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SYNTHESIS OF ELECTRON-POOR TETRASUBSTITUTED OLEFINS AND THEIR REACTIONS WITH ELECTRON-RICH COMONOMERS

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SYNTHESIS OF ELECTRON-POOR TETRASUBSTITUTED OLEFINS

AND THEIR REACTIONS WITH ELECTRON-RICH COMONOMERS

by

Robert Craig Sentman

_____

A Dissertation Submitted to the Faculty of the

DEPARTMENT OF CHEMISTRY

In Partial Fulfillment of the Requirements
For the Degree of

DOCTOR OF PHILOSOPHY

In the Graduate College

THE UNIVERSITY OF ARIZONA

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THE UNIVERSITY OF ARIZONA
GRADUATE COLLEGE

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

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_____and their Reactions with Electron-Rich Comonomers_____

and recommend that it be accepted as fulfilling the dissertation requirement

for the Degree of _____Doctor of Philosophy_____ .

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                                          Date

_John T. Funai_____   _2 Mar 82_____
                                          Date

_____   _2 28 82_____
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_H. K. Hall, Jr._____   _2/26/82_____
                                          Date

Final approval and acceptance of this dissertation is contingent upon the
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SIGNED: _Robert Craig Sentman_

To my Wife, Judy

ACKNOWLEDGMENTS

TABLE OF CONTENTS

TABLE OF CONTENTS--<u>Continued</u>

TABLE OF CONTENTS--<u>Continued</u>

LIST OF TABLES

LIST OF ILLUSTRATIONS

ABSTRACT

Six electron-poor tetrasubstituted olefins were
reacted with electron-rich comonomers. Of these, three
[dimethyl dicyanofumarate (DDCF), dimethyl 1,1-dicyano-
ethylene-2,2-dicarboxylate (DDED), and dicarbomethoxymaleic
anhydride (DCMA)] were found to polymerize with styrenes
and vinyl ethers to form 1:1 alternating copolymers of low
molecular weight. All polymerizations with vinyl ethers
and DCMA required initiation, while the copolymerizations
of DDED and DDCF with styrenes were spontaneous. Tetra-
methyl ethylenetetracarboxylate, diisopropylidene ethylene-
tetracarboxylate, and trimethyl cyanoethylenetricarboxylate
failed to copolymerize under any conditions.

The spontaneous reactions of these tetrasubstituted
olefins can best be explained as proceeding via tetramethylene
intermediates, resonance hybrids of biradicals and zwitter-
ions. Spontaneous copolymerizations occur from biradical
intermediates; cycloadduct formation occurs from both.

Tetramethylene formation is electronically controlled
during the reaction of DDED and electron-rich comonomers, as
reflected by the structure of the isolated cyclobutanes.
The orientation of this monomer in the copolymer with styrene
is sterically controlled, as suggested by ^{13}C NMR.

Methyl 3,3-dicyanoacrylate, a new tetrasubstituted olefin, was found to spontaneously copolymerize with styrenes, and to form cyclobutanes with vinyl ethers. It could be copolymerized with vinyl ethers with radical initiation.

CHAPTER 1

INTRODUCTION AND BACKGROUND

The thermal reactions of electron-poor and electron-rich olefins have been reported to yield a wide variety of products, ranging from small molecule dimers to high polymers. Homopolymers of both types of olefin, as well as 1:1 alternating copolymers, have been isolated. Small molecules produced include cyclobutanes, cyclohexanes, and 1-butenes. A universally accepted mechanistic picture explaining this array of products has not been developed, although several schemes have been proposed.

From the nature of the polymeric products, being both 1:1 alternating copolymers via a radical process and homopolymers via an ionic pathway (Shirota, Yoshimura, et al. 1974), any unifying mechanism must account for both radical and ionic species in the initiation reactions. This requirement places a severe limitation on the nature of a proposed reaction scheme.

Background

Charge-Transfer Complexation

Electron-poor olefins are known to form charge-transfer complexes with electron-rich olefins, as witnessed

1

by the appeance of bright colors upon mixing. Equilibrium
constants for these complexes are relatively large, ranging
from 0.1 1/mole for maleic anhydride and vinyl ethers
(Iwatsuki and Yamashita 1967) to 1.63 1/mole for tetracyano-
ethylene and indene (Cooper, Crowne, and Farrell 1966). The
equilibrium constants for vinylidene cyanide with sytrene
and ethyl vinyl ether have been estimated as 0.1 and 0.3
1/mole, respectively (Stille and Chung 1975b).

Are charge-transfer complexes true intermediates or
is complex formation an unrelated side reaction with no
mechanistic meaning? While most authors agree on the former
there is little direct evidence. Kinetic studies are unable
to distinguish between routes 1a and 1b, below:

Route 1a $\qquad$ A + D $\rightleftharpoons$ (AD) $\longrightarrow$ P

Route 1b $\qquad$ (AD) $\rightleftharpoons$ A + D $\longrightarrow$ P
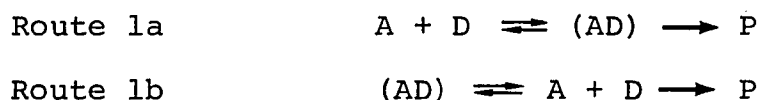
For example, Rappoport (1963) found the reaction of tetra-
cyanoethylene with N,N-dimethylaniline to proceed in a
stepwise fashion, as follows: immediately upon mixing, a
charge-transfer complex is formed which rapidly and irrever-
sibly disappears to another complex (a σ complex), which in
turn slowly converts to product (Mechanism A). The overall
kinetics were found to be first-order in charge-transfer
complex and quadratic in the concentration of the amine, as
predicted. Other mechanisms, however, are also consistent
with these results (Mechanism B: Shirota, Nogami, et al.

1974). Pathway C, not involving the charge-transfer complex as an intermediate but with two competing rapid equilibria, cannot be discounted.

Kiselev and Miller (1975) have shown that a charge-transfer complex is indeed a true intermediate in the Diels-Alder reaction of tetracyanoethylene and 9,10-dimethyl-anthracene. By measuring the temperature dependence of the observed rate constant, they were able to calculate the activation enthalpies for the reaction. In nonaromatic, polar solvents $\Delta H^{\ddagger}_{exp}$ is negative, a result only consistent with route 1a (Figure 1).
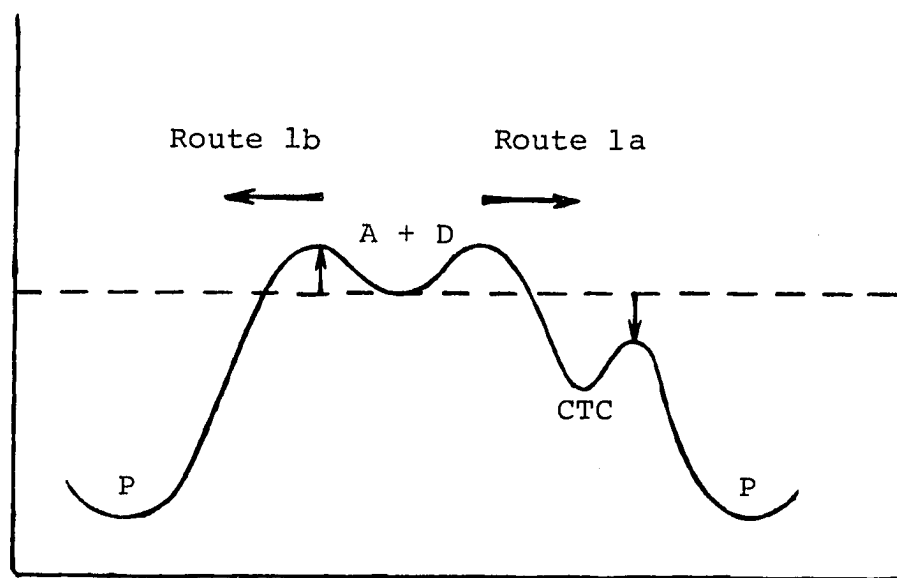
Figure 1. Enthalpy profile for reaction with CTC as intermediate and as side product.

H_3C \ N / CH_3

K

Charge
Transfer
Complex

$ArMe_2$
k_1

H_3C $\overset{+}{N}$ CH_3

CN
CN
H
NC $\overset{-}{}$ CN

Mechanism A

+

NC   CN

NC   CN

k_2 | $-HCN$
(slow)

H_3C \ N / CH_3

NC
CN
NC

Charge
Transfer
Complex

K

$ArMe_2$
+
TCNE

Mechanism C

K'

k_2 | $ArMe_2$

H_3C \ N / CH_3

+

H_3C $\overset{+}{N}$ CH_3

+

NC   CN

NC   CN

K

Charge
Transfer
Complex

k_1
k_{-1}

CN
CN
H
NC $\overset{-}{}$ CN

Mechanism B
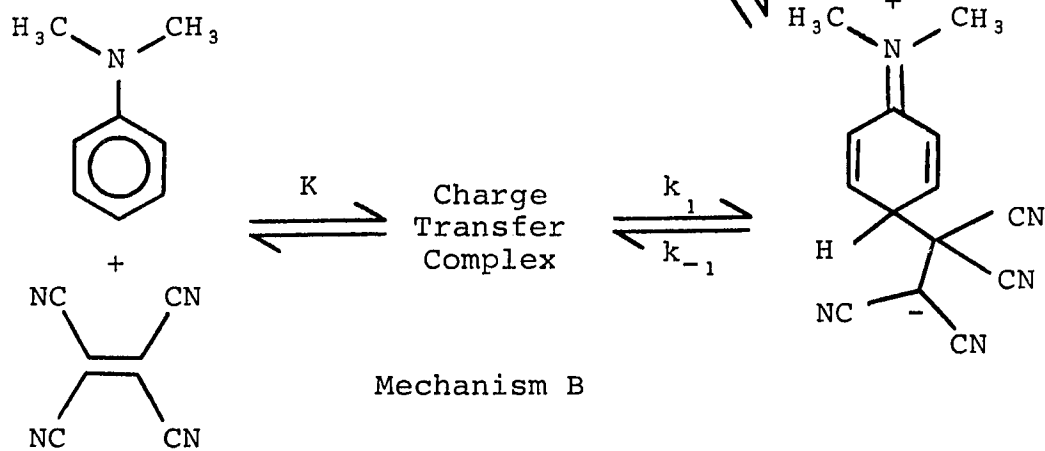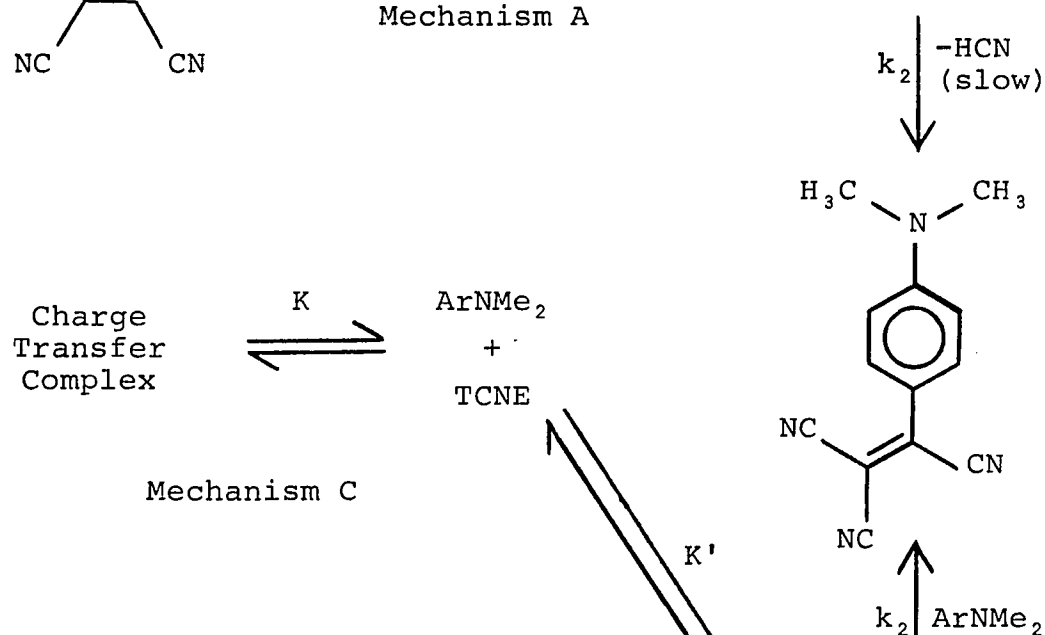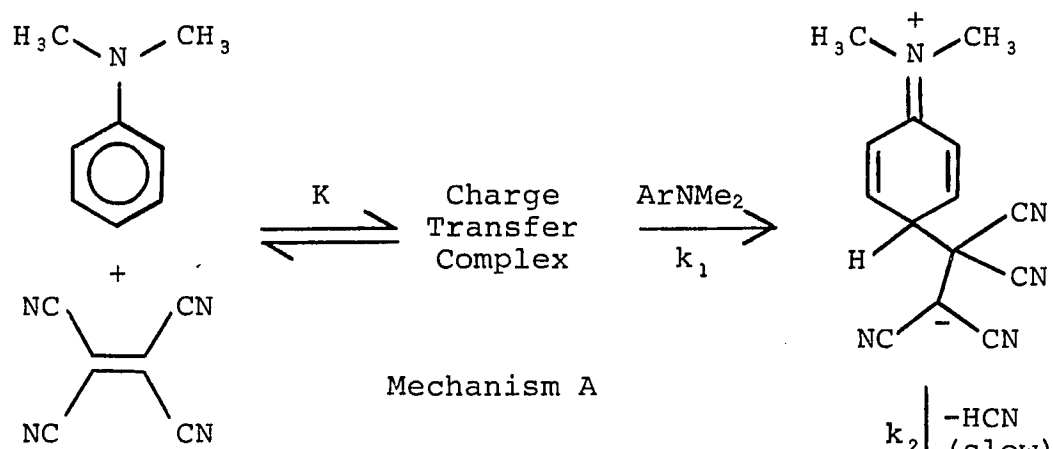
A distinction should be maintained between charge-transfer complexation and electron transfer. The wave function for the ground state of the charge-transfer complex is $\psi(AD) = a\psi(A\text{---}D) + b\psi(A^-\text{——}D^+)$, $a > b$. While electron donation from the HOMO of the electron-rich olefin into the LUMO of the electron-poor olefin is involved in holding the complex together, it is not the dominant factor (Hanna and Lippert 1973). The complex is not a highly polar species, and does not resemble a cation-radical/anion-radical pair.

Initiation Via Electron Transfer

The wave function for the lowest excited state of a charge-transfer complex is $\psi(AD)^* = -b\psi(A\text{---}D) + a\psi(A^-\text{——}D^+)$, $a > b$. This species is highly polar and can dissociate under proper conditions to yield a cation-radical/anion-radical pair. Many of the photochemical reactions of charge-transfer complexes have been shown to proceed from these ion-radicals (Gordon and Ware 1975; Shirota and Mikawa 1977-1978).

Some thermal reactions of charge-transfer complexes have also been shown to involve ion-radicals. Bawn, Ledwith, and Sambhi (1971) detected the ESR signal of TCNE$^-$ in the reaction of TCNE with N-vinylcarbazole. The anion-radical of tetracyanoquinodimethane (TCNQ) was identified in the TCNQ-initiated polymerization of t-butyl vinyl ether (Tarvin, Aoki, and Stille 1972). Stable salts have been isolated for

TCNE⁻ with several stable cation-radicals (Wheland and Gillson 1976).

