%	0	65.5%
	70°C	DPPH[b]	29.9%	0	11.9%
	116°C	None	0	0	67.7%
	116°C	DPPH	0	32.2%	0
Benzene	70°C	None	Trace	0	5.8%
	70°C	DPPH or DPS[c]	Trace	0	0
	116°C	DPPH	0	28.2%	0
1,2-Di-chloro-ethane	70°C	None	17.2%	0	17.6%
	70°C	DPPH	18.3%	0	0
	70°C	DPS	24.2%	0	0
	116°C	DPPH	0	20.8%	0
Aceto-nitrile	70°C	None	Trace	0	5.8%
	70°C	DPPH	18.1%	0	0
	70°C	DPS	21.7%	0	0
	116°C	DPPH	0	17.1%	0
Benzal-dehyde[d]	70°C	DPPH	0	10.4%	0
DMSO[e]	75°C	DPPH	0	32.8%	0

a. Conditions: Reagents 0.67M, additives 1×10^{-3}M, reaction times 19 hours, nitrogen atmosphere (except as noted).
b. DPPH = diphenylpicrylhydrazyl.
c. DPS = Di-(4-hydroxy-3-t-butyl-5-methylphenyl) sulfide.
d. 90 hours.
e. 48 hours.

di-(4-hydroxy-3-t-butyl-5-methylphenyl) sulfide (DPS) effectively in-

hibited the formation of copolymer 5 in solution (Table 1). Yields of 3

and 4 were much higher in these inhibited reactions. Variation in DPPH

concentrations in benzene had no apparent changes in yields. The free

radical initiator azobisisobutyronitrile (AIBN) gave good yield of the

1:1 alternating copolymer 5 and negligible yields of 3 and 4.

Solvent Effect. Apparently no solvent effect was observed. At

70° C 1,2-dichloroethane or acetonitrile gave only slightly higher

yields than benzene (Table 1). The only solvents which gave the 1-butene

at 70 - 75° C were dimethylsulfoxide (DMSO) and benzaldehyde, due proba-

bly to the longer reaction time allowing 3 by cycloreversion to give the

thermodynamically stable compound 4. At 116° C the yield of 1-butene

was similar in 1,2-dichloroethane, benzene, and acetonitrile.

Trapping Attempts. A variety of polar reagents used as solvents

was examined as potential agents for polar tetramethylene intermediates

in the reaction of 1 with 2. These included thiophenol, methanol,

methoxyaceticacid, formic acid, and trifluoroethanol, but these reacted

with 1 or 2. Thiophenol and methanol reacted with triester to give the

addition adduct:

$$CH_3OOC \quad COOCH_3 \\ \diagdown \diagup \\ + \quad R-X-H \quad \longrightarrow \\ \diagup \\ COOCH_3$$

$$\begin{array}{ccc} RX & H & CO_2CH_3 \\ \diagdown & | & \diagup \\ & C——C & \\ | & & \diagdown H \\ CH_3O_2C & CO_2CH_3 \end{array}$$

R-X- = CH_3O - , —⟨O⟩—OCH_3

Methoxyacetic acid, formic acid and trifluoroethanol polymerized p-methoxystyrene 1.

Acetonitrile or benzaldehyde had been used by Schug and Huisgen (1975) with success, but did not give heterocyclic adduct in this work. Dimethyl maleate, N-phenylmaleimide and maleic anhydride have been used in excess to intercept a non-polar tetramethylene of 1 and 2 at 70 - 75° C, but failed again to yield the expected cyclohexanes. They yielded copolymer of 1 and dimethyl maleate; 1 and N-phenylmaleimide; and homo-poly-p-methoxystyrene, respectively.

Nitrosobenzene or NO, potential traps of polar and non-polar tetramethylene, failed to yield the expected heterocyclic adduct. Nitro-sobenzene reacted with 1 to give a double Diels-Alder product from two molecules of nitrobenzene and one of p-methoxystyrene. With NO the 1-butene 4 and unidentified oligomers formed.

Cycloreversions and Solvolyses of Dihydropyran 3. Heating 3 alone at 75° C overnight gave copolymer 5 and also traces of 1 and 2. Heating 3 at 115° C in the presence of DPPH converted it completely to 1-butene 4. Vacuum distillation of 3 gave back reactants 1 and 2. Heating 3 in deuteroacetonitrile for 43 hours at 75° C in the presence of DPPH gave 1-butene 4 and traces of 1 and 2.

Heating 3 in methanol at 86° C for 5 hours gave no reaction, but at 126° C for 16 hours gave p-methoxystyrene and the methanol adduct of 2. Left in methanol at 28° C for 10 days, 3 gave 1-butene 4.

Heating 3 at 70° C in acetic acid and DPPH for 48 hours gave
acetate 6 in good yield. The latter, heated alone, gave 1-butene 4 and
acetic acid:
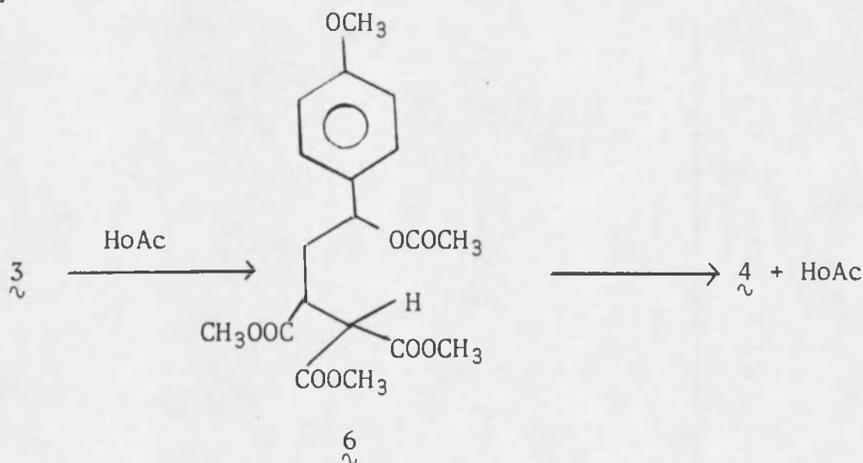
Acetic acid, in blank experiments, did not react with triester
and only very slowly with p-methoxystyrene. A mixture of the monomers
in acetic acid in the presence of DPPH at 75° C gave acetate 6 (30.7%).
This probably formed by acetolysis of 3:
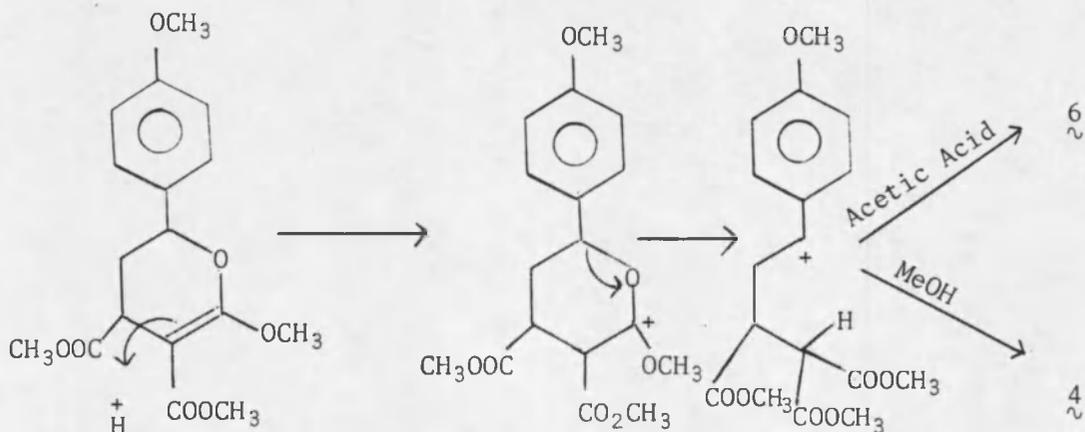
Photochemical and One-Electron Oxidation Reactions. p-Methoxy-
styrene 1 and triester 2 were irradiated by UV light at 40° C in aceto-
nitrile (Table 2). Irradiating 1 and 2 in the presence of

Table 2.   Photochemical reactions of p-methoxystyrene with trimethyl ethylenetricarboxylate.[a]

Additives	Time (hr)	Cyclobutane dimer 7	Cyclobutane adduct 9	Copolymer 5	Homo-polymer 8
air, 1,4-dicyano-benzene	46.5	0.13g 24.25%	0	0.211g 31.4%	0
air	162	0	0	0.005g and oligomer	0
air, 4',4'-di-methoxy benzophenone	144	0	Trace	0.241g 35.86%	0
air, 4,4'-di-methoxy benzophenone DPPH	144	0	0.019g 3%	0	Trace

[a]See Experimental for conditions.

1,4-dicyanobenzene (DCB) gave the trans-cyclodimer 7, previously synthe-
sized by Yamamoto, Asamuma and Nishijima (1975), along with copolymer
5. p-Methoxystyrene and triester in acetonitrile in the presence of
ferric perchlorate, following Ledwith's process (1972) to create cation-
radicals, at 28° C yielded homopolymer 8 of 1 and left triester 2 un-
reacted:
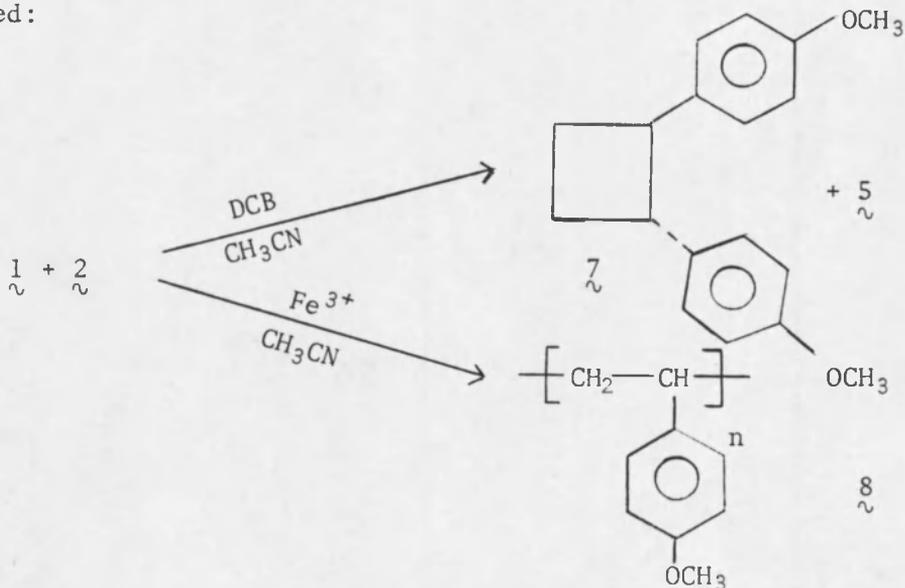
Ultraviolet irradiation of 1 and 2 in acetonitrile in the presence of
4,4'-dimethoxybenzophenone and DPPH gave a low yield of cyclobutane adduct
9, mp 133 - 134°. Its structure was confirmed by nmr, which showed
shielded carbomethoxy absorption at δ 3.25 and coupling constants of 8
and 10 Hz for the hydrogen α to the phenyl group.
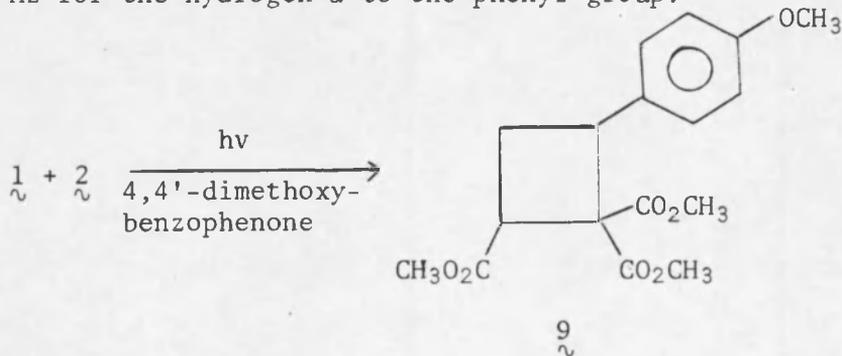
Dimethyl Cyanofumarate

A trisubstituted electrophilic olefin of greater reactivity examined previously by Hall and Daly (1975), dimethyl cyanofumarate 10, was allowed to react with p-methoxystyrene (Table 3). In bulk the reagents formed a bright yellow mixture, then an immediate exothermic reaction occurred to form 1:1 alternating copolymer 11 in 98% yield.

In acetonitrile-d_3 solution containing DPS inhibitor, after 48 hr at 28° C, dihydropyran 12, along with other products, was observed by nmr. Radical inhibitors, DPS and di-t-butylnitroxide, inhibited the formation of copolymer 11, but DPPH failed (Table 3).
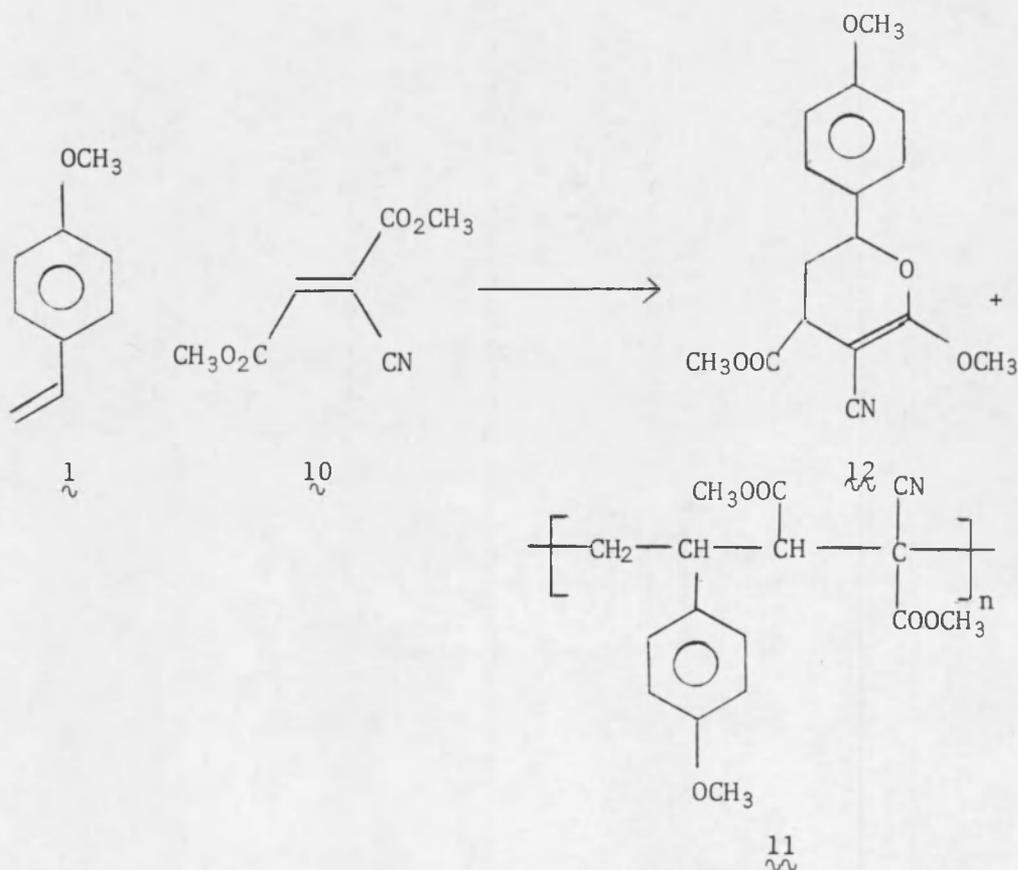
Table 3. Reaction of dimethyl cyanofumarate with p-methoxystyrene.[a]

Solvent	Additives	Time (hr)	Dihydropyran 12	Copolymer 11
None	None	0.1	0	98%
CD_3CN	DPPH (0.01g)	118	33.7%	28.1%
CH_3CN	DPS (0.01g)	114.5	50.8%	0
CH_3CN	di-t-butyl-nitroxide	114.5	49.5%	0

[a]See Experimental for details.

Dihydropyran 12 was isolated from pentane at -50° as a mixture of isomers and was stable for few hours at room temperature. Its infrared and nmr spectra confirmed the structure assigned. Infrared showed an absorption at 1660 cm^{-1} (C=CO$_2$) and nmr gave a quartet a low field (δ 5.1) with coupling constants 4 and 8 Hz.

Cycloreversions and Solvolysis of Dihydropyran 12. The isolated dihydropyran 12 led to the copolymer 11 after a few hours at 28° C even in the presence of DPPH. After a few days in methanol at 28°, 12 yielded the solvolysis product 13:
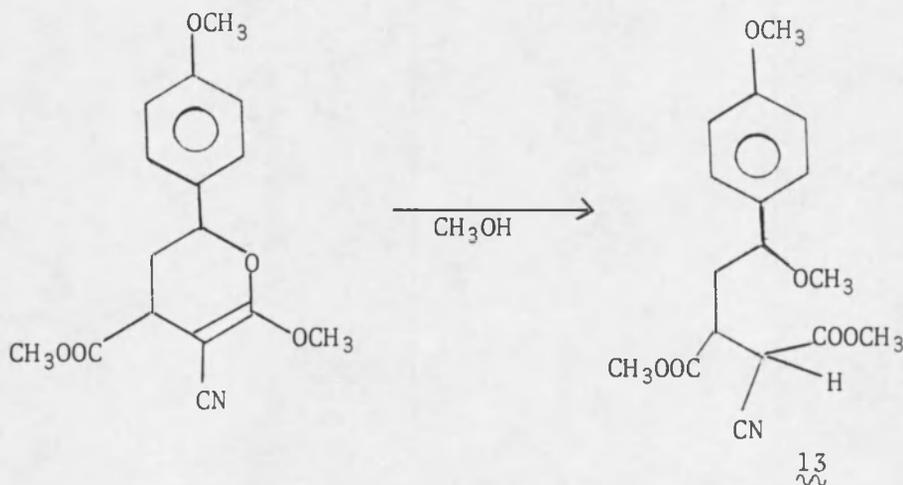
Trapping Attempts. N-Phenylmaleimide (2:1 mole excess) was used to try to trap the tetramethylene from 10 and 1 at room temperature (28° C) but yielded copolymer of 1 and the maleimide.

Maleic anhydride and dimethyl maleate were also used. They stopped the copolymerization of 1 and 10 but did not stop the formation of 12. The reaction of dimethyl cyanofumarate 10 and p-methoxystyrene 1 in the presence of 2-methyl-2-nitrosopropane in benzene showed an esr absorption (Figure 1).

$1 \times 10^2 G$
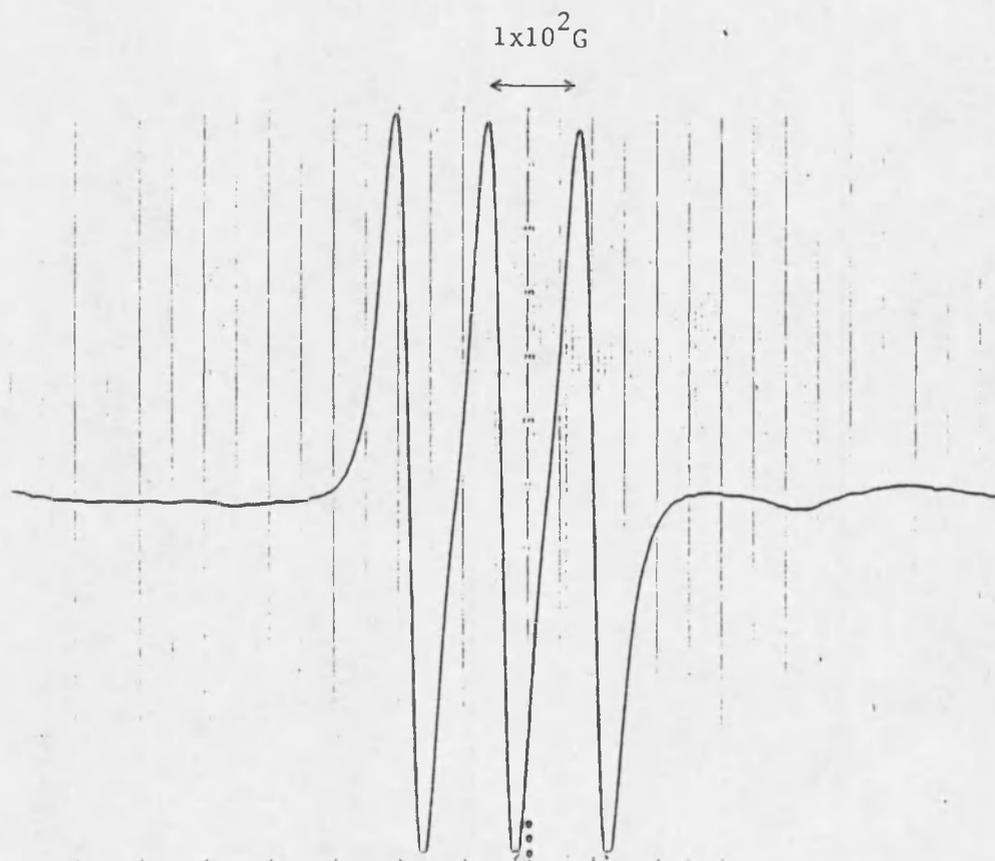
Figure 1.   Esr spectrum obtained after one hour of reaction of
1 with 10 spin trapped with 2-methyl-2-nitrosopropane.

Tetramethyl Ethylenetetracarboxylate

Tetramethyl ethylenetetracarboxylate 14 was less reactive than trimethyl ethylenetricarboxylate, requiring higher temperatures to react. It gave cyclobutane adduct 15 at 116° C (Table 4) in bulk. When 1,2-dichloroethane was used as solvent, the product was homopoly-p-methoxy-styrene 8:
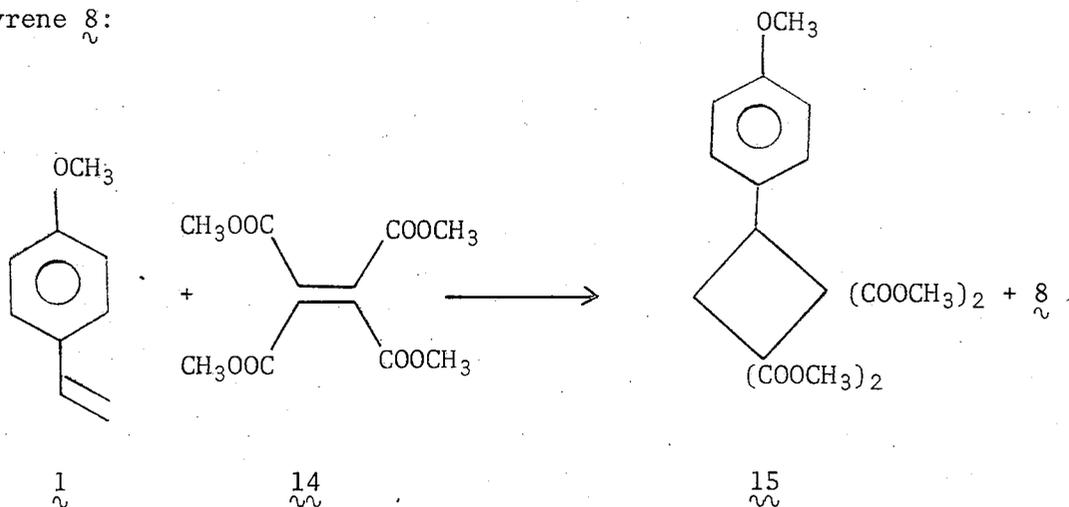
Cyclobutane 15 was obtained in crystalline form, mp 136 - 137° C. Infrared, nmr, and elemental analysis were consistent with the structure. Nmr spectrum showed a shielded carbomethoxy absorption at δ 3.3 and coupling constants of 8 and 12 Hz for the proton α to the phenyl group. Homopolymer 8, a white powder, was characterized by comparison of its nmr spectrum with that of authentic poly-p-methoxystyrene. Its infrared spectrum showed a carbonyl absorption peak even after repeated refluxing with methanol to remove unreacted 14. Exposure of a mixture of 1 and 14 in solution (benzene) to free radicals from AIBN at 70° C gave no polymer.

Table 4. Reaction of p-methoxystyrene with tetracarbomethoxyethylene at 116° C.[a]

Time (hr)	Solvent	Cyclobutane 15	Homopolymer 8
40	None	Trace	4.1%
44.5	None	3.7%	0
65.5	None	9.3%	0
40	1,2-dichloroethane	Trace	5.6%
44.5	1,2-dichloroethane	Trace	7.1%

[a]See Experimental for details.