One obvious feature of this mechanism is its ability to account for simultaneous occurrence of both ionic and radical reactions. Stille and Chung (1975b) used this feature to explain the reactions of vinylidene cyanide with vinyl ethers. Glogowski and Hall (1979) used a similar scheme for their results in the reactions of N-vinylcarbazole and trimethyl ethylenetricarboxylate.
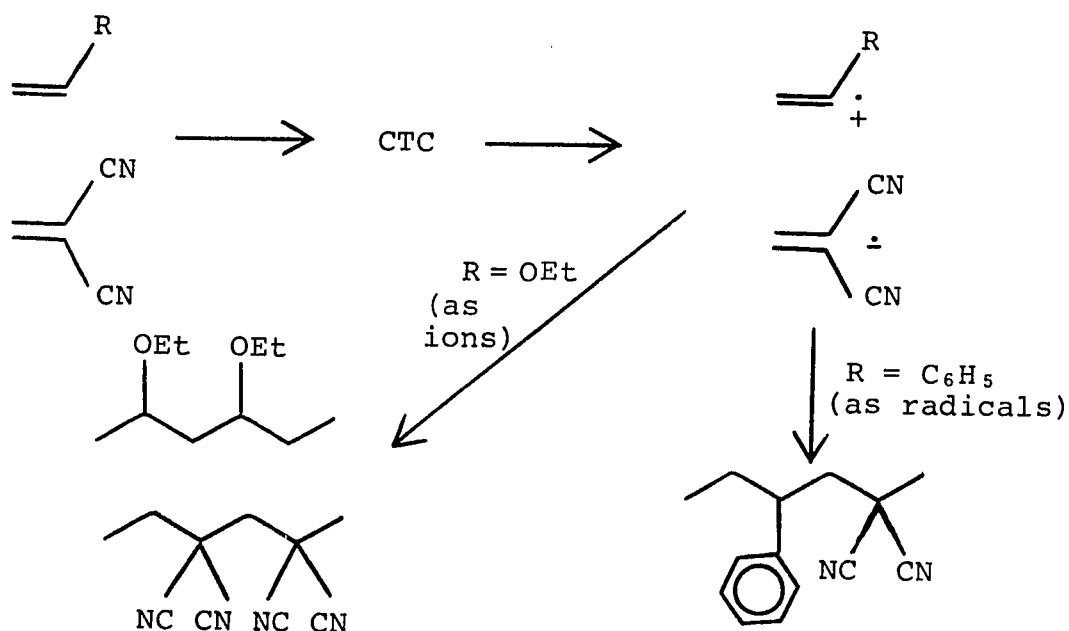
However, electron transfer is energetically favorable only for extremely electrophilic or nucleophilic olefins, where a ≃ b in the ground state wave functions of the complex. Even with solvent assistance it is unlikely

electron transfer can account for the majority of reactions

involving moderately electron-poor ethylenes (Foster 1969).

In addition, cation-radicals are known to dimerize

to cyclobutanes in the presence of electron acceptors in

moderately basic solvents. N-vinylcarbazole cation-radical

cyclizes to trans-1,2-dicarbazol-9-yl-cyclobutane in the

presence of maleic anhydride (Shirota and Mikawa 1977-1978)

and p-methoxystyrene cation-radical forms an analogous cyclo-

butane in the presence of trimethyl ethylenetricarboxylate

(Hall and Abdelkader 1981). The cyclobutanes usually

isolated from electron-rich/electron-poor olefin pairs are

1:1 adducts.
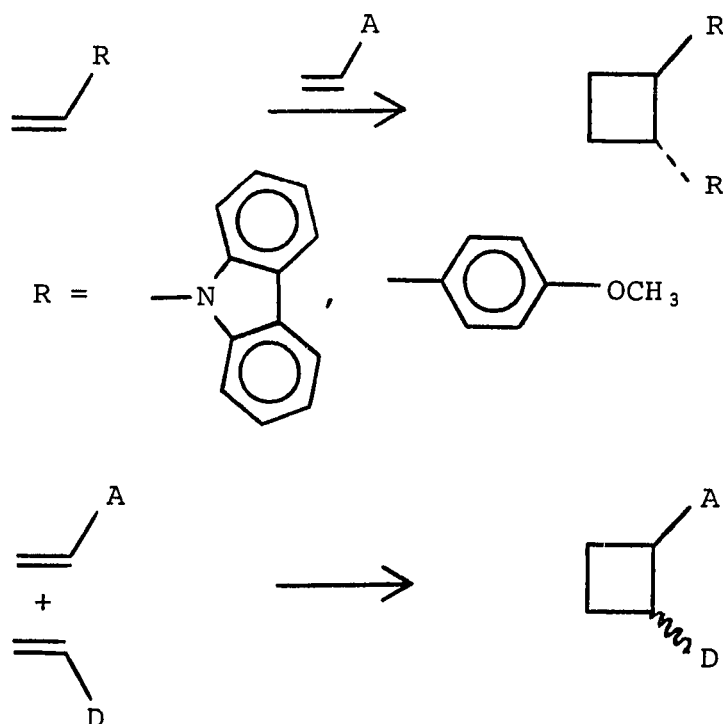
Reactions Through a Zwitterionic Intermediate

Reactions of electron-poor/electron-rich olefins have been suggested to involve zwitterionic intermediates since the early work of Brannock et al. (1964). These reactions typically show an increase in rate with increasing solvent polarity, and substituent effects for polar states. Several ionic intermediates have been trapped.

Kramer (1968) studied the addition of TCNE to para-substituted styrenes, with electron-rich groups as substituents. Plotting the logarithm of the second-order rate constants versus σ^+ for the substituents, he found ρ equal to -7.1 ± 0.5. This large value strongly indicates a polar intermediate is involved in this reaction.

Other researchers have also noted increases of reactivity as ionic character increases. Middleton (1965) noted that the reactivity of an electron-poor olefin toward an electron-rich olefin depends on its electrophilicity. 1,1-Dicyano-2,2-bis(trifluoromethyl)ethylene reacts with methyl vinyl ether instantaneously at $-78°C$, while TCNE takes 1.5 hours at room temperature. Similar results were obtained with sytrene.

The reactivity of an electron-rich olefin toward an electron-poor one depends on its nucleophilicity. The rate of reaction between vinyl ethers and TCNE increased 60,000 times as the vinyl ether changed from phenyl to t-butyl vinyl ether (Huisgen and Steiner 1973). Hall and Ykman

(1975) found a similar pattern in the reactions of a series of trisubstituted (with CN or CO_2CH_3) electron-poor olefins with a series of electron-rich olefins.

Many of the above authors also studied solvent effects on reaction rates. Invariably there is a marked increase in rate with increasing solvent polarity. The dependence of TCNE cycloaddition on solvent polarity is immense: k(acetonitrile)/k(cyclohexane) amounts to 63,000 for p-methoxystyrene, 29,000 for anethole, and 10,800 for ethyl isobutenyl ether (Huisgen 1977a).

The small molecule products usually obtained from a zwitterionic intermediate are cyclobutanes arising from collapse of the 1,4-dipole:
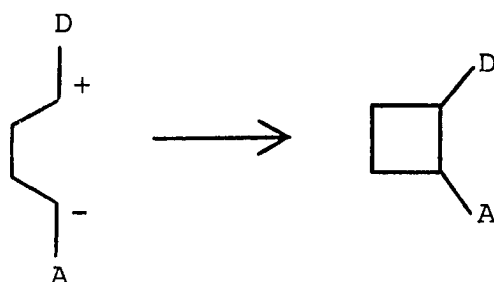
Some of the cyclobutanes so produced are shown below:
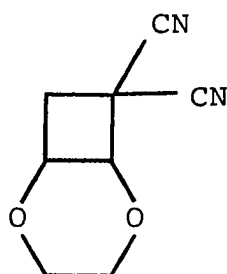
Stille et al.
(1975)

Huisgen and Steiner
(1973)

CH$_3$O$_2$C

CO$_2$CH$_3$

CO$_2$CH$_3$

N

CH$_3$O$_2$C

CO$_2$CH$_3$CO$_2$CH$_3$

CO$_2$CH$_3$

N —CH$_3$
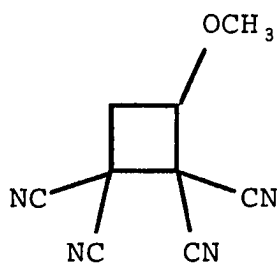
CH$_3$
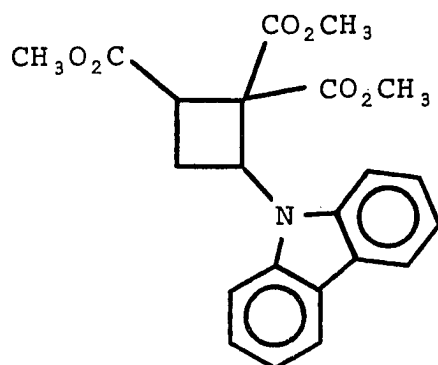
Glogowski and Hall
(1979)
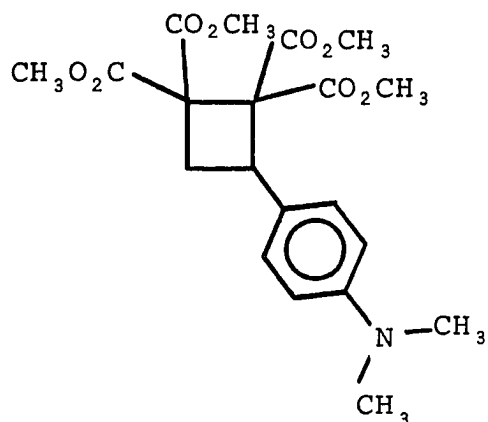
Hall, Dunn, and Padias
(1980)

The ultimate proof of the existence of an inter-
mediate is its isolation or trapping from a reaction mixture
(Huisgen 1970). This has been done in a number of systems,
both as side products and by external agents.

Certain systems form cyclohexanes by addition of
another molecule of olefin across the 1,4-dipole, essen-
tially trapping the intermediate. The extra ethylene unit
can be electron-poor, as in the reaction of N,N-dimethyliso-
butenylamine with diethyl ethylene-1,1-dicarboxylate
(Brannock et al. 1964).

N(CH$_3$)$_2$

+
N(CH$_3$)$_2$

E

E

(CH$_3$)$_2$N

E

E

E

E

+

E

E

E = COOCH$_3$
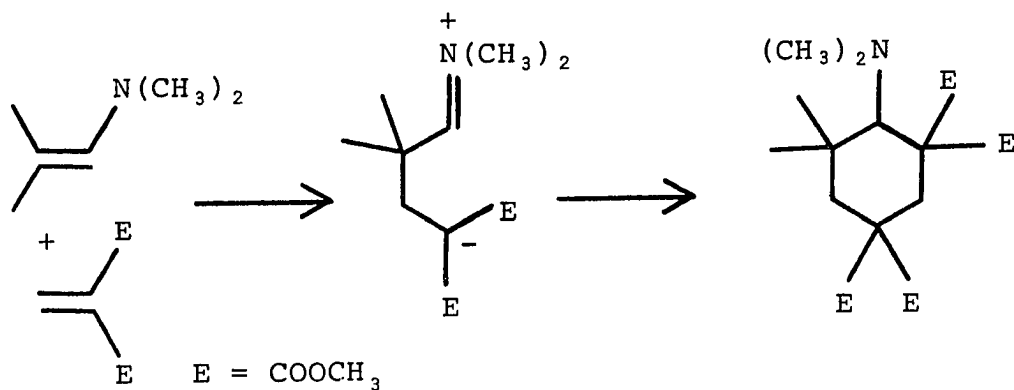
Other examples are afforded by vinylidene cyanide and
styrene (Stille and Chung 1975a), vinylidene cyanide and
ketene diethyl acetal (Still and Chung 1975b), and tricyano-
ethylene and N,N-dimethylisobutenylamine (Hall and Ykman
1975).

$R_1 = C_6H_5, \quad R_2 = H$
$R_1 = R_2 = OCH_2CH_3$
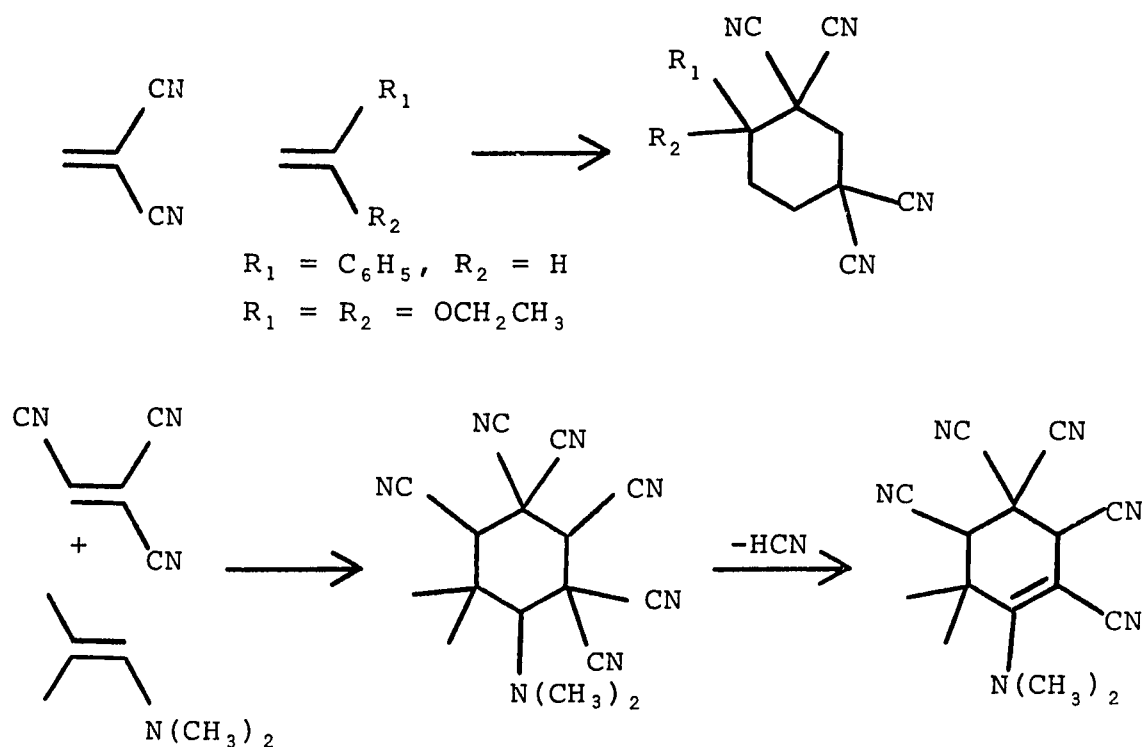
The extra olefin can also be electron-rich, as in the reac-
tion of tetracyanoethylene with styrene (Williams, Wiley,
and McKusick 1962a).
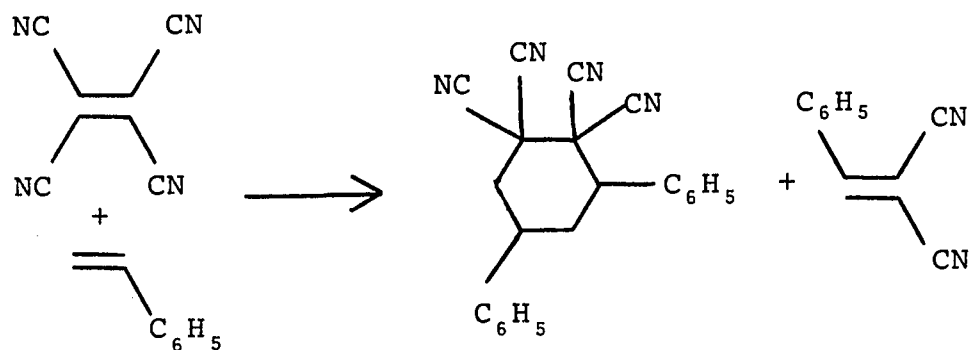
Similar cyclohexanes were isolated by Glogowski and Hall (1979) with N-vinylcarbazole and electron-poor olefins.