Reaction of N-Ethyl-3-vinylcarbazole
with Acceptors

Trimethyl Ethylenetricarboxylate

N-Ethyl-3-vinylcarbazole 16 with trimethyl ethylenetricarboxylate
2 gave a transient yellow color and yielded cyclobutane adduct 17 as the
major product and homopolymer 18:
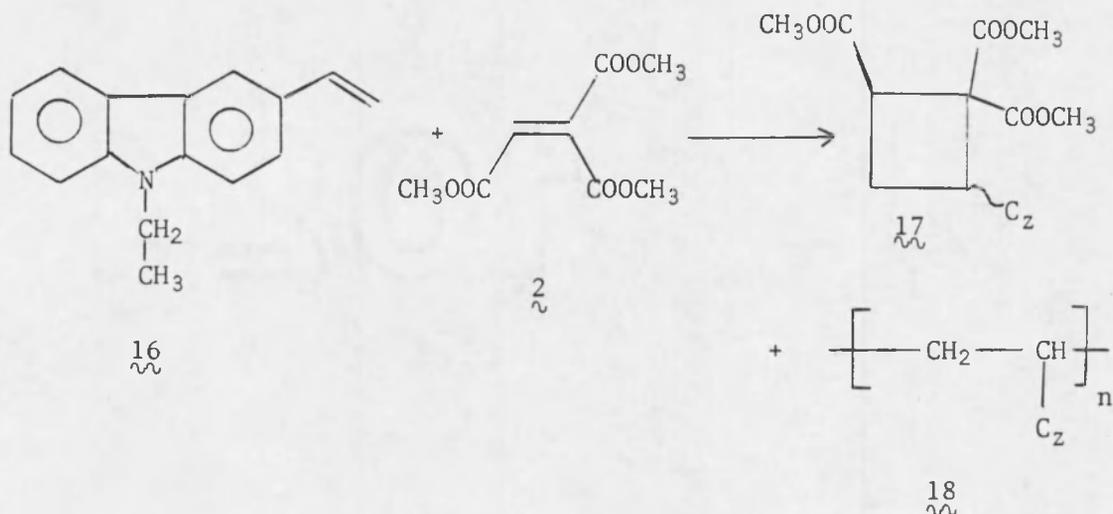
The reaction yields depended on the reaction conditions (Table 5).
Cyclobutane adduct 17 was composed of cis and trans isomers in a 1:1
ratio. The isomers were separated by chromatography. Both were obtained
as oils, and attempts to crystallize them from many solvents failed. In-
frared and nmr spectra, as well as elemental analysis, confirmed the
assigned structures. The nmr spectra showed two shielded carbomethoxy
absorption at δ 3.1 and 3.23 and coupling constants of J=10, 10 Hz and
J=8, 14 Hz for the hydrogen α to the carbazyl group in trans and cis
cyclobutane adduct, respectively. The homopolymer 18, a white powder,
showed a carbonyl absorption even after refluxing with methanol.

Table 5. Reaction of N-ethyl-3-vinylcarbazole with trimethyl ethylene-
tricarboxylate.[a]

Solvent	Additives	Temper-ature	Time in hours	Cyclo-butane adduct 17	Copoly-mer 19	Homo-polymer[b] 18
Aceto-nitrile	Nitrogen	28° C	66.5	20.9%	0	16.3%
Aceto-nitrile	Degassed	50° C	16	37.5%	0	4.3%
Benzene	---	50° C	16	20.5%	0	1.4%
1,2-Di chloro-ethane	---	50° C	16	38.9%	0	4.7%
Di-methyl-sulfoxide	---	50° C	16	36.7%	0	0
1,2-Di-chloro-ethane	Degassed, DPS (0.02g)	50° C	22	49.9%	0	6.8%
1,2-Di-chloro-ethane	Degassed, triethyl-amine (1 ml)	50° C	21	24.3%	0	0
Phenyl isocyanate	Degassed	50° C	92.5	0	0	0.153g[c]
Propional-dehyde	---	58° C	92.5	33.7%	0	0.050g[d]
Benzal-dehyde	---	68° C	26	59.7%	0	0.073g[e]
Benzene	Degassed AIBN (0.01g)	72° C	45	15.1%	77%	0

Table 5.--<u>Continued</u>

Solvent	Additives	Temperature	Time in hours	Cyclobutane adduct 17	Copolymer 19	Homopolymer[b] 18
Acetonitrile	Nitrogen	76° C	42.5	80%	0	trace
None	Air	116° C	24	98.1%	0	1.8%

[a]Conditions as in Experimental. Concentration of each olefin 5×10^{-1} mole/l.

[b]Homopolymer 18 was insoluble in acetone, acetonitrile, ether and methanol. It showed in the ir an ester carbonyl absorption. Its calculated composition: C, 86.8; H, 6.8; N, 6.3.

[c]Polymer analysis: C, 82.6; H, 6.6; N, 6.1; O, 4.5.

[d]Polymer analysis: C, 70.4; H, 6.1; N, 4.0; O, 19.5.

[e]Polymer analysis: C, 82.5; H, 6.8; N, 5.4; O, 5.2.

Temperature Effect. Below 76° C the reactions were incomplete in 16 hours (Table 5) and gave both 17 and homopolymer 18. At 116° C the reactions were practically complete giving a good yield of 17 and only traces of 18.

Free Radical Inhibitor Effect. DPS did not affect the formation of 17 and 18.

Free Radical Initiator Effect. AIBN gave a good yield of 1:1 alternating copolymer 19 (Table 5), along with 17, but no homopolymer 18.

$$16 + 2 \xrightarrow[\Delta]{\text{AIBN}} 17 + \left[CH_2-\underset{CH_3OOC}{\overset{C_z}{\underset{|}{\overset{|}{CH}}}}-CH-\underset{COOCH_3}{\overset{COOCH_3}{\underset{|}{\overset{|}{C}}}} \right]_n$$

19
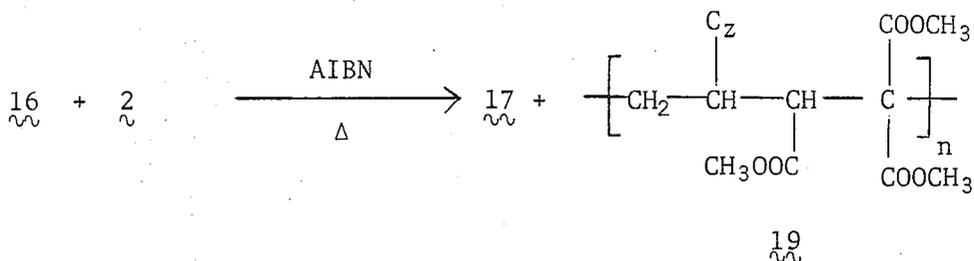
Cationic Inhibitor Effect. Triethylamine stopped the formation of 18 and diminished the yield of 17 (Table 5).

Solvents Effects. The yield of cyclobutane adduct 17 was higher in polar solvents. Homopolymer 18, generally a minor product, was favored in 1,2-dichloroethane and suppressed in basic solvent DMSO.

Trapping Attempt. A variety of potential trapping polar reagents were used as solvents. These included acetonitrile, propionaldehyde, and benzaldehyde, which have been used by Schug and Huisgen (1975) to trap a 1,4-zwitterion, and phenyl isocyanate. No heterocyclic adduct small molecules were obtained. The aldehydes and phenyl isocyanate allowed the formation of polymer of undetermined structures (Table 5). The cyclobutane 17 was not formed only in the case of phenyl isocyanate.

Photochemical and One-Electron Reactions of 16. Irradiating 16 in the presence of 1,4-dicyanobenzene or 4,4'-dimethoxylbenzophenone in solution failed to give cyclobutane dimer of 16 by analogy to the work done by Yamamoto et al. (1975)-with p-methoxystyrene and Bell, Crellin, and Ledwith (1969) with N-ethyl-3-vinylcarbazole. The reaction yielded only homopolymer of 16 which was inhibited by triethylamine (Table 6). N-Ethyl-3-vinylcarbazole 16 with trimethyl ethylenetricarboxylate 2 in acetonitrile and in the presence of 1,4-dicyanobenzene was irradiated by ultraviolet light to yield the homopolymer 18 and cyclobutane 17.

Finally, 16 alone with trimethyl ethylenetricarboxylate and in the presence of ferric perchlorate without light at 28° C yielded only polymer and oligomer of 16.

Dimethyl Cyanofumarate

The more reactive olefin, dimethyl cyanofumarate 10 was allowed to react with 16 (Table 7). In solution the reagents formed an orange-red solution which became colorless overnight. The reaction was complete and formed homopolymer 18 and cyclobutane 20:

20
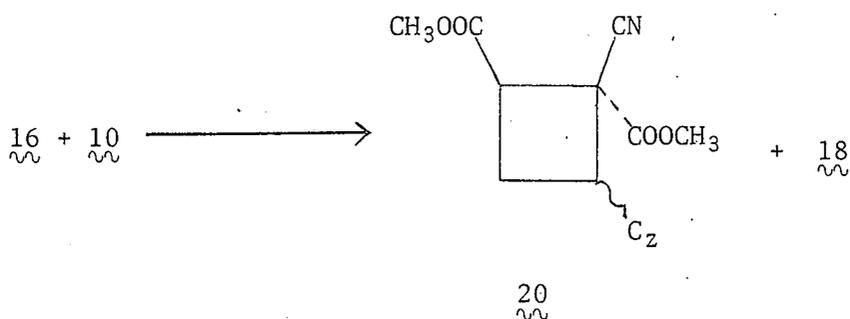
Table 6. Photochemical reaction of N-ethyl-3-vinylcarbazole.[a]

Solvent	Additives	Time in Hours	Homopolymer 18
Acetonitrile	1,4-dicyano-benzene 10 mg	69	56%
Acetonitrile	---	68.5	66.1%
Acetonitrile	1,4-dicyano-benzene 10 mg and triethylamine	6 days	0
Benzene	---	139	20.3%
Benzene	4,4'-dimethoxy-benzophenone	144	19.4%

[a]4,4'-Dimethoxybenzophenone (0.5g). Concentration in acetonitrile 0.5 mole/ℓ, and in benzene 0.33 mole/ℓ.

Table 7. Reactions of N-ethyl-3-vinylcarbazole with dimethyl cyanofumarate.[a]

Solvent	Time in Hours	Homopolymer[c] 18	Cyclobutane 20	Ratio Trans/cis of 20
Aceto-nitrile	16.5	8.1%	91.8%	2.9
1,2-Di-chloro ethane[b]	45.5	60.1%	39%	1.8

[a]As in Experimental; concentration in acetonitrile 0.25 mole/ℓ.

[b]Non-degassed reaction, concentration 0.35 mole/ℓ.

[c]Homopolymer 18 showed a carbonyl absorption in the ir.

The homopolymer showed a carbonyl absorption in the ir spectrum, and was favored in 1,2-dichloroethane (Table 7). The cyclobutane adduct was a mixture of only two isomers, the 1,2 trans and cis (the carbomethoxy at the third position was always cis to the cyano group).

The trans was always the major product, and isolated as crystal (mp 144.5 - 145.5° C); the cis isomer was isolated as an oil. The cis showed shielded carbomethoxy at δ 3.2 in the nmr spectrum.

Tetramethyl Ethylenetetracarboxylate

The more sterically hindered olefin tetramethyl ethylenetetra-carboxylate was less reactive. It did not react at 28° C or even at 85° C, but it reacted at 130° C with 16 for 21.5 hours to give cyclobutane adduct 21 in 64.8% yield:

16 + 14 ⟶

CH₃O₂C, CO₂CH₃, CH₃O₂C, CO₂CH₃, C_z

21
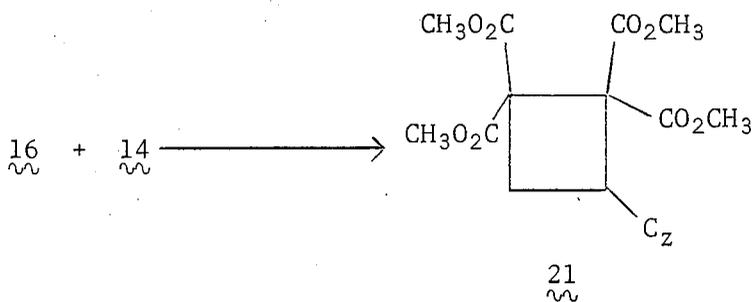
Cyclobutane adduct 21 was isolated as crystals, mp 68 - 70° C. Infrared, nmr and elemental analysis were consistent with the structure. The nmr spectrum showed a shielded carbomethoxy at δ 3.15.

Reaction of Dimethylvinylamine with
Trimethyl Ethylenetricarboxylate

Previously Glogowski (1976) reacted dimethylvinylamine with trimethyl ethylenetricarboxylate in a 1:1 ratio at low temperature (-78° C). Then he added alkylating agents, to get in general a mono-salt or disalt of a cyclohexane composed of 2 molecules of dimethylvinylamine and 1 molecule of trimethyl ethylenetricarboxylate:

$$X^- = CF_3SO_3^-$$
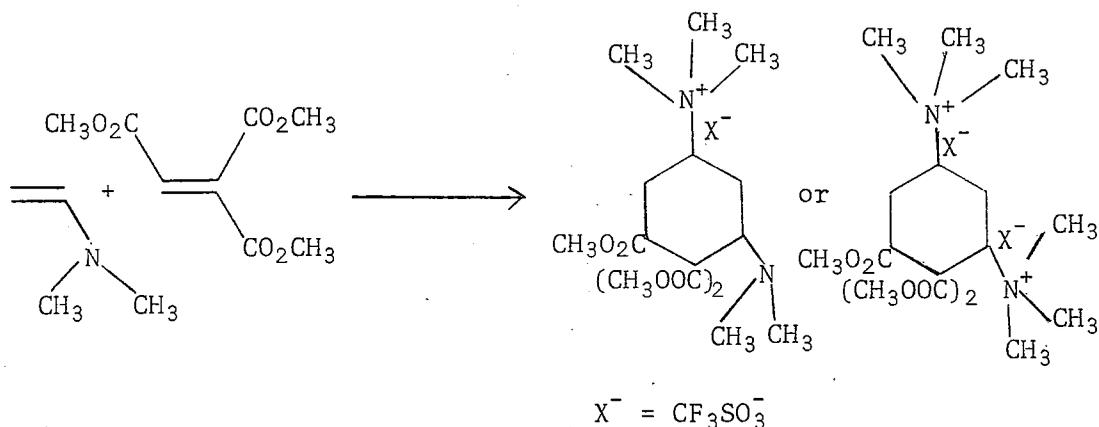
In the present work we reacted trimethyl ethylenetricarboxylate and dimethylvinylamine in a 1:2 ratio, respectively. After 48 hours of reaction at -50° C, trans 1-butene 23 was isolated as crystals from pentane-ether. The nmr showed a doublet for the proton α to the amino group at δ 6.1 with a coupling constant of 14 Hz. The other product showed multiplets at δ 2.3 and 3.8.
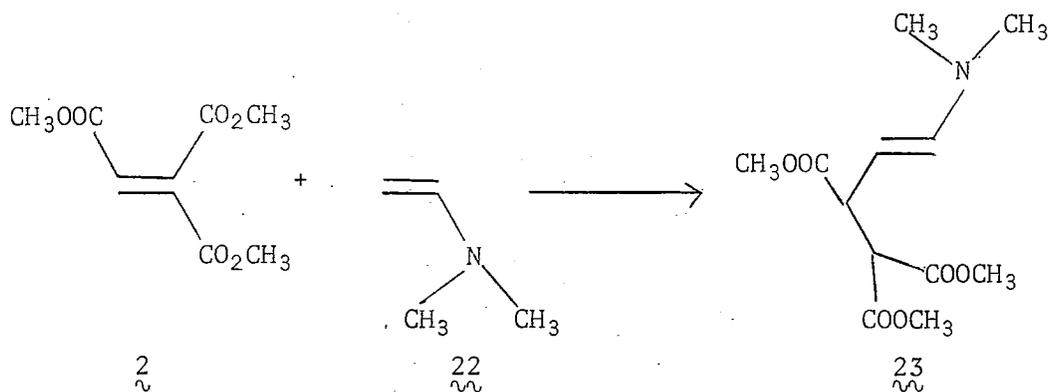
When the 1-butene was left at room temperature and observed by nmr, the olefin absorption at 6.1 disappeared, and a singlet appeared at δ 9.9. When the mixture was treated with ether we isolated a soluble part which showed a singlet at δ 9.9 and no dimethylamine absorption, and an insoluble part which showed just the dimethylamine absorption.

Solvent and Temperature Effect. The yield of 1-butene was higher at -50° than 0° C (Table 8). It was higher in toluene than in THF.

Discussion

Biradical Character of Tetramethylene Intermediates

When p-methoxystyrene 1 and trimethyl ethylenetricarboxylate react at 70 - 116° C, small molecules 3 and 4 and alternating copolymer 5 are formed. Dihydropyran 3, formed at 75° C, is the kinetically controlled product. It isomerizes to the more thermodynamically stable 1-butene at 115° C and even at room temperature (at atmospheric pressure). Heating 3 under vacuum regenerates 1 and 2. These results can be

Table 8. Reaction of trimethyl ethylenetricarboxylate with dimethyl-
vinylamine.[a]

Solvent	Temperature	1-butene 23	Others
1,2 dichloro-ethane	0°	24.7%	1.148 g
THF	-50° C	39.7%	1.11 g
Toluene	-50° C	51.9%	0.764 g

[a]Reaction time 48 hours. Ratio DMVA/Triester (2:1).

accommodated by considering the conformational isomers of a tetra-methylene intermediate 24 (Scheme 1). Following Chmurny and Cram (1973), cis face-to-face 24 a stabilized by overlap of the p orbitals, may form first. This can undergo facile rotation of 90° around the C_3-C_4 bond, giving cis edge-to-face 24 b which can reversibly collapse to 3. Rotation of 180° around the C_2-C_3 bond gives trans-24 c and leads to 1-butene 4 by an internal abstraction of hydrogen. The internal abstraction is supported by the use of radical chain inhibitors.

Biradical character is indicated by the spontaneous formation of alternating copolymer identical with that formed by deliberate free-radical induced copolymerization of 1 and 2. The copolymer is formed either from the forward reaction of 1 and 2 or in the cycloreversion of 3. Biradical character for 24 is further supported by the comparable yields of 3 and 4 obtained in polar solvent with those in benzene. Trapping experiments did not succeed, indicating that 24 is highly reactive and too short-lived to trap. Moreover, the trapping agents used were probably more suitable for zwitterionic than biradical intermediates, and reacted preferentially with p-methoxystyrene 1 or trimethyl ethylenetricarboxylate 2.

Formation of dihydropyran 3 and 12 by internal O-alkylation of an ester is very unusual. Presumably the avoidance of cyclobutane ring strain in the [2 + 2] cycloadducts is involved.

Dimethyl cyanofumarate 10 reacts similarly with p-methoxystyrene. The biradical nature of tetramethylene intermediate 25 is strongly

Scheme 1

trans (staggered)

rotate around
C_2-C_3 bond

cis, face-to-face (eclipsed)

rotate around
C_3-C_4 bond

cis, edge-to-face (gauche)
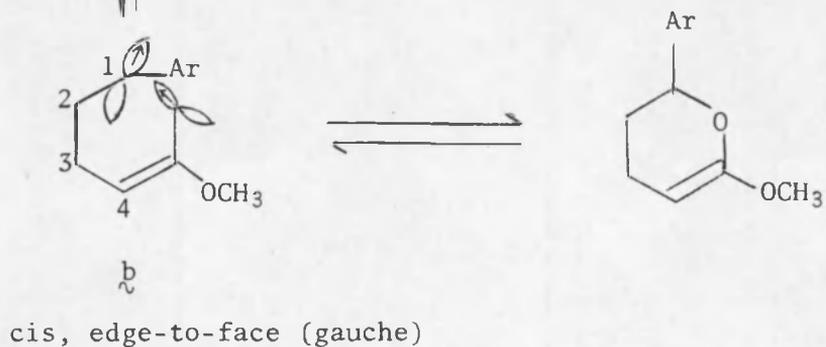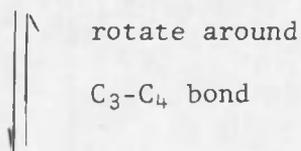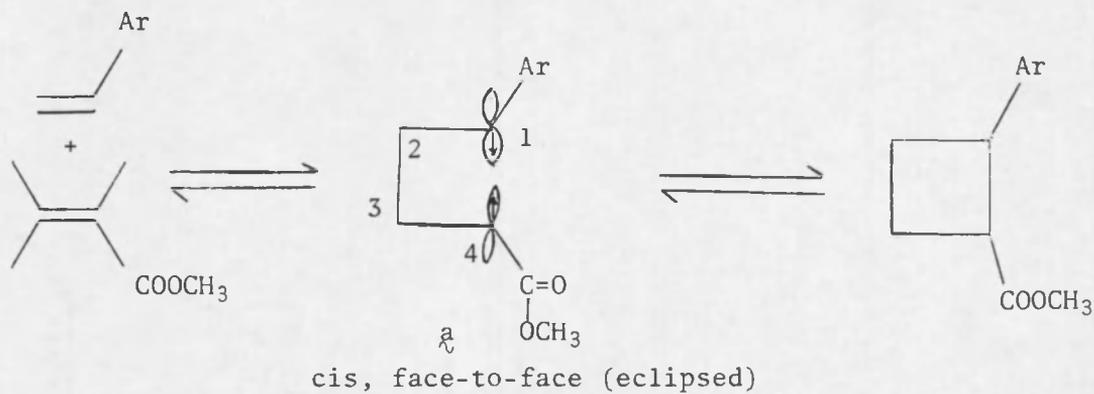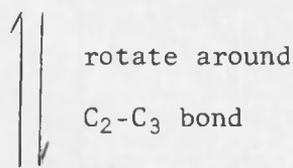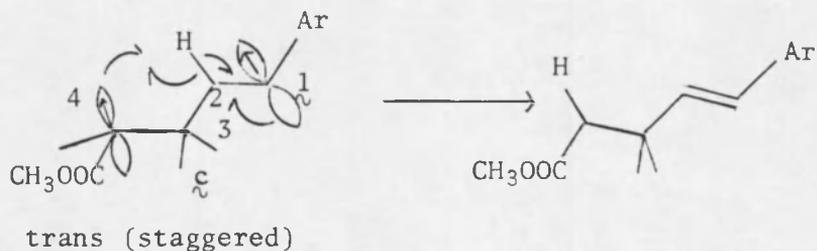
24 a-c   Tetramethylene from 1 and 2
25 a-c   Tetramethylene from 1 and 10
26 a-c   Tetramethylene from 1 and 14   Ar = p-methoxyphenyl

demonstrated by esr and by the spontaneous formation of copolymer $\underset{\sim}{11}$ at 25° C, where no adventitious thermal initiation is possible. Maleic anhydride and dimethyl maleate failed to trap the tetramethylene, but spin trapping was successful.

Dihydropyran $\underset{\sim}{12}$ formation is kinetically favored and no cyclo-butane forms. The 1-butene does not form in this case, due to the higher rate of 180° rotation around C_2-C_3 compared to the back formation of starting materials $\underset{\sim}{1}$ and $\underset{\sim}{10}$. Here, tetramethyl ethylenetetracarboxy-late did not copolymerize with p-methoxystyrene even when free radical initiator was deliberately added, so that in this case we could not test for the biradical nature of tetramethylene $\underset{\sim}{26}$ by copolymer formation.

Here cis face-to-face $\underset{\sim}{26}$ does collapse to cyclobutane adduct be-cause of the additional carbomethoxy substituent. Rotation around the C_3-C_4 bond may be impeded, or $\underset{\sim}{26}a$ may be favored by a conformational "gem-dimethyl effect." Moreover, a 1,3-diaxial carbomethoxy-aryl inter-action in a putative dihydropyran may intervene. Rotation around C_2-C_3 is also difficult, as evidenced by failure to form 1-butene.

Inasmuch as the stabilizing groups in tetramethylene $\underset{\sim}{26}$ are identical to those in $\underset{\sim}{24}$, trapping experiments failed as before.

The contrast between the results with trimethyl ethylenetri-carboxylate $\underset{\sim}{2}$ and tetramethyl ethylenetetracarboxylate $\underset{\sim}{14}$ shows that the groups at positions 1 and 4 of the tetramethylene do not alone deter-mine its behavior. This can also be seen by contrast with Cram's tri-methylene (b) which, although having similar terminal groups to trimethylene $\underset{\sim}{25}$, behaved as zwitterion.