Zwitterionic intermediates also undergo rearrangements. The reaction of TCNE with 2-ethoxy-3,4-dihydro-2H-pyran undergoes a rearrangement to form cyclohexane as shown (Williams, Wiley, and McKusick 1962a):
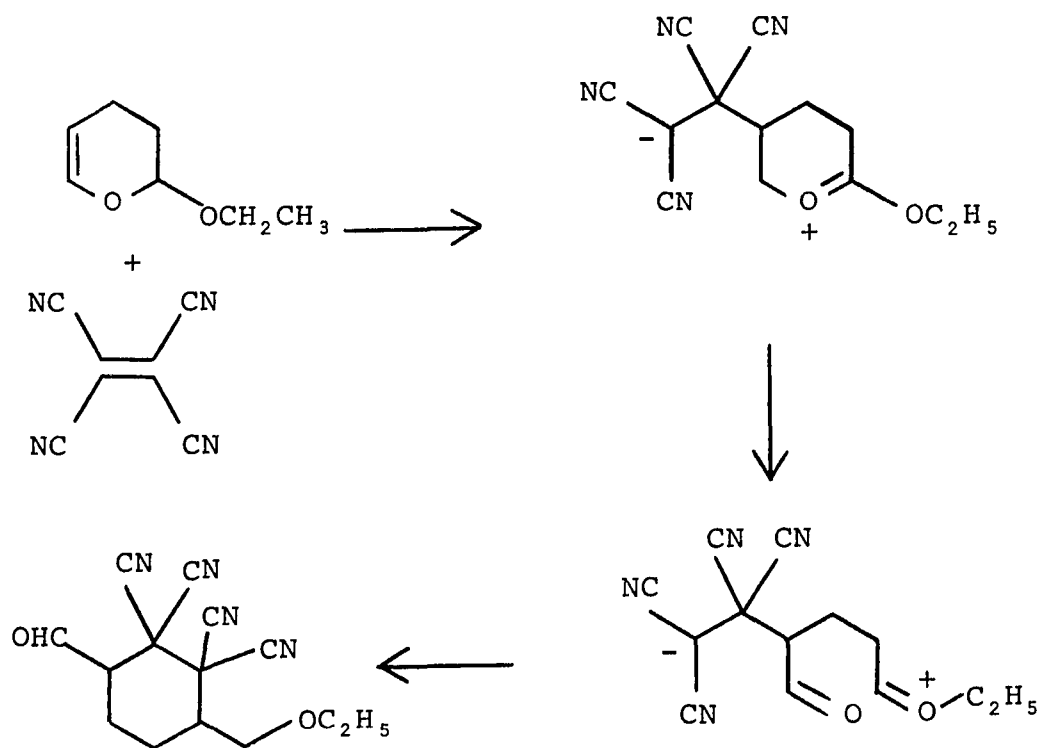
Another rearrangement seen for 1,4-zwitterionic intermediates is a 2,4 hydrogen shift to 1-butene. This reaction has been reported by Hall and Ykman (1975) and Glogowski and Hall (1979) for a number of olefin pairs.
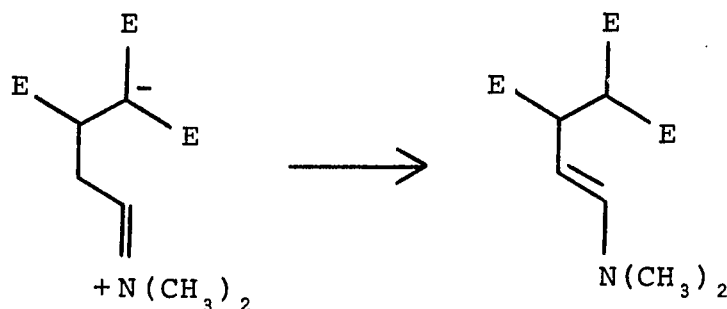
Another route available to the 1,4-zwitterion is expulsion of a stable anion. 1,2,2-Tricyanovinyl chloride reacts with p-methoxystyrene to form 1,2,2-tricyano-4-(p-methoxyphenol)-butadiene (Williams, Wiley, and McKusick 1962b).

$$R = pCH_3OC_6H_4-$$
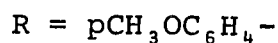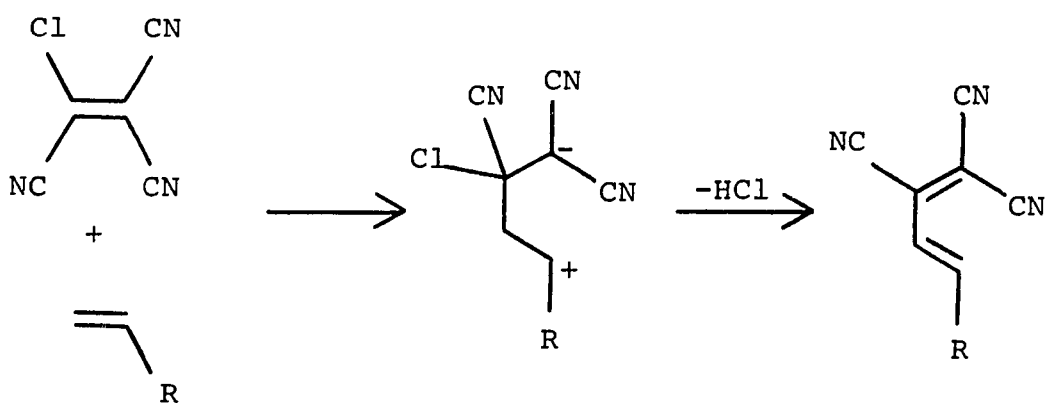
Hall et al. (1979) reported the isolation of cyclopropanes from zwitterions bearing a 3 halo substituent:

E = COOCH$_2$CH$_3$

R = CH$_2$CH$_3$
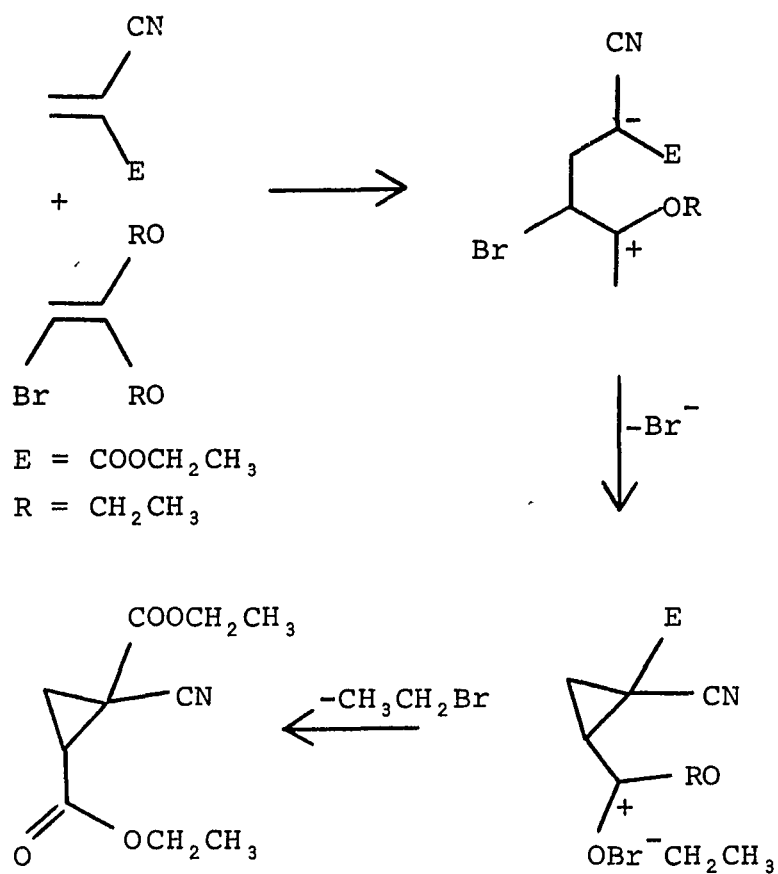
Recently Rasoul and Hall (1980) have used this chemistry to synthesize efficient cationic initiators.

R = C$_6$H$_5$, OR'
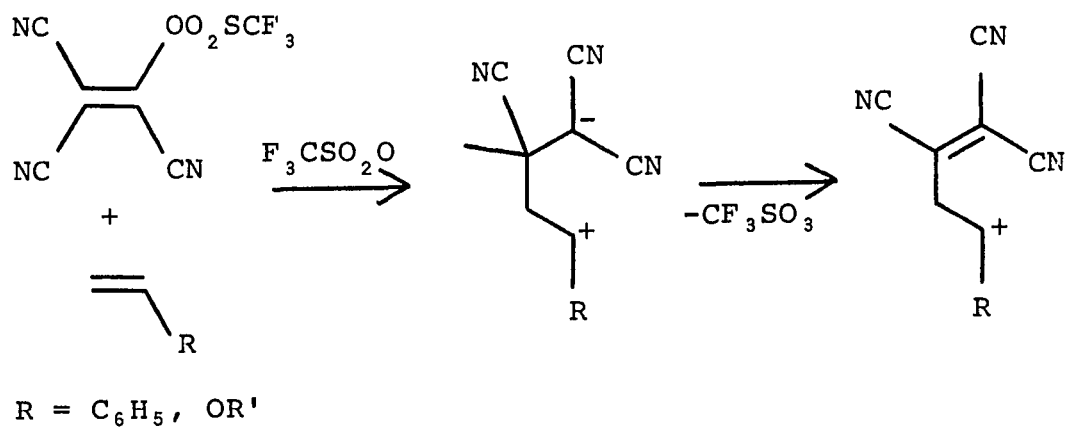
Zwitterionic intermediates from the reaction of electron-poor/electron-rich olefin pairs have also been trapped by external agents. Schug and Huisgen (1975) reported trapping the zwitterion of tetracyanoethylene and ethyl vinyl ether with acetonitrile, acetone, and N-benzylidenemethylamine. While only trace amounts are trapped under conditions of kinetic control (4% with acetonitrile, 6% from acetone), the reactions are nearly quantitative if allowed to reach equilibrium. The cyclobutane originally formed is slowly converted to the more stable six-membered ring through a small equilibrium concentration of zwitterion.
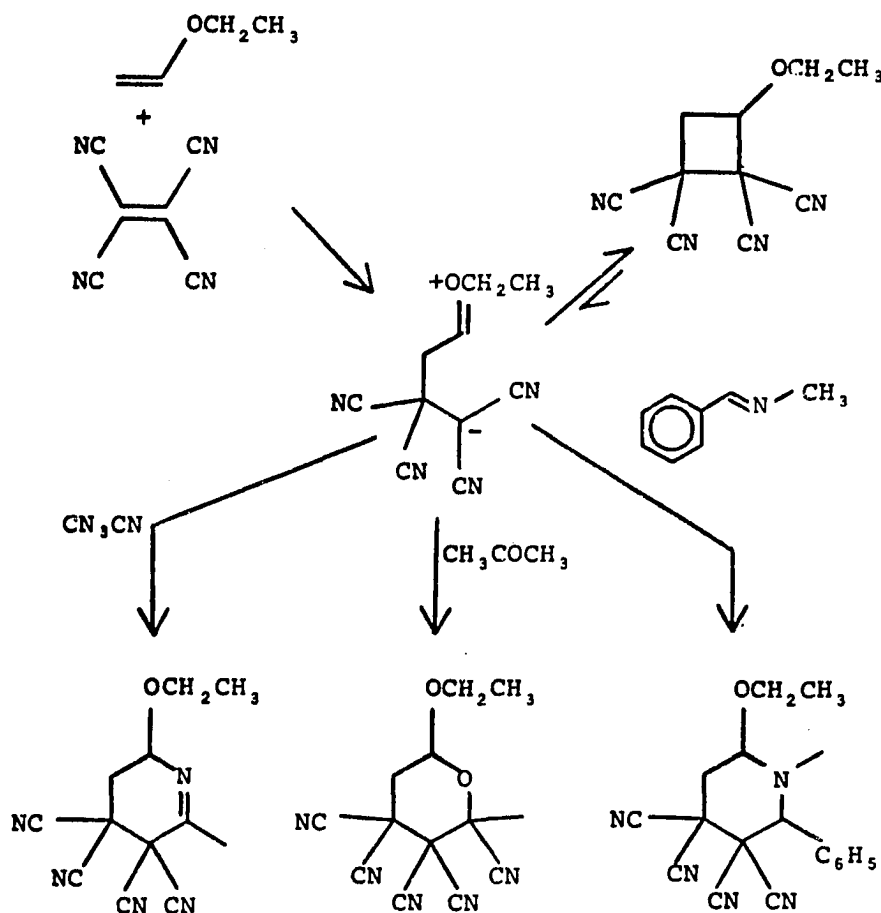
Trapping can also be accomplished with methanol.
Huisgen, Schug, and Steiner (1974) first trapped the zwitter-
ion from TCNE and vinyl ethers. A detailed analysis of the
stereochemistry of this reaction has shown it to proceed via
electrophilic attack by the intramolecular contact ion pair,
the zwitterion existing as a self-solvating gauche configura-
tion (Huisgen 1977b).
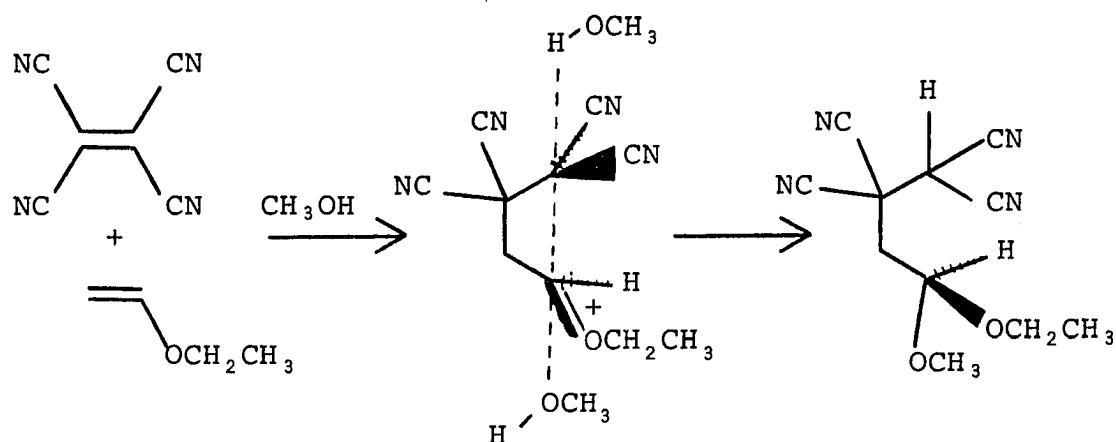
Other methanol adducts have been isolated from TCNE and
N-vinylcarbazole (Glogowski and Hall 1979) and dimethyl
cyanofumarate and p-methoxystyrene (Hall and Abdelkader
1981).

Zwitterionic intermediates have also been implicated
as the actual initiating species in a number of homopolymer-
izations. Tarvin, Aoki, and Stille (1972) trapped several
zwitterionic dimers during their investigation of the
initiation of alkyl vinyl ethers by electron acceptors.
They also isolated oligomers containing both

tetracyanoquinodimethane and vinyl ether, again indicating

a zwitterionic initiator.