Evidence Against Dihydropyran Formation
by Concerted Cycloaddition

Dihydropyran 3 and 12 might form through a hetero-Diels-Alder
[4 + 2] cycloaddition. Following the principle of microscopic reversi-
bility, the retro-Diels-Alder mechanism should occur to form 1 and 2
only. But the opening of 3 in CD_3CN and methanol in the presence of
DPPH yielded mostly 1-butene 4, and the opening of 12 yielded the co-
polymer 11. These results (as well as the spontaneous copolymerization
seen in both forward and reverse reactions and the esr absorption) are
against a Diels-Alder mechanism.
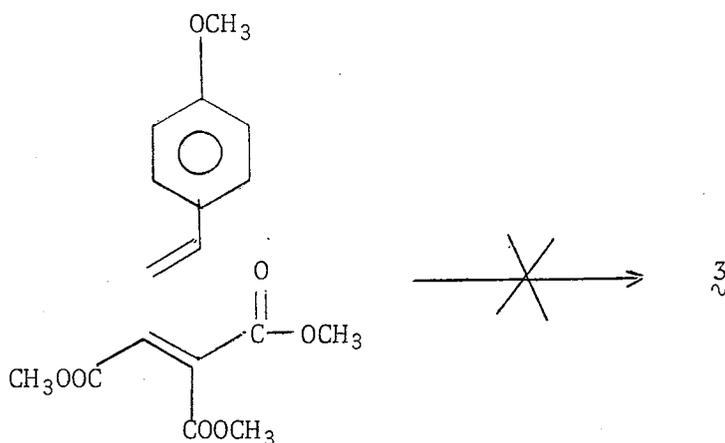
Zwitterionic Character of Tetramethylene
Intermediates

We have stressed the biradical character of tetramethylenes.
However, as stated in the introduction, the tetramethylene must be re-
garded as resonance hybrids of zwitterion and spin-paired biradical
following Salem and Rowland's theory. The concept resonance hybrid is
explained by Huisgen and others (1977) by a weak overlap between the

orbitals at positions 1 and 4 of the tetramethylene, since the two centers are close enough in the cis face-to-face intermediate, and a π type overlap between the terminal p orbitals and the sp^3 hybrid orbitals at C2 and C3 carbons "through-bond coupling" is possible even in the trans intermediates.

The zwitterionic character for tetramethylene 26 was demonstrated by the cationic homopolymerization of p-methoxystyrene. 1,2-Dichloro-ethane promoted homopolymerization, as is often observed, and mentioned by Kennedy (1975). Because radical copolymerization does not occur be-tween p-methoxystyrene 1 and tetramethyl ethylenetetracarboxylate 14, homopolymerization and zwitterionic character can be detected.

In the reactions of N-ethyl-3-vinylcarbazole 16 with trimethyl ethylenetricarboxylate only cyclobutane adduct 17 and homopolymer 18 are formed. Since [2 + 2] cycloaddition is forbidden by a concerted mechanism, the formation of 17 presumably involves a tetramethylene intermediate 27 (Scheme 2). Following Chmurny and Cram (1973) again, a cis face-to-face adduct 27 forms first. The zwitterionic character of the tetramethylene is indicated by solvent effect (cyclobutane 17 is favored in polar solvents), and is supported by the cationic homopoly-merization of N-ethyl-3-vinylcarbazole.

Even the free radical copolymerication gave mostly the alterna-ting copolymer of 16 and 2 accompanied by small amounts of cyclobutane 17.

Scheme 2
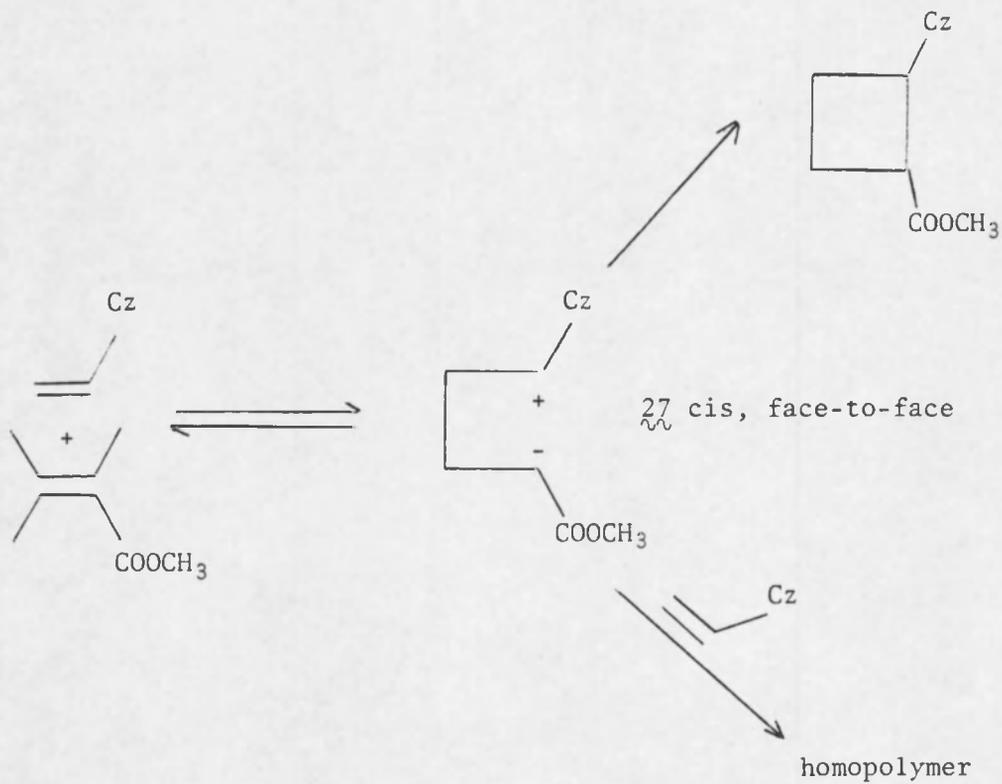
Cz = N-Ethyl-3-Carbazyl

Dimethyl cyanofumarate 10 reacts similarly with N-ethyl-3-vinylcarbazole. The zwitterionic nature of intermediate 27 is strongly demonstrated by the cationic polymerization of 16 being more important in 1,2-dichloroethane than in acetonitrile. A further support is the formation of only two isomers of cyclobutane 20, the 1,3-trans and cis (the ester group being always trans): no dihydropyran or 1-butenes were noted. This can be explained by strong coulombic interaction which inhibits any rotations. And finally the sterically hindered tetramethyl ethylenetetracarboxylate reacts similarly with N-ethyl-3-vinylcarbazole without any polymer formation.

Dimethylvinylamine, with lower potential of ionization than N-ethyl-3-vinylcarbazole, has been reacted with trimethyl ethylenetricarboxylate to expect cation-radical anion-radical pair. But the mechanism goes through a tetramethylene, supported by 1-butene formation, with a zwitterionic character due to nitrogen, which can stabilize the positive charge (Scheme 3). This stabilization will diminish the coulombic attraction, permitting rotations around the C_2-C_3 bond to form a trans tetramethylene which abstracts a hydrogen to form the 1-butene.

Evidence Against Cation-Radical
Intermediates

Ferric perchlorate and 1,4-dicyanobenzene have been used by Ledwith (1972) and Yamamoto et al. (1975) to form cation-radicals from donor olefins thermally and photochemically, respectively. Deliberately generated p-methoxystyrene cation-radical and N-ethyl-3-vinylcarbazole

Scheme 3

COOCH$_3$

CH$_3$

CH$_3$

N

CH$_3$

CH$_3$

N$^+$

CH$_3$

CH$_3$

2   1

3   4

COOCH$_3$

COOCH$_3$

cis face-to-face

rotation around
C$_2$-C$_3$

CH$_3$ CH$_3$

N$^+$

H

CH$_3$OOC

CH$_3$ CH$_3$

N

H

CO$_2$CH$_3$
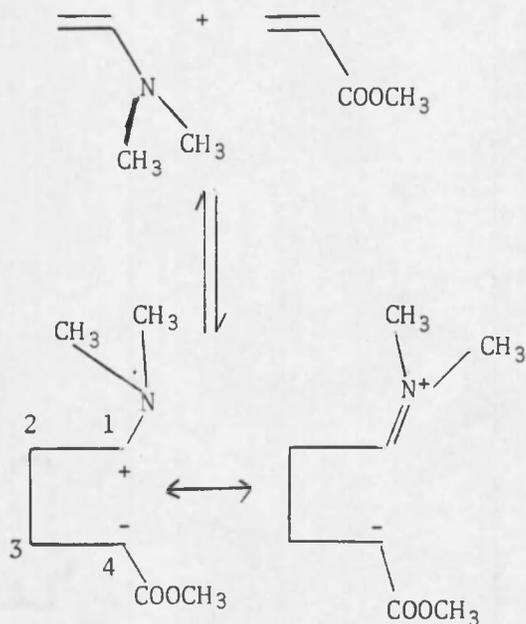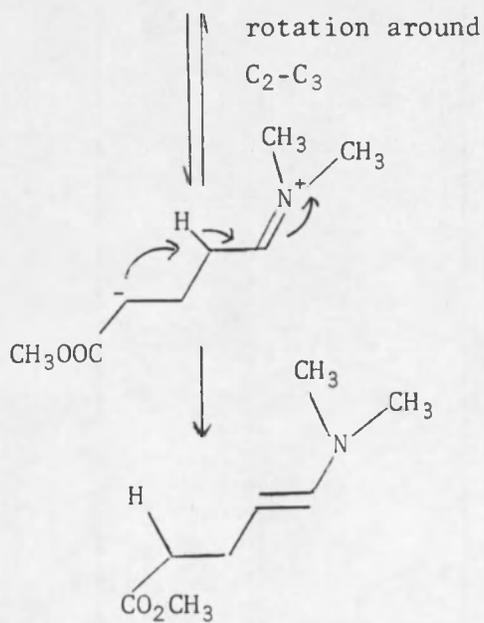
cation-radical reacted perferentially with the parent donor olefin to form the corresponding cyclodimer and homopolymer, respectively, even in the presence of trisubstituted olefin. Only when the known triplet transfer agent 4,4'-dimethoxybenzophenone in the presence of DPPH was added could a low yield of cyclobutane 9 be isolated, clearly by a different mechanism:

$$\text{sensitizer} \xrightarrow{h\nu} \text{sens}^{*3} \xrightarrow{1} 1^{*3}$$

cyclobutane adduct ← ← copolymer ← triplet biradical
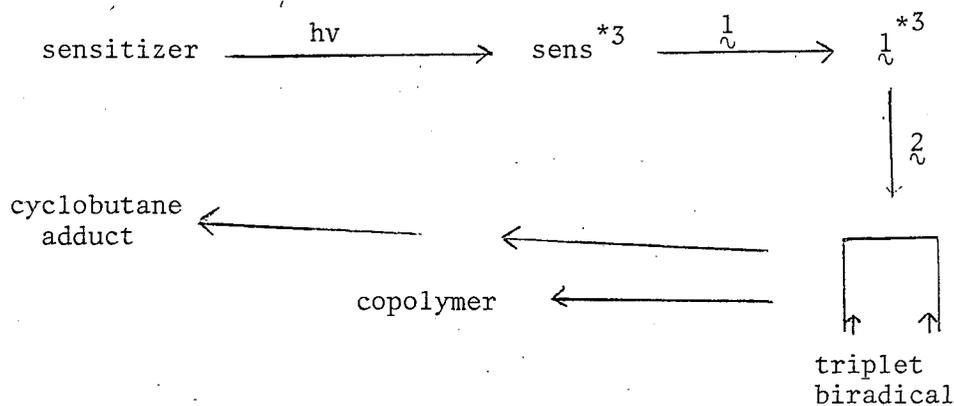
A second criterion also speaks against electron-transfer and ion-radical involvement. Because of the known larger electron affinity of a cyano group versus a carbomethoxy group, according to Salem and Rowland (1972), the rate sequence in that case should be:

dimethyl cyanofumarate ⟩ tetraester ⟩ triester.

However, this is not observed. Tetraester 14 was less reactive than triester 2. This is attributed to greater steric hindrance at the β-position of 14. This is incidental evidence for bond formation and a tetramethylene intermediate, inasmuch as 14 would be more reactive than 2 if single electron transfer were occurring.

Conclusion

Thermal reactions of electron-rich olefins with electron-poor olefins go through tetramethylene intermediates. These intermediates can have extreme biradical character, or be purely zwitterionic, or be anywhere in between. The biradical will not show any strong coulombic attractions, permitting free rotations under certain conditions. The zwitterions are of two kinds. The one with strong coulombic attractions has a short life-time and cannot be trapped, e.g., the one formed from tetracyanoethylene and p-methoxystyrene by Huisgen and the one formed by p-dimethylaminostyrene and triester by Hall et al. (1980):
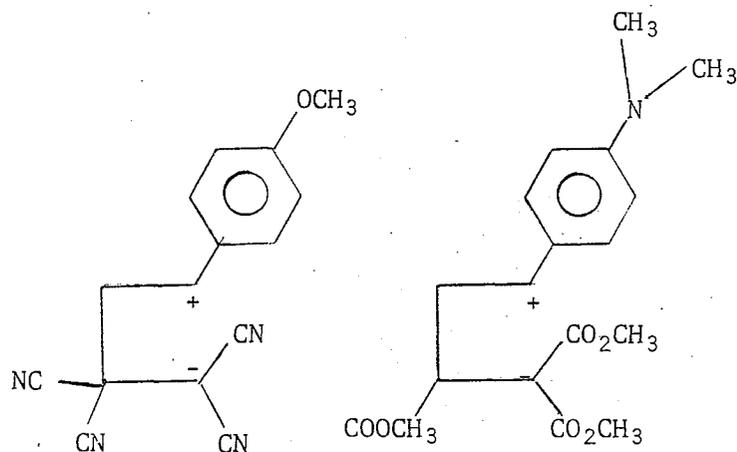
In contrast highly stabilized zwitterions with long life-time occur and can be trapped. These contain a heteroatom (O,N,S) which stabilizes the positive charge, and where rotations are possible, their negative charge may be stabilized by cyano groups, too.

CHAPTER 3

EXPERIMENTAL

Instrumentation

Melting points were obtained from a Thomas-Hoover capillary melting point apparatus and were uncorrected. ^{1}H nmr spectra were taken with Varian T-60 and EM360L nuclear magnetic resonance spectrometers at 60 MHz using TMS as an internal reference. Infrared spectra were recorded on Perkin-Elmer 710A and 398 spectrometers standardized with polystyrene. Photochemical reactions were run in a Rayonet reactor at 40° C. Analyses were performed at the University of Arizona Analytical Center, Tucson.

Solvents

Solvents were dried and distilled before use. Acetonitrile, benzene, 1,2-dichloroethane, dichloromethane and toluene were refluxed with CaH_2, fractionally distilled from it and stored under nitrogen atmosphere and over molecular sieves. All other solvents were dried and stored over molecular sieves.

Chemicals

All chemicals were from Aldrich Chemical Co., Inc., and used without any further purification, unless mentioned.

Reactants

p-Methoxystyrene was distilled from calcium hydride and stored under nitrogen at -15°. Tetramethyl ethylenetetracarboxylate was synthesized and purified by J. Ried following Hall and Daly's procedure (1975).

Trimethyl ethylenetricarboxylate, dimethyl cyanofumarate, N-ethyl-3-vinylcarbazole, and dimethylvinylamine have been synthesized (with some modifications) according to Hall and Daly (1975) for the first and second monomers, Limburg and Williams (1973) for the third, and Chang and Dittmer (1969) for the last one.

Synthesis of Trimethyl Ethylenetricarboxylate

Trimethyl Ethane-1,1,2-tricarboxylate. Absolute methanol (1.25ℓ) was placed in a 3-1, three-necked round bottom flask equipped with a mechanical stirrer. The reaction vessel was placed in an ice-bath. After reacting sodium (28.8 g; 1.25 moles) in small pieces with cold methanol dimethyl malonate (330 g; 2.5 moles) was added with stirring. Through an additional funnel methyl chloroacetate (136 g; 1.25 mole) was added dropwise with stirring for 1.5 hours. The three previous steps were protected with a current of nitrogen and the reaction vessel was kept in an ice-bath. After stirring the mixture overnight the solvent was rotaevaporated, and 400 ml of distilled water was added to dissolve NaCl. The organic phase was extracted with 3 200 ml-portions of ether, and dried with K_2CO_3. After filtration and rotaevaporation, the oil left was distilled using a spinning band column. Trimethyl

ethane-1,1,2-tricarboxylate came over at 100-110° C at 1.5mm of pressure

in 65.6% yield (162g).

Trimethyl 1-bromoethane-1,1,2-tricarboxylate. In a 2ℓ three-

necked round bottom flask, equipped with a mechanical stirrer and a re-

flux condenser was placed trimethyl ethane-1,1,2-tricarboxylate (162 g;

0.81 mole) and 750 ml of carbon tetrachloride. The reaction vessel was

irradiated by UV light, and through an additional funnel bromine (141 g;

0.88 mole) was added dropwise with stirring. Irradiation and stirring

were continued overnight, and the solvent was rotaevaporated to leave

crude bromide (238.34 g; 0.84 mole).

Trimethyl ethylenetricarboxylate (2). The crude bromide (238.34

g; 0.84 mole) was dissolved in 750 ml of ether and cooled in ice-bath.

To the solution was added dropwise through an additional funnel 84.8 g

(0.84 mole) of triethylamine with stirring. The stirring was continued

for 2 hours and the solvent was rotaevaporated to leave an oil. Tri-

methyl ethylenetricarboxylate distilled over at 105° C and 0.7 mm of

pressure crystallized in the receiver at room temperature and was re-

crystallized from ether to yield 86.40 g (50.9%) of trimethyl ethylene-

tricarboxylate (2) mp 39-40° C, nmr (CDCl$_3$) δ: 3.85, 3.9, 3.95

(3s, 9H, CO$_2$CH$_3$), and 6.9 (1s, 1H).

Synthesis of Dimethyl Cyanofumarate

Dimethyl cyanosuccinate. A 3ℓ three-necked round bottom flask

equipped with a mechanical stirrer was filled with 1.8ℓ of anhydrous

methanol and placed in an ice-bath. Sodium (46 g; 2 moles) was added

slowly to the cold methanol. To the cold solution of sodium methoxide, was added 198 g (2 moles) of methyl cyanoacetate to give a pale yellow solution. A solution of methyl chloroacetate (162 g; 1.5 moles) in 200 ml of methanol was added dropwise over a period of 3 hours with stirring. All the previous steps had been protected with a current of nitrogen. Stirring was continued overnight to give a yellow solution with a white precipitate. The solvent was rotaevaporated to leave a residue which was poured onto 1 kg of ice and water and acidified to litmus with con-centrated hydrochloric acid to give a pink mixture. The organic phase was extracted with 4 125 ml-fractions of dichloromethane, dried over $MgSO_4$, filtered and decolorized with activated charcoal. The dichloro-methane was rotaevaporated and the mixture was distilled. Dimethyl succinate (85.74 g) came out in 33% yield at 95° C at 0.35 mm of pressure.

Dimethyl 1-cyano-1-bromosuccinate. In a 2ℓ two-necked round bottom flask was placed dimethyl cyanosuccinate (122.84 g; 0.72 mole), acetic acid (43.08 g; 0.72 mole) and 300 ml of water. The reaction vessel was placed in an ice-bath. Through an additional funnel 251 ml of 2.86 M sodium hypobromite (0.72 mole) was added dropwise with stirring over 30 minutes. The stirring was continued for 2.5 hours to get a yellow solution which turned red when adding concentrated hydrochloric acid. The organic phase was extracted with 4 100 ml-portions of ether, dried over $MgSO_4$ and filtered. Charcoal was added to the filtrate, and the mixture was stirred for 30 minutes. Charcoal was filtered off and the solvent was rotaevaporated to yield the crude bromide (170.2 g; 95%).

Dimethyl cyanofumarate. In a 2ℓ two-necked round bottom flask, the crude bromide (155 g; 0.62 mole) was dissolved in 300 ml of anhydrous ether. The reaction vessel was kept in an ice-bath, and a solution of triethylamine (62.74 g; 0.62 mole) in 50 ml of anhydrous ether chilled with Dry-Ice acetone bath was added dropwise through an additional funnel for 1 hour with stirring. The stirring was continued for another hour at 0°, and hydrochloric acid (gas) in ether was added. The salt was filtrated off and washed with ether and the precipitate discarded. Charcoal was added and the solution was stirred for 1 hour. The charcoal was filtrated off and 2 drops of HCl were added to the solution, which was placed at -15° C. After crystallization and recrystallization from ether, dimethyl cyanofumarate (35.37 g; 33.8%) mp 59-60° C was obtained pure nmr (CDCl$_3$) δ: 3.9 and 3.92 (2s, 6H, CO$_2$CH$_3$), and 7.4 (s,1H).

Synthesis of N-Ethyl-3-vinylcarbazole

Triphenylmethylphosphonium iodide. Triphenylphosphine (50 g; 0.19 mole) was dissolved in 200 ml of benzene. To the solution was added (27 g; 0.19 mole) of iodomethane in 100 ml of benzene with stirring. The stirring was continued for 19 hours at room temperature. The salt was filtered and washed with benzene to yield 73.19 g (94.9%) of triphenyl-methylphosphonium iodide.

N-Ethyl-3-vinylcarbazole. In a 1ℓ three-necked round bottom flask equipped with a reflux condenser triphenylmethylphosphonium iodide (40.4 g; 0.1 mole) was dissolved in 400 ml of anhydrous tetrahydrofuran and protected with a current of nitrogen. Through an addition funnel

was added 46 ml of 2.4 M solution of butyllithium in hexane (0.1 mole)
with stirring over a period of 20 minutes. The reaction mixture was
allowed to react for 2 hours and finally a solution of N-ethylcarbazole-
3-carboxaldehyde (22.33 g; 0.1 mole) in 200 ml of THF was added dropwise
over 10 minutes. The reaction mixture was heated to reflux for 2 hours
then cooled to room temperature and treated with 800 ml of hexane. The
precipitate was filtered, washed with 100 ml of hexane and discarded.
The filtrate was rotaevaporated to leave a crude oil, which was crystal-
lized from 200 ml of ethanol containing one drop of ammonium hydroxide
and recrystallized from 100 ml of ethanol to yield 10.6 g (48%) of
N-ethyl-3-vinylcarbazole (mp 66-67° C; nmr (CDCl$_3$) δ: 1.5 (t,3H,CH$_3$),
4.4 (q,2H,CH$_2$), 5.15-5.9 (dd,2H, C=C), 6.7-8.25 (m,8H).

Synthesis of Dimethylvinylamine

2-Dimethylaminoethyl chloride. 2-Dimethylaminoethyl chloride
hydrochloride (70 g; 0.486 mole) was dissolved in 50 ml of distilled
water in a 500 ml Erlenmeyer flask. In a second flask 40.9 g (0.725
mole) of KOH was dissolved in 25 ml of distilled water. The two solutions
were cooled in an ice-bath, then mixed. An oil formed rapidly, and was
extracted with 3 100 ml-portions of anhydrous ethyl ether. The etherate
solution was dried over MgSO$_4$ for 15 minutes. The solution was filtrated
and the solvent rotaevaporated to yield 38.69 g (70%) of the crude free
amine.

Dimethylvinylamine. In a 2ℓ two-necked round bottom flask
equipped with a magnetic bar, and distilling apparatus (lubricated with
Lubriseal), was placed 44.44 g (0.396 mole) of potassium t-butoxide and

500 ml of purified dimethylformamide. The reaction vessel was placed in

a methanol-ice-bath. The crude amine (38.69 g; 0.36 mole) was added

with stirring to the cold solution of butoxide with protection by a

current of argon and the reaction was left for 20 minutes. Then a

vacuum (2 mm) was applied to obtain 100 ml of a solution of t-butanol

and dimethylvinylamine in dimethylformamide in a receiver cooled by a

Dry-Ice-acetone bath. The 100 ml solution was placed in a methanol-ice-

bath and fractionally distilled using a Vigreux column, a condenser and

a receiver chilled by Dry-Ice-acetone. Dimethylvinylamine (10.08 g;

39.4%) was obtained pure at 25° and .35 mm of pressure (it was stored at

-50° and used within 24 hours). nmr (DMF) δ: 2.7 (s,6H,$N<^{CH_3}_{CH_3}$),

3.15-3.6 (m,2H, $\diagup\!\!=\!\!\diagdown^H_H$), and 5.9 (q,J=8, 14HZ, 1H, $\diagup\!\!=\!\!\diagdown^H_N$).

<div align="center">General Procedure</div>

The reactions were run in pressure tubes previously degassed or

under nitrogen or argon atmosphere. The tubes were placed at the desired

temperature which was maintained at ± 1° C by a temperature control

apparatus. The polymers were precipitated with anhydrous ether or

methanol, redissolved in 2 ml of acetone, reprecipitated by the same

solvent, filtered, washed and dried under vacuum. They were weighed and

compared to authentic samples or analyzed. The yield of copolymer was

calculated from the total weight of the acceptor and donor olefins. The

yield of homopolymer was calculated from the feed of the donor olefin.

Methanol or ether was rotaevaporated off the filtrate. The latter was

weighed and an nmr spectra was taken from which the yield of small

molecules was calculated.