R' = CH₂CH₃
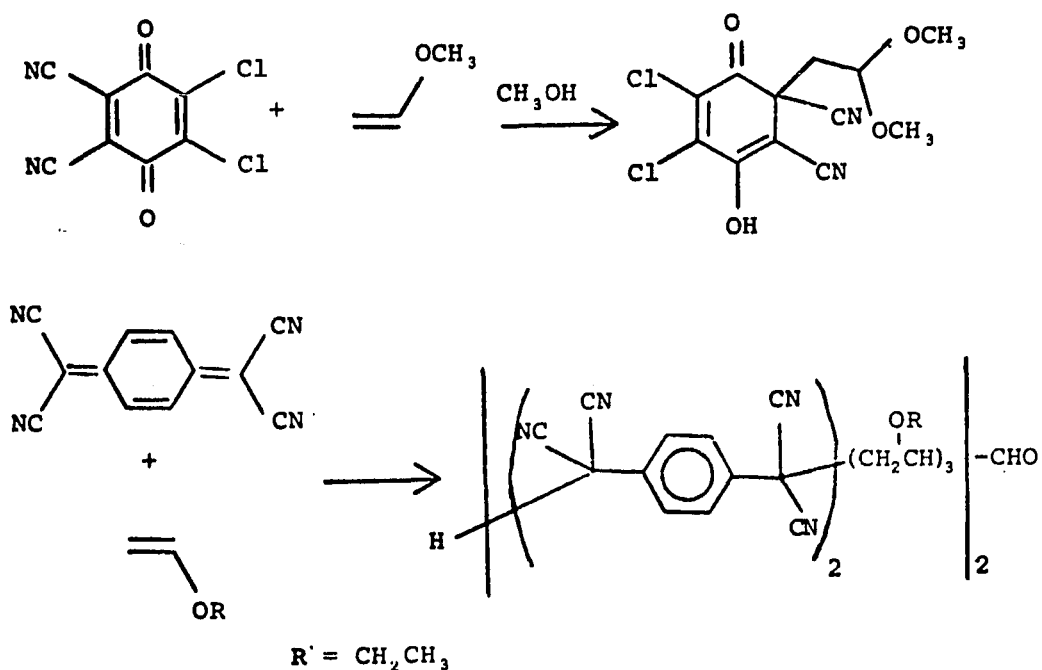
The actual initiator in vinylcarbazole polymeriza-
tions catalyzed by chloranil has been identified as hydrogen
halide generated from an initially formed zwitterion
(Natsuume et al. 1970). This acid also causes devinylation
of N-vinylcarbazole to produce free carbazole. The rate of
carbazole formation and polymerization increase as chloranil
is replaced by bromanil indicating a common intermediate.
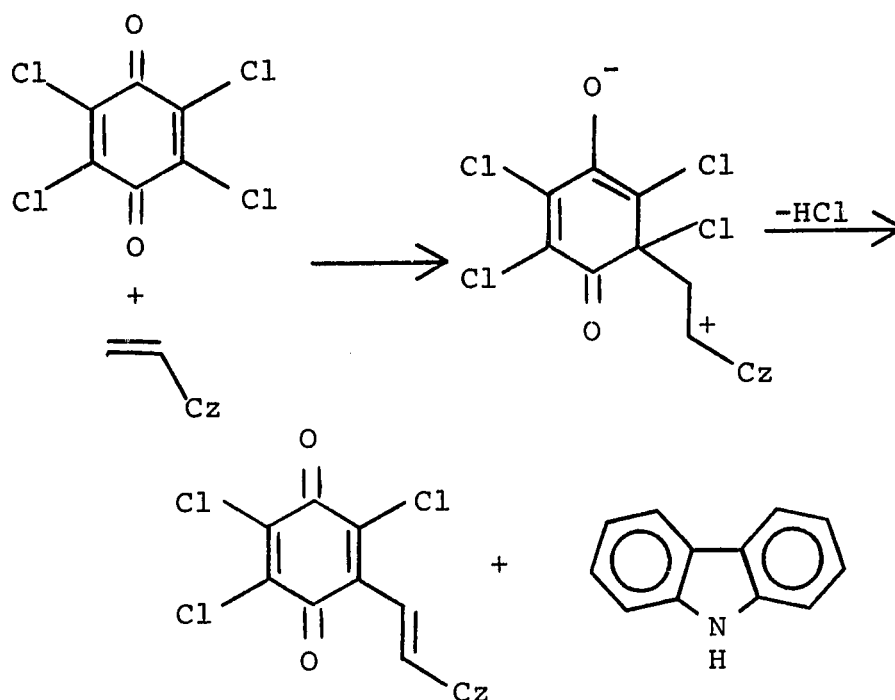
Hall and Ykman (1977) noted that the electron-poor olefin was incorporated into polystyrene initiated by such electron-poor olefins as 2,2-dicyanovinyl chloride, implying a zwitterionic intermediate. Such an intermediate is also postulated for the polymerization of vinylcarbazole initiated by fumaronitrile (Shirota, Matsumoto, and Mikawa 1972), and many other polymerizations.

Some of the reactions of 1,4-zwitterions are summarized below:

There is some evidence the zwitterions themselves arise from coupling of a cation-radical/anion-radical pair. Tarvin, Aoki, and Stille (1972) detected the ESR spectra of several anion-radicals as precursors to a zwitterionic species.
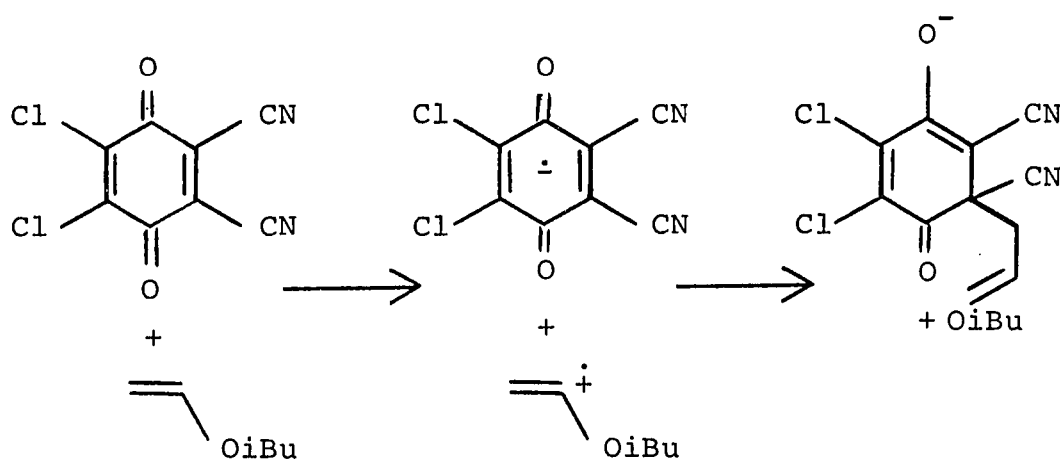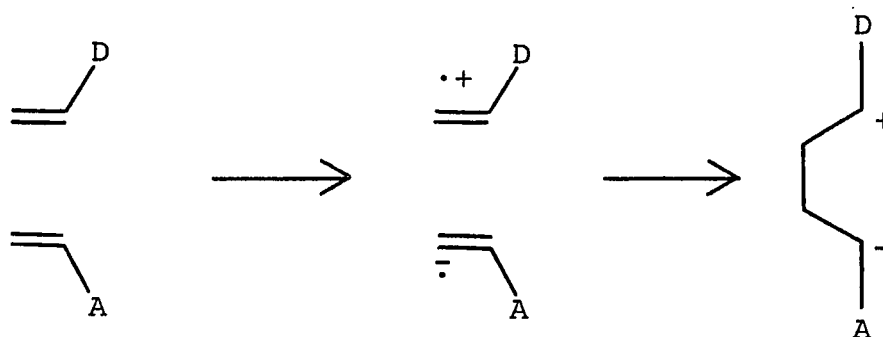
Natsuume et al. (1970), on the other hand, found no evidence of ion-radicals in the formation of a similar zwitterion from chloranil and N-vinylcarbazole.
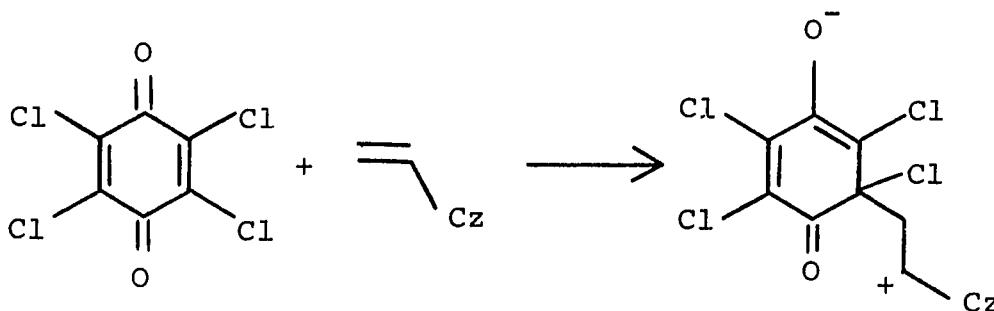
In any event, collapse of the intimate ion pair, if it is
present at all, to zwitterion is rapid compared to other
reactions. In most systems the chemistry of ion-radicals
is not observed.

Reaction Via Diradical Intermediates

Zwitterions are not the only suggested intermediates
for the 2+2 cycloadditions of olefins. Dimerization of poly-
halo and other substituted olefins has been suggested to
involve a diradical intermediate (Roberts and Sharts 1962).

The fluorinated olefins tetrafluoroethylene and
1,1-dichloro-2,2-difluoroethylene react with butadiene to
give predominantly cyclobutanes (Bartlett 1968).
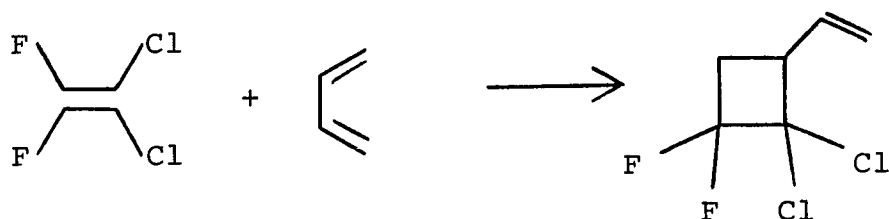
The rate of this reaction shows little solvent dependence,
for 1,1-dichloro-2,2-difluoroethylene only increasing by a
factor of 2.8 as the solvent changes from hexane to nitro-
methane, thus emphatically confirming the nonionic character
of this reaction (Bartlett 1970).

Diradicals have also been implicated as potential
initiating species for the spontaneous polymerization of
pentafluorostyrene and methyl methacrylate (Pryor 1971).

Initiation via a Diels-Alder adduct, as seen for styrene itself, is unlikely in these systems, but formation of a 1,4 diradical is compatible with the kinetics of the polymerizations.
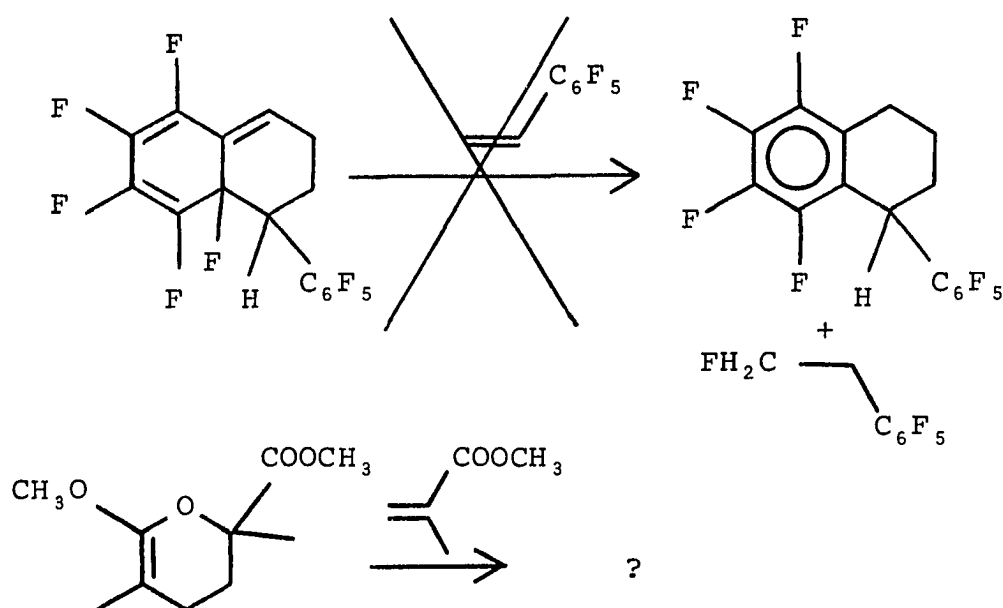
Many electron-rich/electron-poor olefin pairs spontaneously copolymerize. Systems showing this ability include styrene/ethyl 2,3-dicyanoacrylate (Noren and Hall 1972), styrene/vinylidene cyanide (Gilbert et al. 1956), and p-dioxene/maleic anhydride (Kokubo, Iwatsuki, and Yamashita 1969). A 1,4 diradical is a likely initiating species for these reactions (Zutty et al. 1965), albeit probably only after chain-transfer to generate two free monoradicals. Other mechanisms have also been proposed for these spontaneous initiations: hydrogen atom abstraction by the

charge-transfer complex from solvent (Matsuda and Abe 1968),
and conversion of the complex into two radicals by an elec-
tron transfer followed by proton transfer to form two
monomer monoradical species (Imoto 1966).

A 1,4 diradical has been trapped in the reverse
reaction of trimethyl ethylenetricarboxylate and p-methoxy-
styrene, which also spontaneously copolymerizes (Hall and
Gillard 1981).
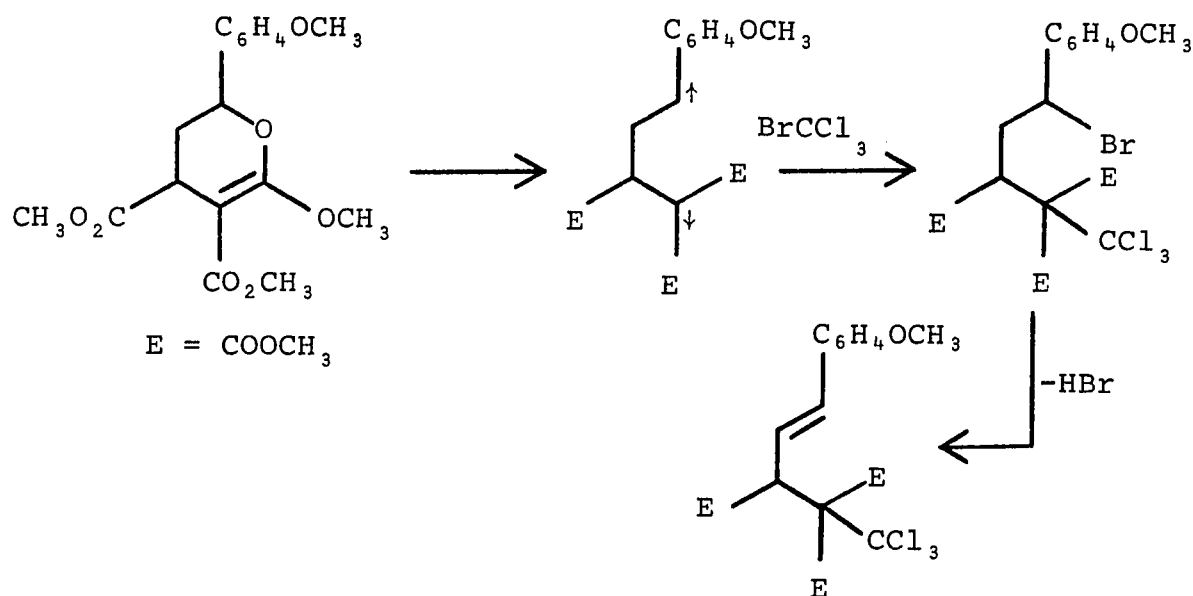
Pryor, Iino, and Newkome (1977) studied the dis-
appearance of the radical scavengers galvinoxyl and 1,3-
bis-(diphenylene)-2-phenylallyl in pentafluorostyrene at
100°C. The reaction was found to be first order in scavenger
and the rate constants for the two were identical. This was
explained by the rapid equilibrium of PFS with 1,4 diradicals
and reaction of the scavengers in a rate limiting step.

The Tetramethylene Intermediate

It was left to Salem and Rowland (1972) to unify the 1,4 zwitterion and diradical into a single species, the tetramethylene intermediate, defined as a resonance hybrid of both structures.
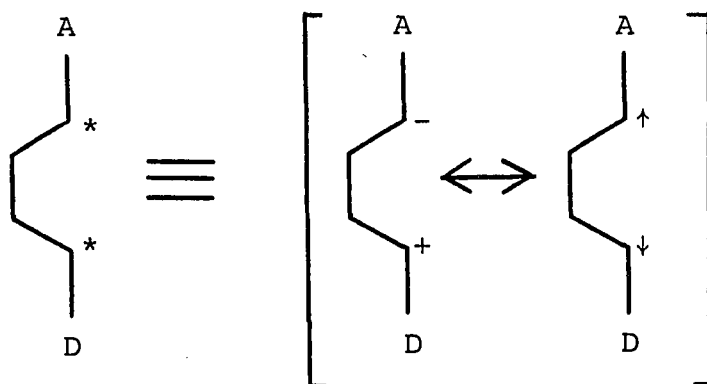
There should be a continuum between highly zwitterionic intermediates and purely diradical ones. Where on the continuum a given tetramethylene intermediate will lie is determined by the substituents at the terminal carbons. That most olefin pairs investigated form intermediates which act as either pure zwitterions or pure diradicals is because the model reactions for which mechanistic criteria have been elaborated were tailor made for one extreme or the other (Huisgen 1977a).