Poly (p-methoxystyrene-alt-trimethyl
ethylenetricarboxylate) (5)

To a solution of 4 mmole (0.536 g) of p-methoxystyrene and 4
mmole (0.808 g) of triester 2 in 6 ml of benzene was added 10 mg of AIBN.
The mixture was placed in a pressure tube which was capped and degassed
with argon. The reaction mixture was heated to $72 \pm 1°$ C overnight.
The copolymer was precipitated in 50 ml of methanol, filtered, dissolved
in 3 ml of acetone and reprecipitated with 30 ml of methanol and finally
washed with 20 ml of methanol. The dried copolymer 5 (0.27 g; 20%) was
obtained as a white powder. ir (KBr): 2950 m, 1740 s, 1650 m cm^{-1}.
nmr (CDCl$_3$) δ: 2.2-3.8 (m, 16H), 6.35-7.2 (m, 4H).

Dimethyl 2-(p-methoxyphenyl)-6-methoxy-3,4-
dihydro-2H-pyran-4,5-dicarboxylate (3)

A solution containing 404 mg (2 mmole) of triester 2, 268 mg
(2 mmole) of p-methoxystyrene, and 10 mg of DPPH in 3 ml of 1,2-dichloro-
ethane under nitrogen was heated in an oil bath at 70° C for 20 hours.
The cooled solution was stirred overnight at 0.5 mm to remove solvent
and p-methoxystyrene. Ether (20 ml) was added and the solution cooled
to -76° C. After 24 hours, crystallization was complete. Ether super-
natant was removed with a pipette. The crystalline materials were
dissolved in chloroform and passed through a silica gel column to remove
polar impurities. The chloroform was rotaevaporated and the residue was
recrystallized from ether at -76° to give 0.123 g (18.3%) of dihydropyran
3:

mp   93-94° C

ir (KBr) showed: 2950 w(C-H), 1730 m (C=O), 1660 m (C=CO$_2$)

1610 s (C=C) cm^{-1}.

nmr (CDCl$_3$) δ: 2.2 (m, 2H, CH$_2$), 3.5 (q, 4, 10Hz, 1H, H-C-CO$_2$CH$_3$),

3.7, 3.75, 3.8 and 3.85 (4s, 12H, -O-CH$_3$), 5.2

(q, 4, 10Hz, 1H, H-C-O), and 6.8-7.4 (A$_2$B$_2$, 4H,

aromatic).

Anal. Calcd. for C$_{17}$H$_{20}$O$_7$: C, 60.7; H, 6.0.

Found: C, 60.7, H, 5.8.

Trimethyl 1-(p-methoxyphenyl)-1-butene-3,4,4-
tricarboxylate (4)

The reaction was carried out as above, but at 116° C. The mix-

ture was cooled and 1,2-dichloroethane was rotaevaporated. The mixture

was heated in a vacuum distillation apparatus to 120° (0.1 mm), whereupon

p-methoxystyrene and triester distilled. The residue was cooled,

dissolved in chloroform, passed through a silica gel column, and the

solvents were rotaevaporated. Crystallization in 20 ml of ether at -76° C

gave 0.14 g (20.8%) of 4 as a white powder:

mp   73-74° C.

ir (KBr): 2950 w (C-H), 1730 s (C=O), 1610 m (C=C) cm^{-1}.

nmr (CDCl$_3$) δ: 3.7, 3.8 and 3.85 (3s, 13H, OCH$_3$ and CH), 4.05

(m, 1H, CH-(CO$_2$CH$_3$)$_2$), 5.95 and 6.05 (dd, 2, 14Hz,

1H, H——C=Cβ to aromatic ring), 6.6 (d, 14Hz, 1H,

C=C—H α to aromatic ring), 6.8-7.4 (A$_2$B$_2$, 4H,

aromatic).

Anal. Calcd. for $C_{17}H_{20}O_7$:   C, 60.7; H, 6.0.

Found: C, 60.6; H, 6.2.

Trimethyl 1-(p-methoxyphenyl)-1-acetoxy-3,4,4-butanetricarboxylate (6)

    The reaction was carried out like the previous ones, at 75° C in acetic acid. The mixture was cooled at room temperature and the solvent and p-methoxystyrene were removed under vacuum at room temperature (0.1 mm). The acetate and triester were separated by chromatography. The mixture was dissolved in chloroform, eluted through a silica gel column by a mixture of 50/50 chloroform and pentane, and the solvents were rota-evaporated to give 0.243 g (30.5%) of the acetate 6 as an oil sensitive to heat. This oil on heating gave the 1-butene 4.

    ir (neat):   2925 w (C-H), 1730 s (C=O), 1660 w (C=O, α to aromatic ring), 1600 w (C=C) cm^{-1}.

    nmr (CDCl$_3$) δ: 2.0-2.5 (m, 2H, CH$_2$), 2.1 and 2.15 (2s, 3H, $\overset{\overset{\text{O}}{\|}}{C}$ - CH$_3$),

3.2 (m, 1H, H-C-CO$_2$Me), 3.75-3.9 (4s, 12H, OCH$_3$),

3.95 (d, 1H, H-C-(CO$_2$Me)$_2$), 5.8 (t, 1H, H-C-O-$\overset{\overset{\text{O}}{\|}}{C}$-CH$_3$),

6.8-7.42 (A$_2$B$_2$, aromatic).

Anal. Calcd. for $C_{19}H_{24}O_9$:   C, 57.6; H, 6.1.

Found: C, 57.1; H, 6.3.

The sample lost weight during the analysis at the rate of 6 ug/min. The acetate was heated to give 4 which gave a better analysis.

Trimethyl 1-(p-methoxyphenyl)-2,2,3-
cyclobutanetricarboxylate (9)

A solution containing 404 mg (2 mmoles) of triester 2, 268 mg
(2 mmoles) of p-methoxystyrene, 226 mg of 4,4'-dimethoxybenzophenone and
10 mg of DPPH in 4 ml of acetonitrile in a quartz tube was irradiated by
UV light at 40° C (in a UV reactor) for 6 days. The mixture was dripped
into 40 ml of methanol to yield a trace of precipitate which is the
homopolymer of p-methoxystyrene. The solvent was rotaevaporated, and
to the mixture is added 50 ml of pentane where the sensitizer was
slightly soluble. The solution was separated from the crystals of 4,4'-
dimethoxybenzophenone. To the solution was added 20 ml of dichloroethane
and the solution was left at -76° C to yield 0.019 g (3%) of cyclobutane
adduct mp, 133-134° C after two successive crystallizations.

ir (KBr): 2750 w (CH), 1730 s (C=O), 1600 w (C=C) cm^{-1}.

nmr (CDCl$_3$) δ: 2.5-3.1 (m, 2H, CH$_2$), 3.45 (q, 1H, CH), 3.25, 3.72,

3.76 and 3.88 (4s, 12H, OCH$_3$), 4.15 (q, 8, 10Hz, 1H,

CH α to phenyl group), 6.7-7.4 (A$_2$B$_2$, 4H, aromatic).

Anal. Calcd. for C$_{17}$H$_{20}$O$_7$: C, 60.7; H, 6.0.

Found: C, 60.7; H, 5.9.

Methyl 2-(p-methoxyphenyl)-6-methoxy-5-cyano-3,4-
dihydro-2H-pyran-4-carboxylate (12) and poly-(p-
methoxystyrene-alt.-dimethyl cyanofumarate) (11)

A solution containing 0.134 g (1 mmole) of 1, 0.169 g (1 mmole)
of 10 and 0.01 g of DPPH in 1.5 ml of CD$_3$CN in an nmr tube was left for
66.5 hours at room temperature. Nmr showed copolymer, dihydropyran and
starting material. After 118 hr the solution was dripped into methanol

to yield 0.085 g (28.1%) of copolymer which was separated by filtration. After rotaevaporation of the solvent, we added acetone-pentane (1:100) and the solution kept at -76° C to yield 0.102 g (33.7%) crystals of 12, which melted at room temperature and copolymerized when left at room temperature overnight. For dihydropyran 12:

ir (neat): 2950 w (CH), 2200 w (CN), 1730 m (C=O), 1660 m (C=CO$_2$), 1610 s (C=C) cm^{-1}.

nmr (CDCl$_3$) δ: 2.08-2.4 (m, 2H, CH$_2$), 3.08-4.4 (m, 10H, OMe and HC-CO$_2$Me), 5.1 (q, 1H, 4, 8Hz, CH), 6.8-7.5 (m, 4H, aromatic).

For copolymer 11:

ir (KBr): 2950 w (CH), 1730 s (C=O), 1660 m (C=C) cm^{-1}.

nmr (CDCl$_3$) δ: 2.45-2.7 (m, 3H), 2.85-3.6 (m, 1H, H-C-CO$_2$CH$_3$), 3.6-3.9 (m, 6H, OCH$_3$), and 6.45-7.10 (m, 4H, aromatic).

Dimethyl 1-(p-methoxyphenyl)-1-methoxy-4-cyano-3,4-butanedicarboxylate (13)

Dimethyl cyanofumarate (0.169 g; 1 mmole) was dissolved in 2 ml of 1,2-dichloroethane, to which was added (0.5 g; 5 mmole) of maleic anyhdride. Separately p-methoxystyrene (0.134 g; 1 mmole) was dissolved in 2 ml of 1,2-dichloroethane. The two solutions were mixed and allowed to react at room temperature (28° C) for 119 hours. The reaction was quenched with 50 ml of methanol; no precipitation occurred. The solution was left at 28° C for a few days; then the solvent was rotaevaporated.

By high pressure chromatography on a silica gel column with pentane/

chloroform (50/50) 0.174 g (51.9%) of $\underset{\sim\sim}{13}$ was isolated as an oil from

this mixture.

ir (neat): 2950 m (C-H), 1730 s $(\overset{\overset{\text{O}}{\|}}{\text{C}})$, 1610 m (C=C).

nmr (CDCl$_3$) δ: 1.9-2.3 (m, 2H, CH$_2$), 3 and 3.1 (s, 3H, O-CH$_3$ α to

phenyl), 3.25-3.5 (m, 1H), 3.6-3.9 (s, 9H, O-CH$_3$),

4-4.25 (m, 2H), 6.7-7.25 (A$_2$B$_2$, 4H, aromatic).

Anal. Calcd. for C$_{17}$H$_{21}$O$_6$N: C, 60.9; H, 6.3; N, 4.2.

Found: C, 61.0; H, 6.3; N, 3.9.

Tetramethyl 1-(p-methoxyphenyl)-2,2,3,3-cyclobutane-
tetracarboxylate $(\underset{\sim\sim}{15})$

A mixture of 268 mg (2 mmoles) of p-methoxystyrene and 520 mg

(2 mmoles) of tetraester $\underset{\sim\sim}{14}$ were placed in a pressure tube which was

capped and heated to 116° C for 65.5 hours. The mixture was dissolved

in 20 ml of ether to remove unreacted tetraester crystals and then the

unreacted p-methoxystyrene was removed under vacuum (0.1 mm) at room

temperature. The cyclobutane was crystallized twice from ether to yield

73 mg (9.3%) of white crystalline of $\underset{\sim\sim}{15}$, mp 136-137° C.

ir (KBr): 2950 m (C-H), 1740 s (C=O), 1610 m(C=C) cm^{-1}.

nmr (CDCl$_3$) δ: 2.35-2.7 (q, 8, 12Hz, 2H, CH$_2$), 3.3, 3.78 and 3.85

(3s, 15H, OCH$_3$), 4.4-4.75 (q, 8, 12Hz, 1H, CH),

6.75-7.4 (A$_2$B$_2$, 4H, aromatic).

Anal. Calcd. for C$_{19}$H$_{22}$O$_9$: C, 57.9; H, 5.6.

Found: C, 58.3; H, 5.8.

Trimethyl 1-(N-ethyl-3-carbazyl)-2,2,3-cyclobutanetricarboxylate (17)

N-Ethyl-3-vinylcarbazole (0.443 g; 2 mmoles) was dissolved in 2 ml of 1,2-dichloroethane; in another container 2 (0.404 g; 2 mmoles) was dissolved in 2 ml of the same solvent. The two solutions are mixed and placed in a Dry-Ice-acetone bath, then degassed and capped. The reaction mixture vessel was placed in an oil bath at 50° C. After 16 hours the reaction was quenched by 200 ml of MeOH to yield 0.021 g of homopolymer, and 0.33 g (38.93%) of cyclobutane adduct (oil, mixture of 1,3-cis and trans isomers) was precipitated at -76° C in hexane.

Anal. Calcd. for $C_{24}H_{25}O_6N$: C, 68.1; H, 6.0; N, 3.3.

Found: C, 67.8; H, 6.1; N, 2.9.