According to this theory, highly electron-rich substituents like vinyl ethers should favor zwitterionic tetramethylenes, while moderately electron-rich groups like phenyl favor less polar intermediates. The same tendency works on

the anionic terminal, where strongly electron-withdrawing
cyano groups favor zwitterionic species, etc. The reactions
of a tetramethylene reflect the effects of these substituents.

The reactions of vinylidene cyanide provide a per-
fect example of these trends. The reaction of vinylidene
cyanide with vinyl ethers produces a highly zwitterionic
tetramethylene, as both alkoxy and cyano substituents pro-
mote a highly dipolar intermediate (Stille and Chung 1975b).
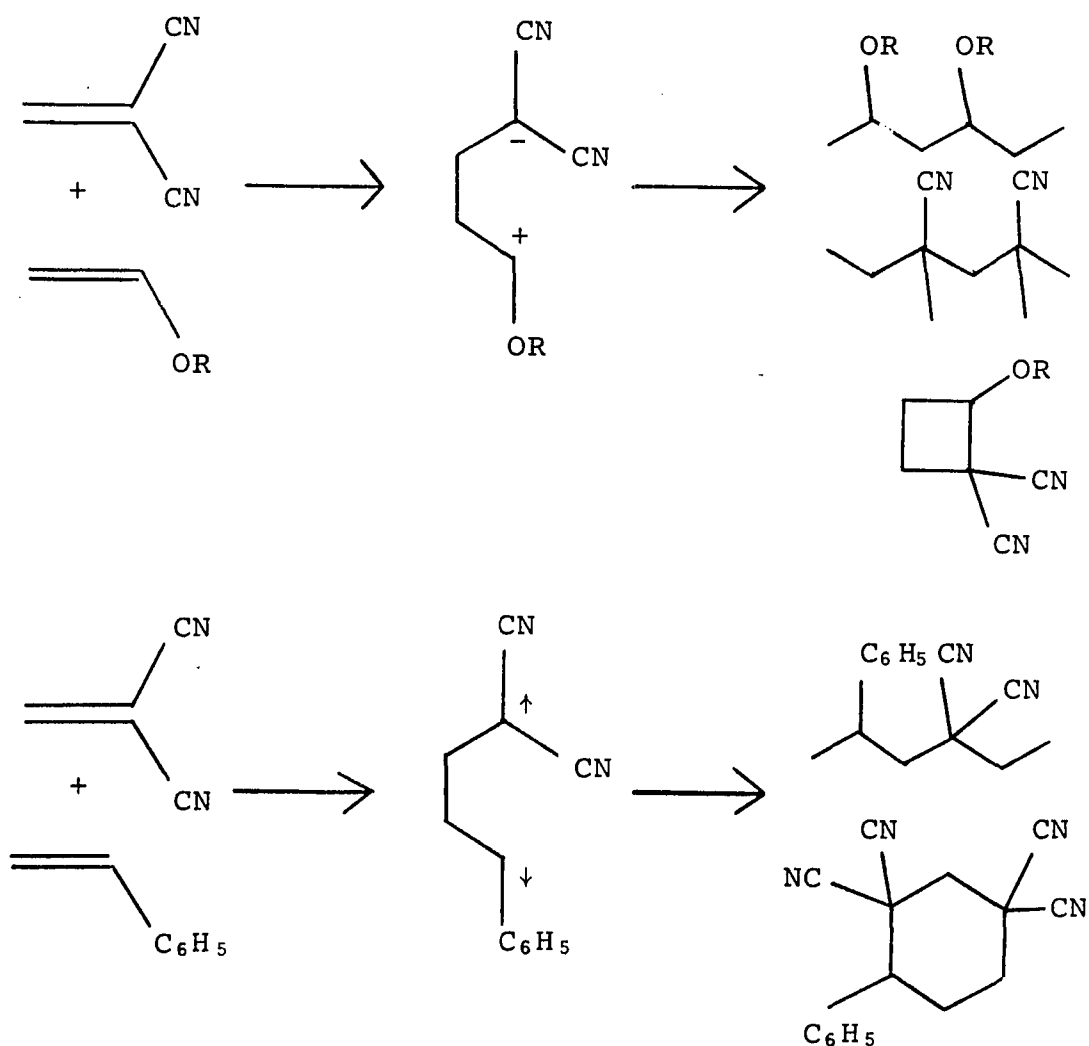
This intermediate initiates ionic homopolymerization of both
olefins or cyclization to cyclobutane. Replacing vinyl
ether with styrene leads to a much less polar tetramethylene
intermediate. The cyano substituents still favor a dipolar
species while the phenyl group tends to prefer a more radical-
like species. This tetramethylene initiates spontaneous
copolymerization of the olefin pair (Stille and Chung 1975a).
Anionic polymerization of vinylidene cyanide starts, but
termination by ring closure to cyclohexane prevents propa-
gation.

A similar situation was encountered by Hall and
coworkers for the reactions of dimethyl cyanofumarate. With
vinyl ethers highly dipolar tetramethylenes are produced
while those from styrenes are much less so, spontaneously
initiating 1:1 copolymerizations (Hall and Daly 1975).

Another approach to measuring where on the continuum
of tetramethylene intermediates a particular species lies is
to monitor the stereochemical leakage during cycloaddition.
As noted earlier, "pure" zwitterions, i.e., those tetra-
methylenes with a very high dipolar nature, exist as self-
solvated intimate ion pairs. Such species undergo quite
stereospecific cyclization, especially in nonpolar solvents.
Hence only 2% inversion occurs for the reaction of cis-1,2-
dicyano-1,2-bis-(trifluoromethyl)ethylene with TCNE in
benzene. A more polar solvent contributes better solvation
and diminished coulombic attraction of the charged centers,

so more isomerization occurs (Huisgen and Steiner 1973).
Diradical tetramethylenes should rotate much faster. The
diradical tetramethylene from the reaction of 1,1-dichloro-
2,2-difluoroethylene with cis,cis-2,4-hexadiene underwent
rotation ten times faster than ring closure (Bartlett,
Montgomery, and Seidel 1964). This technique has thus far
been used only to differentiate concerted from stepwise
reactions but should be able to distinguish zwitterionic
and radical tetramethylene intermediates also.

Similar results have been obtained for the three
carbon analogue, the trimethylene intermediate. Chmurny
and Cram (1973) found the trimethylene derived from the ring
opening of methyl 1,2-diphenylcyclopropanecarboxylate to be
best described as a diradical, whereas that from methyl
1-cyano-2-phenylcyclopropanecarboxylate is better thought
of as a zwitterion (Howe, Yankee, and Cram 1973).
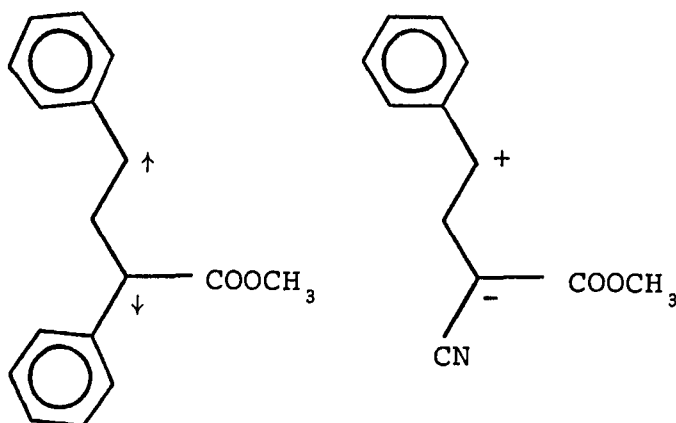
Propagation in Charge-Transfer Polymerization

Alternation in radical polymerization is generally attributed to a preference for cross propagation over homopropagation. This preference is quantified in empirical reactivity ratios. From these ratios and the relative monomer concentrations, the composition of a copolymer can be calculated. Electron-rich/electron-poor olefin pairs show a more marked tendency toward 1:1 alternation regardless of the monomer feed ratio.

Iwatsuki and Yamashita (1971), after reviewing the chemistry of three component copolymerizations, suggested alternating copolymerization is better thought of as homopolymerization of the charge-transfer complex. Attempts to calculate terpolymer composition for the system maleic anhydride, p-dioxene, and acrylonitrile from known reactivity ratios led to conclusions contrary to the facts (predicting no acrylonitrile incorporation), while the system is easily handled by treatment as a two component copolymerization of maleic anhydride/p-dioxene complex and acrylonitrile. The essential feature of this approach is that in the terpolymerization system, a pair of monomers should appear as a constant 1:1 ratio with amounts of the third comonomer varying with its monomer feed. This is in agreement with the experimental facts. Many other terpolymerization systems were also reported to be amenable to this

approach and reactivity ratios for the complexes have been calculated for a number of these systems.

Recently Yoshimura, Mikawa, and Shirota (1978) studied the kinetics of the copolymerization of N-vinyl-carbazole with diethyl fumarate and fumaronitrile in detail. Their results indicate both propagation of charge-transfer complex and free monomer are significant, but that in these systems propagation of free monomer was found to be more important. That the mechanism of propagation involving a monomer pair which forms a weak complex is complicated is not surprising. While the reactivity of the complex may be higher, its concentration at any time would be fairly low. The overall kinetics seen would be a function of monomer feed ratio, equilibrium constant of complex formation (complex concentration), and reactivity ratios of free mono-mer and complex. It is likely that participation of free monomers becomes more important as the complex formed between them is weaker. Such systems also show deviation from a 1:1 composition with monomer feed, the vinylcarbazole content of copolymer of VCZ and diethyl fumarate becoming increasingly rich as the VCZ content of the monomer feed increases. The concentration of complex is low, cross propagation from VCZ to fumarate low, while to complex high. The results are understandable using the approach of Iwatsuki and Yamashita described previously.

Termination of Charge-Transfer Polymerizations

It is assumed that termination reactions in poly-
merizations involving charge-transfer complexes are analo-
gous to those of other radical polymerizations, namely
disproportionation and recombination. Yoshimura et al.
(1978) have proven the termination of vinylcarbazole and
diethyl fumarate to be bimolecular as expected.

Scope of the Present Study

Steric hindrance prevents the formation of highly
functionally-substituted vinyl polymers. This takes two
related forms. First, steric hindrance at the reaction site
slows the propagation rate. Second, the resulting polymer,
if formed, is sterically congested and has a low ceiling
temperature, leading to depolymerization. As a result, the
highest average degree of functional groups in vinyl poly-
mers turns out to be 1.0 (Table 1). These results apply to
ordinary laboratory conditions. Under very high pressures,
even tetrasubstituted ethylenes can be homopolymerized
(Anderson, Hoover, and Vogl 1979). Successful copolymeri-
zation of mono and tetrasubstituted olefins would give
copolymers with 1.25 functional groups per chain carbon atom.

Steric hindrance can be minimized by use of planar
structures. For example, maleic anhydride and maleimide are
much more reactive monomers than the corresponding 1,2-
disubstituted ethylenes. Similarly carbomethoxymaleic

Table 1. Degrees of substitution for various vinyl polymers.

Structure	Source	Average Functional Substitution per Carbon Chain Atom
$\sim CH_2CX_2\sim$	Homopolymers of 1,1-disubstituted ethylenes	1.0
$\sim CHXCHX\sim$	Homopolymers of 1,2-disubstituted ethylenes	1.0
$\sim CX_2CX_2CH_2CH_2\sim$	Alternating copolymer of tetrachloroethylene with ethylene[1]	1.0
$\sim CHXCX_2CH_2CHY\sim$	Alternating copolymers of trisubstituted ethylenes and monosubstituted ethylenes[2,3]	1.0

[1]Hopff and Balint (1972).

[2]Hall and Daly (1975).

[3]Hall and Ykman (1977).

31

anhydride is far more reactive than trimethyl ethylene-tricarboxylate (Hall et al. 1981). Carbomethoxy and nitrile groups are largely coplanar, and would also have less steric hindrance. In addition, the increased tendency toward alternation seen in electron-rich/electron-poor olefin copolymerizations would favor incorporation of olefins bearing such substituents into copolymers with electron-rich comonomers.

A series of cyano and carboalkoxy-bearing tetra-substituted olefins were synthesized and their reactions with styrenes and vinyl ethers, particularly with regard to copolymerizability, were investigated. Ethylenes studied were tetramethyl ethylenetetracarboxylate (TMET), trimethyl cyanoethylenetricarboxylate (TCET), dimethyl dicyanofumarate (DDCF), diethyl dicyanofumarate, dimethyl 1,1-dicyanoethylene-2,2-dicarboxylate (DDED), dicarbomethoxymaleic anhydride (DCMA), and, briefly, diisopropylidene ethylenetetracarboxylate. Attempts to synthesize methyl tricyanoacrylate have thus far failed.

Hall and coworkers (1975, 1977) have, over the last ten years, successfully synthesized almost every possible permutation of CN- and CO_2CH_3 bearing trisubstituted ethylene. One isomer which had not previously been made is methyl 3,3-dicyanoacrylate (MDA). This trisubstituted olefin was synthesized and some of its chemistry studied.

CHAPTER 2

RESULTS

A series of tetrasubstituted electron-poor olefins
was synthesized and their copolymerizability with sytrenes
and vinyl ethers was studied. Four of the seven formed 1:1
copolymers (three spontaneously) with styrene. Methyl
3,3-dicyanoacrylate was found to behave as expected for a
trisubstituted electron-poor olefin, forming copolymers with
electron-rich comonomers. Polymerization was spontaneous
for styrene, but more electron-rich olefins gave only cyclo-
butanes unless initiated with AIBN.

Synthesis of Electron-Poor Olefins

Methyl Glyoxylate

This compound was prepared by the method of Dyroff
and Papanu (1980).
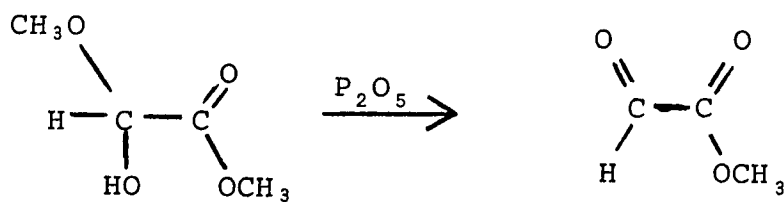
Carbonyl Cyanide

Carbonyl cyanide was prepared by the nucleophilic ring opening of tetracyanoethylene oxide (Linn, Webster, and Benson 1965).
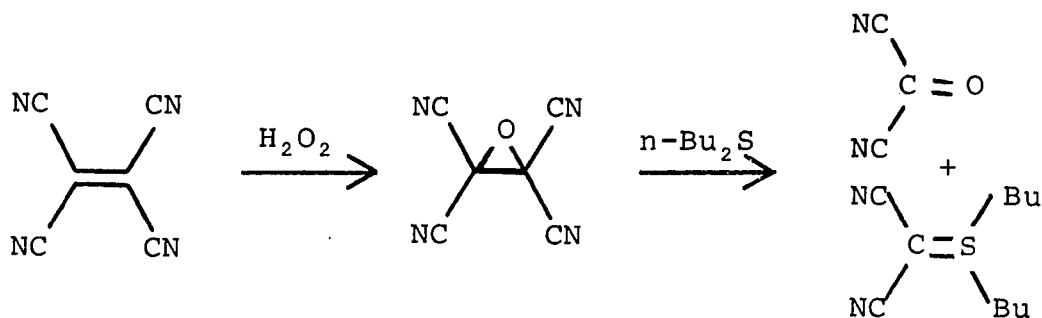
Dimethyl Ketomalonate

This compound was prepared by a method analogous to that used by Pardo and Salomon (1981) for diethyl ketomalonate.
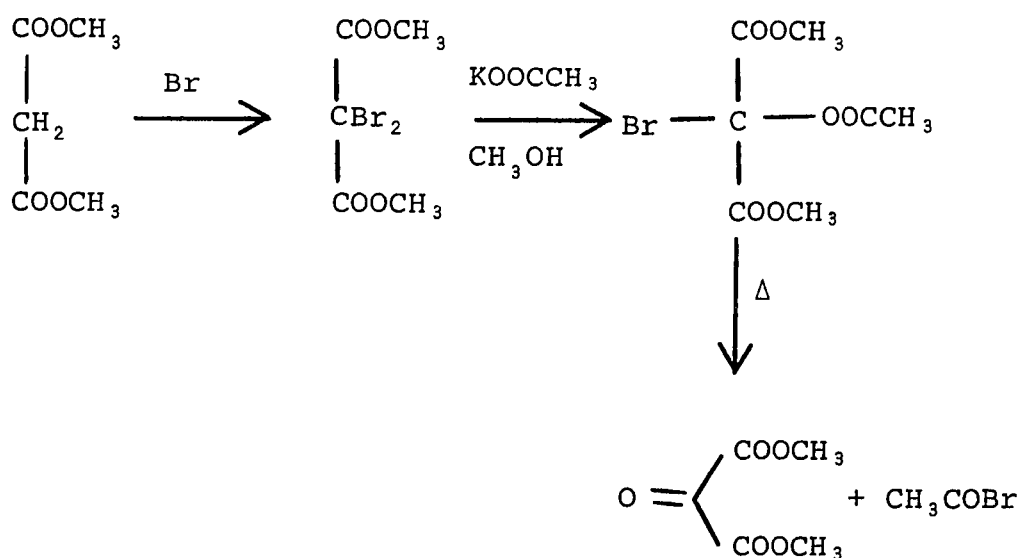
Methyl Cyanoglyoxylate

Attempts to synthesize this ketone from dimethyl dicyanofumarate oxide and n-butyl sulfide failed, as did pyrolysis of methyl acetoxybromocyanoacetate.

Tetramethyl Ethylenetetracarboxylate

TMET was readily prepared by dehydrobromination of dimethyl bromomalonate (Hall and Daly 1975).

$$
\begin{array}{c}
COOCH_3 \\
| \\
CHBr \\
| \\
COOCH_3
\end{array}
\xrightarrow[DMF]{K_2CO_3}
\qquad\qquad E = COOCH_3
$$
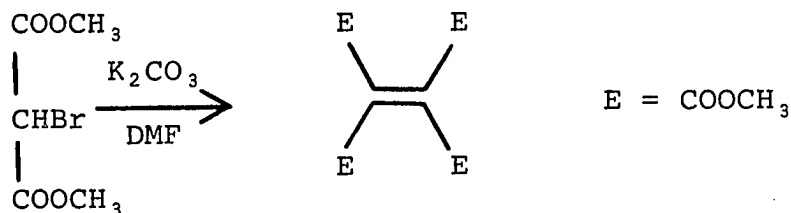
Trimethyl Cyanoethylenetricarboxylate and Dimethyl 1,1-Dicyanoethylene-2,2-dicarboxylate

These new olefins were prepared via Knoevenagel condensations between dimethyl ketomalonate and methyl cyanoacetate or malononitrile, respectively. A 5:1 ratio of ketone to malonate was found to optimize the yield of DDED; at 1:1 a second equivalent of malononitrile adds to olefin.

$$
\begin{array}{c}
CH_3OOC \\

\end{array}
\!\!\!\!\!\! = O \;\; + \;\;
\xrightarrow[C_6H_5CH_3]{\beta\text{-alanine}}
$$

R = CN, CO_2CH_3
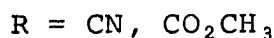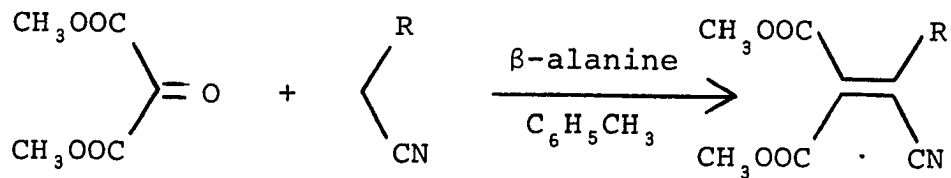
Dimethyl and Diethyl Dicyanofumarates

These olefins were made by the method of Ireland et al. (1976).
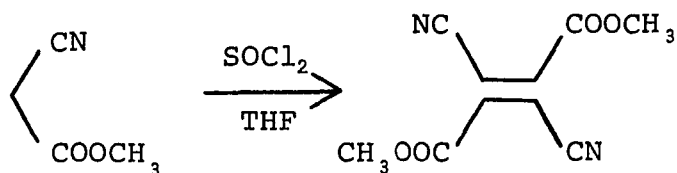
Diisopropylidene Ethylenetetracarboxylate

This ethylene was prepared in low yield by the method of Snyder and Kruse (1958).
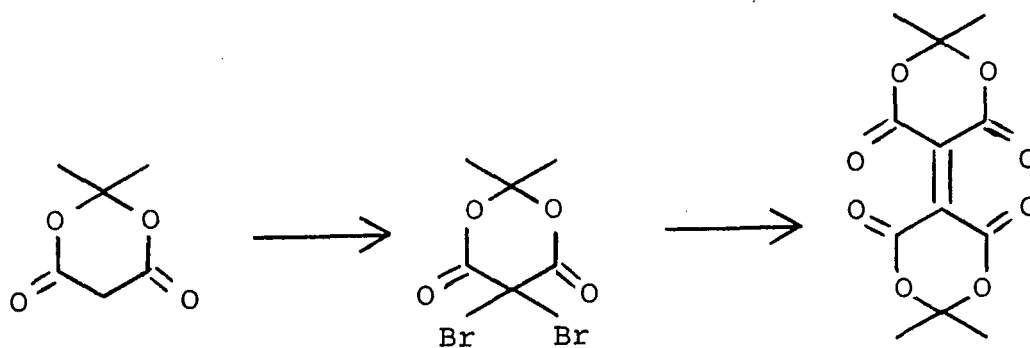
Dicarbomethoxymaleic Anhydride

DCMA was prepared from TMET in moderate yield by heating the latter in the presence of phosphorus pentoxide at 160°C for 24 hours.
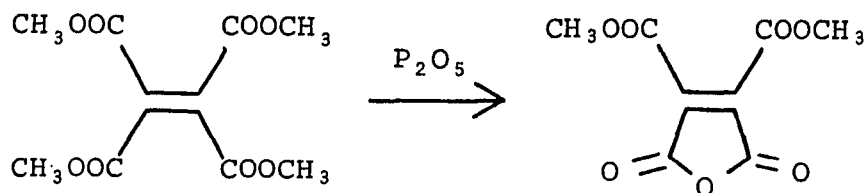
Methyl 3,3-Dicyanoacrylate

This new trisubstituted olefin was synthesized by a Knoevenagel condensation of methyl glyoxylate and malononitrile. A 1:1 ratio of reagents works for this condensation.

$$
\underset{COOCH_3}{\overset{CHO}{|}} \;+\; CH_2(CN)_2 \;\xrightarrow[C_6H_6]{\beta\text{-alanine}}\;
\underset{CH_3OOC}{\overset{H}{\diagdown}}C=C\underset{CN}{\overset{CN}{\diagup}}
$$
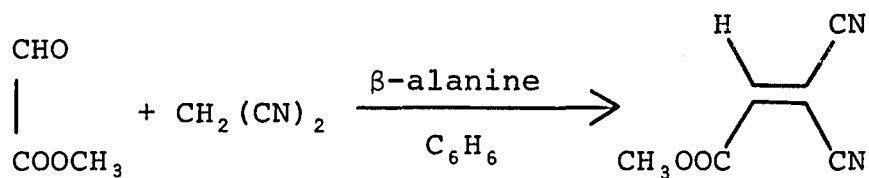
Dimethyl Cyanofumarate and Trimethyl Ethylenetricarboxylate

These compounds were synthesized by the literature method of Hall and Daly (1975).

$$
\underset{R}{\overset{CH_3OOC}{\diagdown}}CH_2 \;
\xrightarrow[\substack{2)\; BrCH_2COOCH_3 \\ 3)\; Br,CCl_4,UV \\ 4)\; N(C_2H_5)_3,\ ether \\ 0^\circ C}]{1)\; Na,CH_3OH}\;
\underset{R}{\overset{CH_3OOC}{\diagdown}}C=C\underset{COOCH_3}{\overset{H}{\diagup}}
$$

$$R = CN,\ CO_2CH_3$$
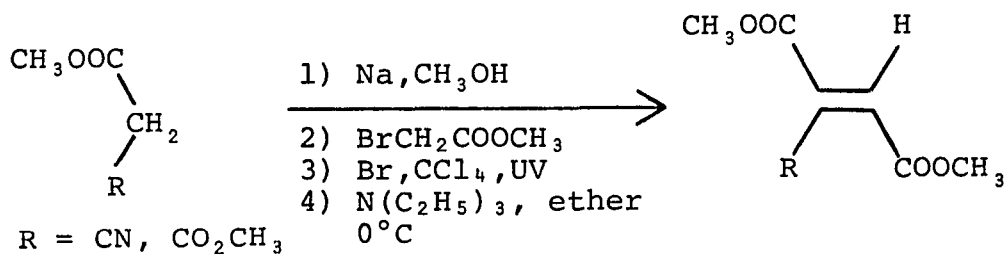
Dimethyl 2-Cyanoethylene-1,1-dicarboxylate

This compound was available in the laboratory. It had been prepared by the Wittig reaction of $((C_6H_5)_3PCH_2CN)Cl$ and dimethyl ketomalonate (Hall and Ykman 1977).

$$
\underset{COOCH_3}{\overset{COOCH_3}{\diagup\!\!\!\diagdown}}C=O \;+\; ((C_6H_5)_3P-CH_2CN)Cl \;\xrightarrow{NaOH}\;
\underset{CH_3OOC}{\overset{CH_3OOC}{\diagdown}}C=C\underset{H}{\overset{CN}{\diagup}}
$$
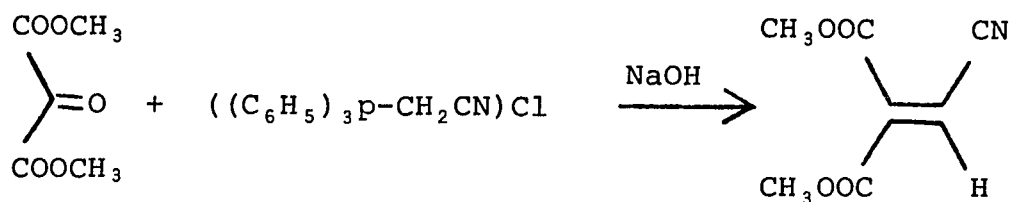
Tricyanoethylene

The precursor to tricyanoethylene, 1-bromo-1,1,2-tricyanoethane, was available in the laboratory. It was prepared by the method of Dickenson, Wiley, and McKusick (1960). Dehydrobromination of this compound at -78°C gave the desired olefin.
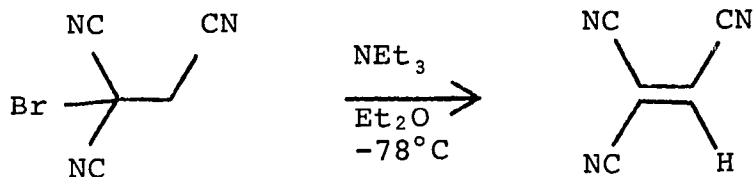
Methyl Tricyanoacrylate

Attempted condensation of methyl cyanoacetate and carbonyl cyanide failed.

Reactions of Tetrasubstituded Electron-Poor Olefins with Styrene and Vinyl Ethers

Tetramethyl Ethylenetetracarboxylate

TMET reacts very slowly with p-methoxystyrene and ethyl vinyl ether at 116°C to form cyclobutanes (Table 2).

$E = COOCH_3$
$R = CH_3CH_2O$, p-$CH_3OC_6H_4$
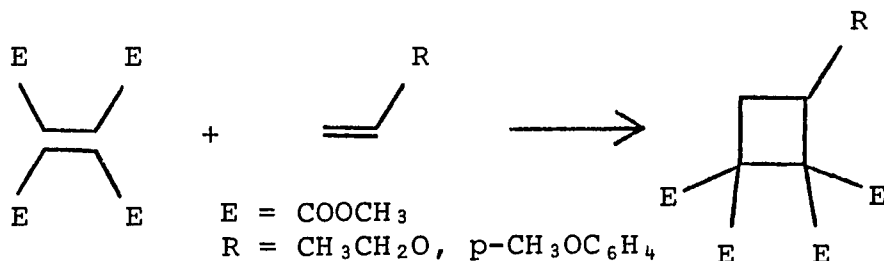
Table 2. Reactions of tetramethyl ethylenetetracarboxylate with electron-rich comonomers.

Electron-Rich Olefin	Feed Ratio[a]	Initiation	Temp. °C	Time Hrs.	% Yield[b] Copolymer	Cyclobutane
p-Methoxystyrene	1:1	None	116	65	0	9.3
Ethyl vinyl ether	1:2	None	116	24	0	26.2
Styrene	1:2	None	116	96	0	0.0
Styrene	1:2	Benzoyl Peroxide	116	24	0[c]	---
Styrene	1:2	AIBN	60	24	0	---

[a] TMET:comonomer

[b] Based on TMET

[c] Polystyrene only

Reactions run in bulk, degassed

No reaction with styrene was observed under these conditions, even after 96 hours. Some homopolystyrenes were isolated, as expected from prolonged heating of styrene at this temperature.

Initiation with AIBN at 60° or benzoyl peroxide at 116° failed to generate copolymers. No polymers were isolated at the lower temperature and only homopolystyrene at 116°.

Trimethyl Cyanoethylenetricarboxylate

TCET reacted with p-methoxystyrene and ethyl vinyl ether at 40°C to form pyran adducts (Table 3). Reaction with styrene required a higher temperature in order to proceed at a reasonable rate. Small amounts of low molecular weight copolymer formed during the reactions with styrenes.

Cycloadduct formation was still the dominant mode of reaction in the presence of radical initiation. Only small amounts of low molecular weight polymers were found in reactions run with AIBN.

$E = COOCH_3$

$R = CH_3CH_2O,\ C_6H_5,\ p\text{-}CH_3OC_6H_4$
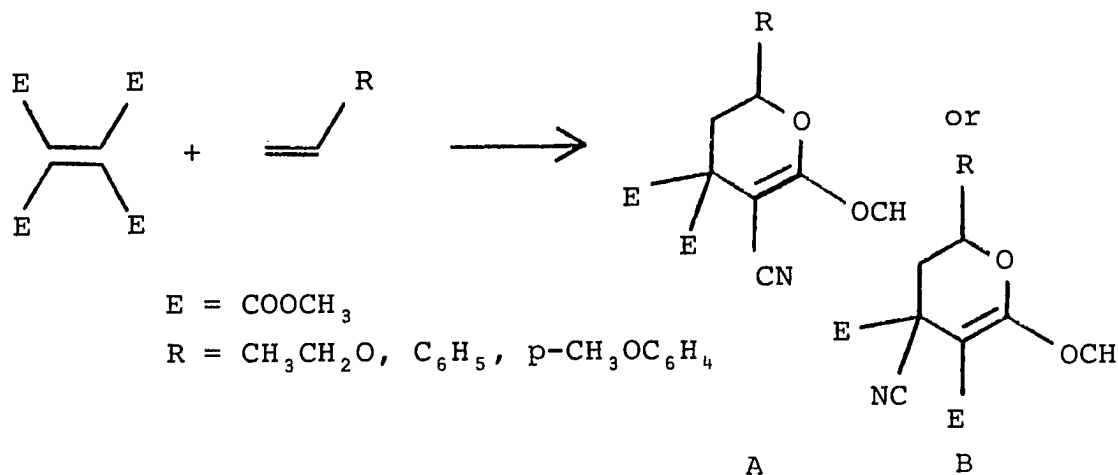
Table 3. Reactions of trimethyl cyanoethylenetricarboxylate
with electron-rich comonomers.[a]

Comonomer	Temp. °C	Time Hrs.	Initiation	% Yield Pyran[b]	% Yield Copolymer
Styrene	40	18	None	0(0)	0
Styrene	60	18	None	36(100)	trace
Styrene	60	18	AIBN	--(90)	10
p-Methoxystyrene	40	18	None	33(90)	5
Ethyl vinyl ether	40	18	None	--(100)	0

[a]1:1 Monomer feed, in bulk

[b]Isolated (NMR)

From the sharpness of the melting point, clean NMR spectra, and ease of recrystallization, it is clear only a single isomer of pyran was produced. Based on the assumption of a stepwise process for formation of these compounds and electronic control of the initially formed tetramethylene intermediate (see results for DDED and Discussion), structure A has been tentatively assigned. No experimental data is available, however, to allow unequivocal assignment of structure.