The separation of the two isomers was done by chromatography on a silica gel column, eluting with hexane.

ir $(CDCl_3)$: 2940 m (CH), 1730 s ($\overset{\text{O}}{\overset{\|}{\text{C}}}$), 1600 m (C=C) cm^{-1}.

nmr δ $(CDCl_3)$: trans isomer; 1.4 (t, 3H, CH_3), 2.87 (t, 10, 10 Hz, 2 H, CH_2), 3.1 and 3.77 (3 s, 9 H, OCH_3), 4.32 (q, 3 H, NCH_2 and $CH-CO_2CH_3$), 4.8 (t, 10, 10 Hz, 1 H, H-C-Ar), 7.2-8.2 (m, 7 H, aromatic).

Cis isomer: 1.5 (t, 3 H, CH_3), 2.65-3 (q, 8, 14 Hz, 2 H, CH_2), 3.23, 3.83, and 3.97 (3 s, 9 H, OCH_3), 3.33-3.8 (q, 8, 14 Hz, 2 H, CH-Ar and $CH-CO_2CH_3$), 7.2-8.2 (m, 7 H, aromatic).

Poly(N-ethyl-3-vinylcarbazole)(18)

In a quartz tube, a mixture of 0.433 g (2 mmoles) of N-ethyl-3-vinylcarbazole 16, and 0.01 g of 1,4-dicyanobenzene was dissolved in 4 ml of acetonitrile. The reaction vessel was irradiated by UV light in a reactor during 69 hours. A precipitate formed. The mixture was dripped into 90 ml of anhydrous ether was filtered to yield 0.248 g (56.0%) of homopolymer 18 (the filtrate contained only starting material).

ir (KBr): 2900 m (CH), 1600 m (C=C) cm^{-1}.

nmr (CDCl$_3$) δ: 0.3-2.6 (m, 6 H, CH$_3$, CH$_2$ and CH), 3.3-4.4 (m, 2 H, N-CH$_2$), 5.5-8.3 (m, 7 H, aromatic).

Anal. Calcd. for C$_{16}$H$_{15}$N: C, 86.8; H, 6.8; N, 6.3.

Found: C, 85.6; H, 6.8; N, 6.0.

Poly(N-ethyl-3-vinylcarbazole-alt.-trimethyl ethylenetricarbozylate)(19)

A mixture composed of 0.404 g (2 mmoles) of triester, 0.443 g (2 mmoles) of N-ethyl-3-vinylcarbazole and (0.01 g) of AIBN was dissolved in 4 ml of benzene, cooled in a Dry-Ice-acetone bath and degassed under full vacuum. The reaction vessel was placed in an oil bath at 72° C for 45 hours. The reaction was quenched with 100 ml of methanol, the precipitate was separated by filtration, washed and dried to yield 0.652 g (77.0%) of copolymer 19. The filtrate after work-up contained 0.12 g (15.1%) of cyclobutane adduct 17 and starting material.

ir (KBr): 2940 m (CH), 1720 s ($\overset{O}{\overset{\|}{C}}$), 1600 m (C=C) cm^{-1}.

nmr (CDCl$_3$) δ: 1-1.6 (m,3H,CH$_3$), 2-4.7 (m, 15H), 6.5-8.5 (m, 7H aromatic).

Anal. Calcd. for $C_{24}H_{25}O_6N$: C, 68.1; H, 6.0; N, 3.3.

Found: ·C, 68.4; H, 5.97; N, 3.52.

Dimethyl 1-(N-ethyl-3-carbazyl)-2-cyano-2,
3-cyclobutanedicarboxylate (20)

A mixture of 0.222 g (1 mmole) of 16 and 0.169 g (1 mmole) of
dimethyl cyanofumarate 10 in a tube was placed in Dry-Ice-acetone, and
degassed under full vacuum. The reaction vessel was left at room temp-
erature for 16.5 hours. The reaction mixture was dropped into 200 ml of
MeOH to yield 0.018 g (8.1%) of homopolymer 18 as a precipitate. The
solvent from the filtrate was rotaevaporated to yield 0.39 g (91.8%) of
cyclobutane adduct 20 as an oily mixture of only two isomers: 1,3-cis
and 1,3-trans.

Anal. of mixed trans and cis calcd. for $C_{23}H_{22}N_2O_4$: C, 70.8; H, 5.7;

N, 7.2.

Found: C, 70.9; H, 5.6; N, 7.1.

The cis isomer crystallized from hexane at room temperature, the solution
contained both the cis and trans isomer. The cis isomer, after recrystal-
lization from hexane, had mp 144.5-145.5° C. The pure trans isomer (oil)
was obtained by evaporating the solution left after precipitating out all
the cis isomer at -76° C.

ir of trans and cis (KBr): 2960 and 2945 m (CH), 2240 w (CN), 1740 ·s
(Ö), 1620 and 1590 s (C=C) cm^{-1}.

nmr of 1,2-trans (CDCl$_3$) δ: 1.4 (t, 3H, CH$_3$), 2.45-3.35 (2t, 10,
10 Hz, 2H, CH$_2$), 3.85 and 3.9 (2s, 6H,

OCH$_3$), 4.3 (q, 4H, CH$_2$-N, CH-Ar, and

CH-CO$_2$CH$_3$), 7.1-8.25 (m, 7H, aromatic).

1,3-cis: 1.4 (t, 3H, CH$_3$), 2.75-3.1 (m, 2H, CH$_2$), 3.2 and 3.8 (2s,

6H, OCH$_3$), 4.2-4.5 (q, 4H, CH$_2$-N, CH-COOCH$_3$, and CH-Ar),

7.2-8.25 (m, 7H, aromatic).

Tetramethyl 1-(N-ethyl-3-carbazyl)-2,2,3,3-
cyclobutanetetracarboxylate (21)

A solution of 222 mg (1 mmole) of 16 and 260 mg (1 mmole) of

tetraester 14 in 2 ml of 1,2-dichloroethane in a vacuum hydrolysis tube

was degassed under vacuum, then placed in an oil bath at 130° C for 21.5

hours. After rotaevaporation of the solvent, the mixture was dissolved

in 30 ml of MeOH, and placed at -76° C to crystallize the unreacted tetra-

ester which was separated. The methanol was rotaevaporated and the mix-

ture was dissolved in 40 ml of hexane and placed at -76° C to give a

precipitate, the cyclobutane adduct (oil), which under vacuum became

solid (0.312 g, 64.8%, mp 68-70°).

nmr (CDCl$_3$) δ: 1.42 (t, 3H, CH$_3$), 2.68 (m, 2H, CH$_2$), 3.15, 3.85 and

3.9 (3s, 12H, OCH$_3$), 4.35 (q, 2H, N-CH$_2$), 4.82 (q,

1H, 10, 12Hz, CH), 7.22-8.2 (m, 7H, aromatic).

ir (CDCl$_3$): 2925 w (CH), 1720 s ($\overset{\overset{\text{O}}{\|}}{\text{C}}$ - OCH$_3$), 1600 w (C=C) cm^{-1}.

Anal. Calcd. for C$_{26}$H$_{27}$O$_8$N: C, 64.85; H, 5.65; N, 2.91.

Found: C, 64.61; H, 5.82; N, 2.86.

Trimethyl 1-dimethylamino-1-butenetricarboxylate (23)

Trimethyl ethylenetricarboxylate (0.951 g; 4.7 mmol.) was reacted with dimethylvinylamine (0.67 g; 9.4 mmol.) in 8 ml of THF, at -50° C in a capped tube protected by argon. After 48 hours, the solvent was rota-evaporated, and the mixture was observed by nmr to reveal the trans-1-butene and another unstable product. The 1-butene 23 (0.511 g; 39.7%, unstable at room temperature) crystallized from a 1:1 mixture of pentane-ether.

ir (KBr): 2925 and 2850 m (CH), 1720 s ($\overset{O}{\overset{\|}{C}}$), 1640 (C=C) cm^{-1}.

nmr (CDCl$_3$) δ: 2.55 (s, 6H, N$\underset{CH_3}{\overset{CH_3}{<}}$), 3.7 (s, 11H, OCH$_3$, H-C-CO$_2CH_3$, and H-C-(CO$_2CH_3$)$_2$), 4 (1dd, 1H, $\underset{H}{\overset{}{}}$═), 6.1 (d, 1H, J=14 Hz, $\underset{N}{\overset{H}{}}$═).

Anal. Calcd. for C$_{12}$H$_{19}$O$_6$N: C, 52.74; H, 7.01; N, 5.13.

Found: C, 52.23; H, 7.08; N, 4.92.

APPENDIX A

NAMES OF COMPOUNDS

1. p-Methoxystyrene

2. Trimethyl ethylenetricarboxylate

3. Dimethyl 2-(p-methoxyphenyl)-6-methoxy-3,4-dihydro-2H-
   pyran-4,5-dicarboxylate

4. Trimethyl 1-(p-methoxyphenyl)-1-butene-3,4,4-tricarboxylate

5. Poly(p-methoxystyrene-alt.-trimethyl ethylenetricarboxylate)

6. Trimethyl 1-(p-methoxyphenyl)-1-acetoxy-3,4,4-butanetricarboxylate

7. Trans 1,2-(p-methoxyphenyl)cyclobutane

8. Poly(p-methoxystyrene)

9. Trimethyl 1-(p-methoxyphenyl)-2,2,3-cyclobutanetricarboxylate

10. Dimethyl cyanofumarate

11. Poly(p-methoxystyrene-alt.-dimethyl cyanofumarate)

12. Methyl 2-(p-methoxyphenyl)-6-methoxy-5-cyano-3,4-dihydro-2H-
    pyran-4-carboxylate

13. Dimethyl 1-(p-methoxyphenyl)-1-methoxy-4-cyano-3,4-butanedicarboxylate

14. Tetramethyl ethylenetetracarboxylate

15. Tetramethyl 1-(p-methoxyphenyl)-2,2,3,3-cyclobutanetetracarboxylate

16. N-Ethyl-3-vinylcarbazole

17. Trimethyl 1-(N-ethyl-3-carbazyl)-2,2,3-cyclobutanetricarboxylate

18. Poly(N-ethyl-3-vinylcarbazole)

19. Poly(N-ethyl-3-vinylcarbazole-alt.-trimethyl ethylenetricarboxylate)

20. Dimethyl 1-(N-ethyl-3-carbazyl)-2-cyano-2,3-cyclobutanedicarboxylate

21. Tetramethyl 1-(N-ethyl-3-carbazyl)-2,2,3,3-cyclobutanetetra-
    carboxylate

22. Dimethylvinylamine

23. Trimethyl 1-dimethylamino-1-butenetricarboxylate

REFERENCES

Bartlett, P. D. Science 1968, Vol. 159, 833.

Bartlett, P. D. Quart. Rev. Chem. Soc. 1970, 24, 473.

Bell, F. A.; Crellin, R. A.; Ledwith, A. Chem. Comm. 1969, 251.

Chang, P. L.; Dittmer, D. C. J. Org. Chem. 1969, 34, 2791.

Chmurny, A. B.; Cram, D. J. J. Amer. Chem. Soc. 1973, 95, 4237.

Glogowski, M. Thesis, 1976.

Glogowski, M.; Hall, H. K., Jr. J. Macromol. Sci. Chem. 1979, A13 (3),
    369.

Hall, H. K., Jr.; Daly, R. C. Macromolecules 1975, 8, 22 and 959.

Hall, H. K., Jr.; Dunn, L. C.; Padias, A. B. J. Org. Chem. 1980, 45,
    835.

Hall, H. K., Jr.; Ykman, P. J. J. Amer. Chem. Soc. 1975, 97, 800.

Huisgen, R. Accts. Chem. Res. 1977, 10, 199.

Huisgen, R.; Steiner, G. J. Amer. Chem. Soc. 1973, 95, 5054.

Kennedy, J. P.; "Cationic Polymerization of Olefins: A Critical Inven-
    tory," Wiley-Interscience: New York, 1975.

Ledwith, A. Accts. Chem. Res. 1972, 5, 133.

Limburg, W. W.; Williams, D. J. Macromolecules 1973, 6, 787.

Little, J. C. J. Amer. Chem. Soc. 1965, 87, 4020.

Salem, L.; Rowland, C. Angew, Chem. Int. Ed. 1972, 11, 92.

Schug, R.; Huisgen, R. J. C. S. Chem. Comm. 1975, 60.

Shirota, Y.; Mikawa, H. J. Macromol. Sci.-Rev. Macromol. Chem. 1977-
    1978, C16 (2), 129.

Stille, J. K.; Oguni, N.; Chung, D. C.; Tarvin, R. F.; Aoki, S.; Kamachi, M. J. Macromol. Sci.-Chem. 1975, <u>A9</u> (5), 745.

Yamamoto, M.; Asanuma, T.; Nishijima, Y. J. C. S. Chem. Comm. 1975, 53.