The pyrans are only somewhat stable at room temperature, turning gummy and intractable after two days. Heating the pyran adduct of TCET and styrene at 120° for 16 hours or running the reaction of TCET/styrene at 120° for 16 hours led to formation of a 1-butene. It is assumed the gummy product from the decomposition of the pyrans described above is a mixture of butene and pyran. (It is not polymeric, but ether soluble.)
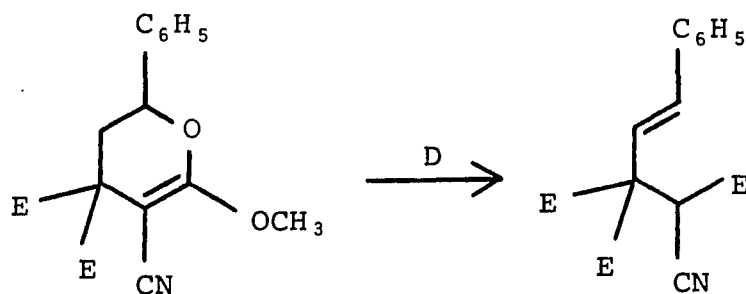
Dimethyl and Diethyl Dicyanofumarates

When heated together in bulk, dimethyl dicyano-
fumarate spontaneously copolymerized with the electron-rich
comonomers styrene, p-methoxystryene, or p-methylstyrene
(Table 4). The order of increasing polymer yield was
p-methylstyrene, p-methoxystyrene, styrene. The remainder
of the product consisted of pyran cycloadducts. Reaction
with vinyl ethers in bulk yielded only pyran adducts unless
initiated with AIBN. Attempted copolymerizations with the
less electron-rich comonomers methyl acrylate and vinyl
acetate resulted in no reaction.

$E = COOCH_3$

$R_1 = C_6H_5$, $p-CH_3C_6H_4$, $p-CH_3OC_6H_4$

$R_2 = OCH_2CH_3$, $OCH_2CH(CH_3)_2$
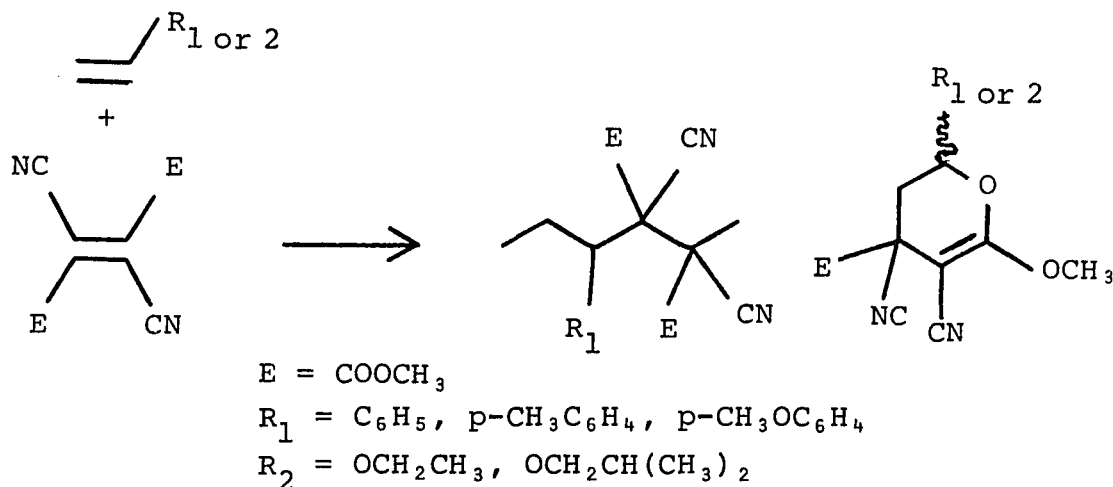
The optimum reaction temperature in each bulk case
was that at which complete liquefication of the reactants
occurred. Increasing reaction temperatures drastically
decreased the yield and molecular weight for the reaction
with p-methoxystyrene and led to discolored polymers in
all cases.

Table 4. Reactions of dimethyl and diethyl dicyanofumarates with electron-rich comonomers.[a]

Fumarate	Comonomer	Monomer Ratio[b]	Temp. °C	Time Hrs.	Initiation	Solvent	% Yield[c] Pyran[e]	% Yield[c] Copolymer	n_{inh}^{d} dl/g
Methyl	Styrene	1:1	150	2.5	None	None	--(71.1)	28.9	0.23
Methyl	Styrene	1:2	150	3.0	None	None	--(--)	16.7	0.12
Methyl	Styrene	1:3	150	3.0	None	None	--(--)	10.6	0.15
Methyl	Styrene	1:1	100	18.0	None	MeCN	30(100)	0.0	--
Methyl	Styrene	1:1	70	18.0	AIBN	MeCN	--(--)	20.4	0.09
Methyl	p-Methylstyrene	1:1	150	2.5	None	None	--(52.3)	47.7	0.28[f]
Methyl	p-Methylstyrene	1:1	70	18.0	AIBN	MeCN	--(--)	9.0	--
Methyl	p-Methoxystyrene	1:1	130	3.0	None	None	--(60.4)	39.6	0.22[g]
Methyl	p-Methoxystyrene	1:1	150	3.0	None	None	--(--)	12.9	0.18
Methyl	Ethyl vinyl ether	1:1	150	3.0	None	None	60(100)	0.0	--
Methyl	Ethyl vinyl ether	1:1	70	18.0	AIBN	MeCN	--(--)	21.4	0.15
Ethyl	Styrene	1:1	110	5.0	None	None	--(--)	23.1	0.16
Ethyl	Styrene	1:1	70	18.0	AIBN	MeCN	--(--)	7.6	--
Ethyl	p-Methylstyrene	1:1	110	5.0	None	None	--(--)	16.3	0.15

[a] 4 mmol fumarate as feed

[b] mmol fumarate:mmol comonomer

[c] Based on fumarate

[d] In acetonitrile

[e] Isolated (NMR)

[f] M_n (by VPO): 3300

[g] M_n (by VPO): 2400

For styrene a 1:1 monomer ratio gave best results.

No spontaneous polymerization occurred if the comonomers were dissolved in acetonitrile and heated overnight at 70°C, although cycloaddition did occur under these conditions. AIBN induced copolymerization in solution, but gave lower yields and viscosities than the bulk copolymerizations.

Both isomers of the pyran cycloadducts of DDCF and vinyl ethers could be seen in the NMR spectra. No attempt was made to separate the isomers. It was impossible to see distinct isomers in the pyrans from styrenes, but melting points of analytically pure samples were broad, so it is probable both isomers are also formed there.
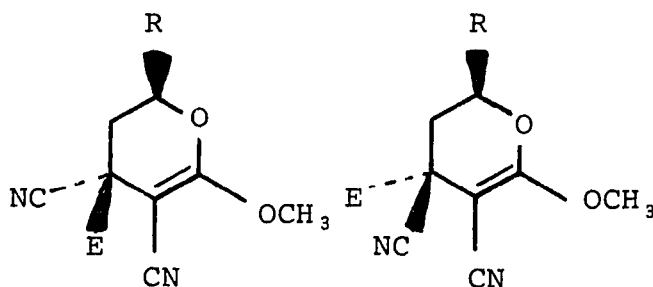
The pyrans of DDCF are comparatively very stable. That of DDCF/IBVE was stored at room temperature for several weeks without a change in melting point or NMR spectra. Others were stable at room temperature for at least two days.

Diethyl dicyanofumarate gave analogous results but with lower yields and molecular weights in all cases studied. A few examples are included in Table 4 for illustration.

The copolymers were obtained in moderate yields and molecular weights. The infrared absorptions of the carbonyl groups in these copolymers lay at higher energy than in the monomers indicating loss of unsaturation as expected.

Attempted homopolymerization of dimethyl and diethyl dicyanofumarate with 0.54 mrad X-radiation at ambient temperature (35°C) or at -78°C failed. No evidence for either polymer or cyclodimer formation was observed.

Dimethyl 1,1-Dicyanoethylene-2,2-dicarboxylate

DDED spontaneously formed 1:1 copolymer when reacted in bulk with styrene or p-methylstyrene at room temperature. Yields of about 60% were obtained and the 1:1 copolymers are of reasonable molecular weight (Table 5). Cyclobutane formation accompanied the polymerization.

E = COOCH$_3$

R = C$_6$H$_5$, p-CH$_3$C$_6$H$_4$, OCH$_2$CH$_3$
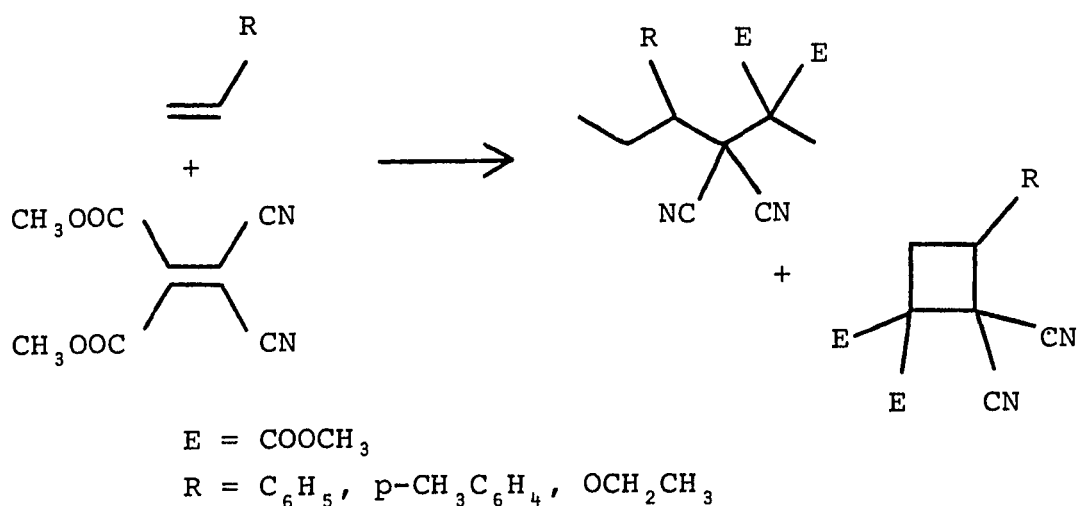
Table 5. Reactions of Dimethyl 1,1-dicyanoethylene-2,2-dicarboxylate with electron-rich comonomers.

Electron-Rich Olefin	Monomer Ratio[a]	Temp. °C	Time Hrs.	Solvent	Initiation	% Yield[b] Cyclobutane[d]	Copolymer	n_{inh}[c] dl/g
Styrene	1:1	25	8	None	None	-- (0)	0	--
Styrene	1:1	25	18	None	None	-- (21)	57	0.38
Styrene	1:2	25	18	None	None	-- (Trace)	48	0.23
Styrene	1:5	25	18	None	None	-- (--)	35	0.17
Styrene	1:1	25	18	MeCN	None	23 (--)	15	0.07
p-Methylstyrene	1:1	25	18	None	None	-- (28)	39	0.32
p-Methylstyrene	1:1	25	18	MeCN	None	56[e] (--)	Trace	--
p-Methoxystyrene	1:1	25	8	None	None	10 (73)	Trace[f]	--
p-Methoxystyrene	1:1	25	18	None	None	-- (33)	0[f]	--
p-Methoxystyrene	1:1	60	18	MeCN	None	39 (--)	0	--
p-Methoxystyrene	1:1	60	18	MeCN	AIBN	-- (--)	42	0.22
Ethyl vinyl ether	1:1	25	8	None	None	97 (100)	0	--
Ethyl vinyl ether	1:1	60	18	MeCN	AIBN	-- (--)	30	0.25
Ethyl vinyl ether	1:1	60	18	None	AIBN	-- (--)	47	0.32
Isobutyl vinyl ether	1:1	25	18	None	None	95 (100)	0	--
Isobutyl vinyl ether	1:50	40	336	None	None	-- (--)	0[g]	--
p-Methoxystyrene	1:50	25 40	168 168	None	None	-- (--)	0[g]	--

[a]DDED:comonomer
[b]Based on DDED
[c]In MeCN
[d]Isolated (NMR)
[e]Impure
[f]Poly-p-methoxystyrene was formed in this reaction.
[g]Attempts to initiate cationic polymerization.

Addition of solvent effectively stopped the poly-merization. Cyclobutane formation proceeded but the rate was very slow. High yields of cyclobutane could be obtained by heating to 50°. Some oligomerization also occurred under these conditions.

No pyran cycloadducts resulting from (4+2) cyclo-additions were observed under any conditions.

With p-methoxystyrene in bulk, DDED reacted to form cyclobutane and poly(p-methoxystyrene). The polymer is oligomeric and the yield is low.

Ethyl or isobutyl vinyl ethers gave only cyclobutane formation, no spontaneous polymerizations occurring. Addi-tion of AIBN to these reactions in bulk, acetonitrile, or benzene led to formation of 1:1 copolymer.

Orientation of DDED in (2+2) cycloadditions. Of the two possible cyclobutanes formed by the reaction of DDED with electron-rich olefins, C and D, structure C has been assigned based on the following observations:

C   D
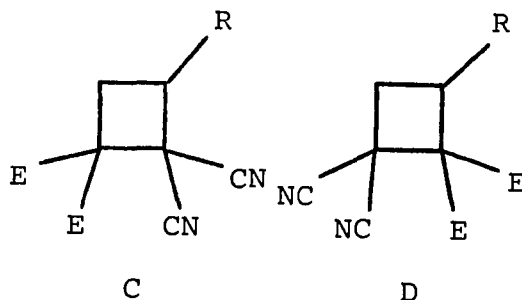
a) In the mass spectrum of the cyclobutanes formed in the reaction of DDED with isobutyl or ethyl vinyl ether, or styrene, the metathesis products were observed. Only
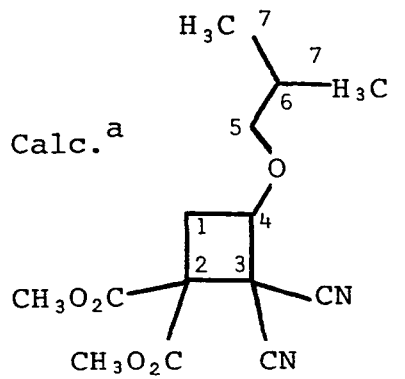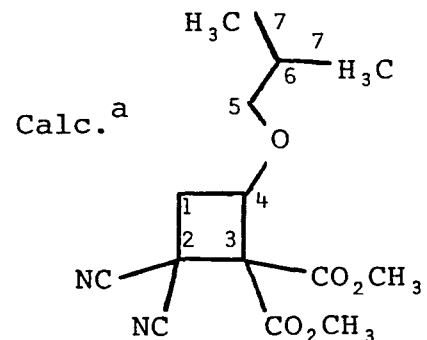
products of the form $(RCHC(CN)_2)^{+}_{\cdot}$ were recorded. Although these peaks are never large (10% for styrene), the complete absence of ions of the structure $(RCHC(COOCH_3)_2)^{+}_{\cdot}$ in all cases is strong evidence for structure C.

b) The chemical shifts in the ^{13}C-NMR spectra of the cyclobutanes do not agree with the values calculated using the method of Levy, Lichter, and Nelson (1980) (Table 6). The spectra do, however, support structure C. For the cyclobutane from DDED and isobutyl vinyl ether, the signals for the carbonyl carbons appear at 166.9 and 165.9 ppm; the nitrile carbons 112.6 and 110.8 ppm. The greater difference in chemical shift for the nitrile signals implies these groups are closer to the point of dissymmetry as in structure C.

c) In the ^{1}H-NMR spectra of several dimethyl α-aryl cyclobutane-1,1-dicarboxylates, one of the ester methyl groups is shifted upfield due to interaction with the aromatic ring current (Hall and Abdelkader 1981). This shift is not seen in the spectra of the cyclobutanes obtained from DDED and several styrenes.

d) Most acrylates carrying·an additional electron-withdrawing group in the α-position form dihydro-2H-pyran adducts with electron-rich olefins (Hall, Rasoul et al. 1982). Thus trimethyl ethylenetricarboxylate, dimethyl cyanofumarate, dimethyl dicyanofumarate, and dimethyl 2-cyanoethylene-1,1-dicarboxylate all form pyrans with

Table 6. Calculated and experimental ^{13}C shifts of cyclobutanes from reaction of DDED with IBVE.

	1 (t)	2 (s)	3 (s)	4 (d)	5 (t)	6 (d)	7 (q)	CN (2)	CO (2)	OCH$_3$ (2)(q)
Calc.[a]	42.6	56.1	32.4	73.3	77.0	27.1	20.6	-	-	-
Calc.[a]	42.6	32.1	56.4	73.3	77.0	27.1	20.6	-	-	-
Exp.	35.9	41.7 52.9		78.9	77.4	28.7	19.3	112.6 110.8	166.9 165.9	54.7 54.0

[a]For method of calculation, see Levy, Lichter, and Nelson (1980).

vinyl ethers and either pyrans or Wagner-Jauregg adducts with styrene. Such adducts have never been observed in the reactions of DDED, implying that in the transition state the two ester groups do not face the electron-rich substituent; the orientation of the two olefins before a reaction will be as in C', and not as in D'.
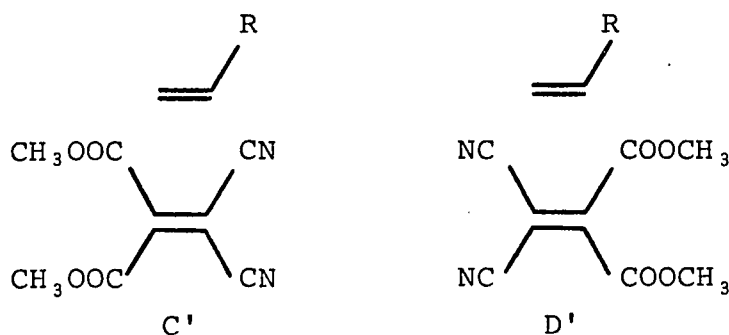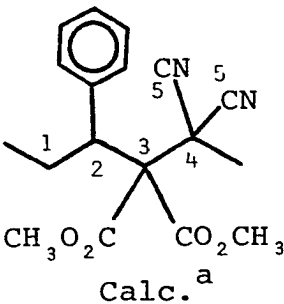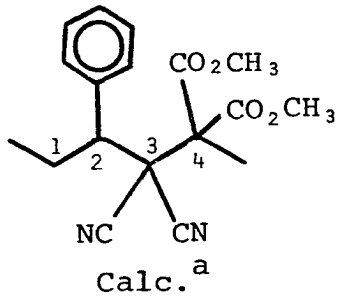
Orientation in the copolymers. There are two possible stereochemistries for an alternating copolymer of DDED and styrene, E and F:

$E = COOCH_3$
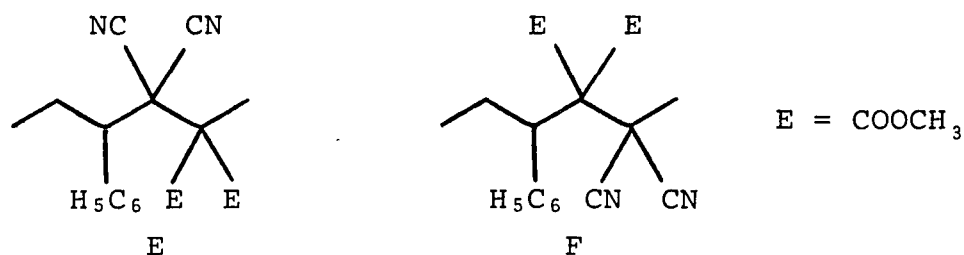
The normal methods used to distinguish between such structures are NMR techniques. Unfortunately the ^{1}H-NMR spectra of E and F are expected to be indistinguishable. Calculations of expected chemical shifts for the backbone carbons via the "additivity rules" of Levy, Lichter, and Nelson (1980) are given in Table 7. The expected values for the two orientations are very similar. In addition,

Table 7. Calculated and experimental ^{13}C shifts of alternating copolymers of DDED and styrene.

	1	2	3	4	CO	CN	Ar	OCH$_3$
Calc.[a]	37.7	33.3	59.8	34.1	–	–	–	–
Calc.[a]	37.7	33.4	35.8	58.1	–	–	–	–
Experimental[b]	46.9	40.8		53.3 69.2	168.3 167.9	114.9 112.1	134.6 132.6 130.0	53.7

[a]For method of calculation, see Levy, Lichter, and Nelson (1980).

[b]In DCCl$_3$, shifts relative to TMS.

experimental and calculated shifts show little correlation. Similar deviations were observed for alternating copolymers of trisubstituted olefins with styrene (Table 8) and p-methoxystyrene (Hall and Gillard 1981).
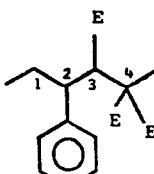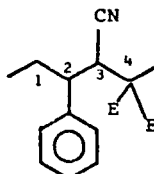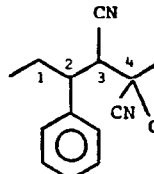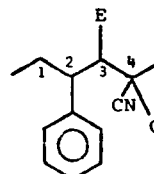
Examination of the data in Table 8 shows that both polymers containing two ester groups in the γ-position have a carbonyl signal at 168-9 ppm. That these polymers contain a characteristic carbonyl peak is not unreasonable since in both cases the signal arises from a carboxyl on a geminal bis carboxylate framework and lies embedded in a sterically congested polymer. There may be a characteristic nitrile signal at 111-112 ppm for polymers containing two cyano groups in a γ-position compared to the phenyl group. Both observations are highly tentative, each being based on two model compounds, but provide the only basis on which to assign an orientation to the DDED/styrene copolymer.

The observed carbonyl signals from the DDED copolymer fall at 167.9 and 168.3 ppm. This correlates well with the carbonyl signals of copolymers of the trisubstituted olefins (Table 9). The cyano shifts at 114.9 and 112.1 do not correlate as well. Based on these observations, orientation E has been assigned to the copolymer.

This assignment assumes the fourth substituent has little effect on the observed carbonyl shift by either steric or electronic effects. This is not too unreasonable. The high degree of substitution along the polymer chain has

Table 8. ^{13}C NMR spectra of copolymers of styrene and trisubstituted electron-poor olefins.

	1	2	3	4	CO	OCH$_3$	CN	Ar
	41.1[a] (38.5)[b]	39.8 (25.8)	42.5 (46.5)	59.0 (60.1)	171.8 169.6	51.6 51.3	–	127.4 130.4 126.5
	45.7 (38.5)	39.4 (25.8)	39.6 (34.5)	58.8 (60.1)	167.6	52.4	117.6	128.4 139.6
	44.6 (38.5)	35.9 (25.8)	36.5 (34.5)	40.3	–	–	112.6 113.3	128.2
	43.8 (38.5)	36.3 (25.8)	56.7 (46.5)	37.4 (36.1)	168.6 168.4	53.5	112.4 112.8	134.5 129.4

E = COOCH$_3$

[a] Experimental value - in DCCl$_3$, relative to TMS.

[b] Calculated value - for method of calculation, see Levy, Lichter, and Nelson (1980).

Table 9. ^{13}C NMR shifts of carbonyl and cyano carbons in copolymers of styrene and electron-poor olefins.

	C=O	CN
CH_3O_2C–CH=C(CO_2CH_3)CO_2CH_3	169.6 168.6 171.8 171.4	--
NC–CH=C(CO_2CH_3)CO_2CH_3	168.2 168.8	117.5
CH_3O_2C–CH=C(CN)CN	168.6 168.4	112.4
NC–CH=C(CN)CN	--	112.6 113.3
$(NC)_2C$=C(CO_2CH_3)CO_2CH_3	168.4 167.9	114.9 112.1

led to a sterically congested polymer where the normal additivity rules are no longer applicable, even for the trisubstituted olefins. Replacement of hydrogen by the sterically undemanding cyano groups should not produce much change in the polymer conformation, and the inductive effect of such a group three bonds away is also expected to be quite small (Levy et al. adjust an alkyl shift by -1 ppm for a C-3 nitrile).

It must be admitted that assignment of structure based on the above type of argument are not definitive, but this assignment is based on the only presently available data. Unequivocal assignment of structure will have to await ^{13}C labeling experiments or some other more definitive approach.

Dimethyl Dicarbomethoxymaleic Anhydride

DCMA was mixed with various electron-rich olefins and the products of the spontaneous reactions were examined.

With most styrenes (including p-methoxystyrene, anethole, divinylbenzene, and diphenylethylene), double Diels-Alder adducts, the so-called "Wagner-Jauregg adducts," were obtained:

R = H, CH$_3$

E = COOCH$_3$
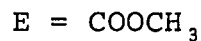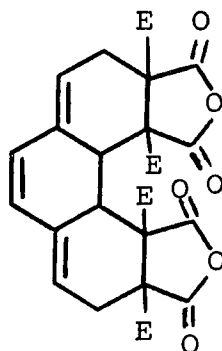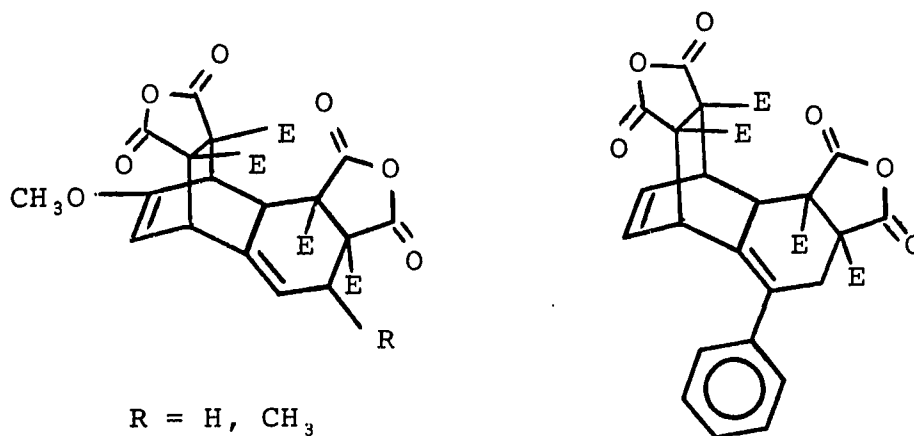
With styrene itself and isobutyl vinyl ether, an inverse electron demand Diels-Alder reaction occurred involving one of the carbonyl groups in the (4+2) cycloaddition leading to the dihydropyran derivatives G and H respectively.

G

H
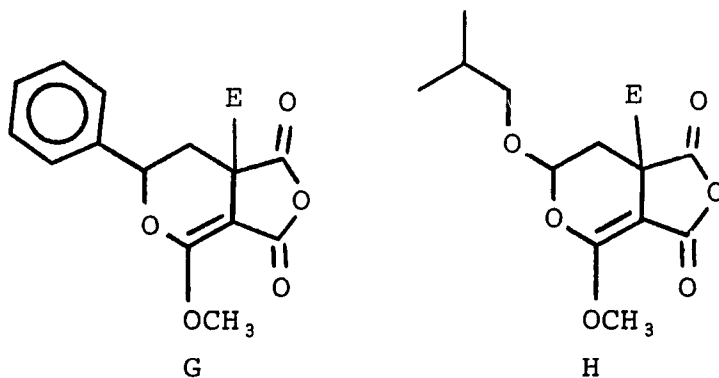
With 2,5-dichlorosytene no reaction occurs.

Isoprene added smoothly to DCMA to give the expected cycloadduct. The reaction followed second-order kinetics with a second order rate constant at 35° of 0.075 M^{-1} sec^{-1}. This is smaller by a factor of 4 than the corresponding value for CMA, which has been more accurately determined in this work (k_2 = 0.293 M^{-1} sec^{-1}).
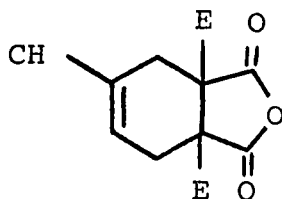
While no polymer forms spontaneously in any of these reactions, 1:1 copolymer was formed with styrene in the presence of AIBN at 80°C. A mixture of 50% polymer, 50% pyran was formed. At lower temperatures the yield of polymer decreased until at 60° only pyran was isolated.

Upon standing for several weeks at room temperature or several days at higher temperature, the pyran was slowly converted to copolymer. Molecular weights in polymers so formed were extremely low, the polymers being soluble in diethyl ether.

No copolymer was formed under analogous conditions with p-methoxystyrene. The DCMA was incorporated into 2:1 adduct and any remaining methoxystyrene homopolymerized.

Diisopropylidene Ethylenetetracarboxylate

Attempted copolymerization of this cyclic tetra-ester with styrene failed. No spontaneous polymerization

occurred at 60°C after 18 hours. Addition of AIBN under similar conditions initiated polystyrene polymerization with no incorporation of the tetraester. No attempt was made to determine if cycloadduct formation had occurred.

Reactions of Methyl 3,3-Dicyanoacrylate with Styrenes and Vinyl Ethers

MDA spontaneously copolymerized with sytrene, p-methylstyrene, and p-methoxystyrene when reacted in bulk at 25°C (Table 10). About 50% conversion to polymer was observed. Unlike with other electron-rich/electron-poor olefin pairs, little cycloadduct accompanied these polymerizations. The copolymers were essentially 1:1 alternating and the composition was independent of the monomer feed ratio.

Addition of solvent slowed the polymerization enough for cyclization to compete. When equimolar amounts of MDA and p-methoxystyrene were reacted in bulk, the ratio of polymer to cyclobutane was 2:1, when 1 mmole each was diluted with 2 ml acetonitrile, the ratio become 1:7; in 5 ml acetonitrile polymerization no longer occurred. Molecular weights of the copolymers also decreased in more dilute polymerization conditions.

Reaction with vinyl ethers produced exclusively cyclobutanes. Copolymerization could be initiated with AIBN.

Attempts to initiate the cationic polymerization of isobutyl vinyl ether and p-methoxystyrene with catalytic

Table 10. Reactions of methyl 3,3-dicyanoacrylate with electron-rich comononers.[a]

Electron-Rich Comonomer	Monomer Ratio[b]	Solvent	Initiation	% Yield[c] Cyclobutane[d]	% Yield[c] Copolymer	dl/g[e]
Styrene	1:1	None	None	--(0)	49.6	0.54
Styrene	1:2	None	None	--(0)	15.0	0.40
Styrene	1:1	MeCN	None	43(80)	0	--
p-Methoxystyrene	1:1	None	None	--(27)	63.0	0.59
p-Methoxystyrene	1:1	None	MeCN[f]	43(70)	9.0	--
p-Methoxystyrene	1:1	None	MeCN[g]	41(75)	0.0	--
p-Methylstyrene	1:1	None	None	--(42)	59.0	0.52
Ethyl vinyl ether	1:1	None	None	96(100)	0.0	--
Ethyl vinyl ether	1:1	MeCN	AIBN	--(--)	45.0	0.46
Isobutyl vinyl ether	1:1	None	None	89(100)	0.0	--
Isobutyl vinyl ether	1:50[h]	None	None	--(--)	0.0	--
p-Methoxystyrene	1:50[h]	None	None	--(--)	0.0	--

[a] All reactions run at 25°C for 18 hours; 1 mmol MDA

[b] MDA;Comonomer

[c] Based on MDA

[d] Isolated(NMR)

[e] In acetonitrile

[f] 2 ml solvent

[g] 5 ml solvent

[h] Attempts to initiate cationic polymerization

amounts of MDA failed. No polymer formation was seen in either case after 48 hours, well after all MDA had reacted, presumably to cyclobutane.

CHAPTER 3

DISCUSSION

The discussion will cover three aspects of the pre-
ceding results: First, the copolymerizability of tetra-
substituted olefins; secondly, the nature of the spontaneous
reactions with respect to the structure of the initially
formed tetramethylene intermediate; finally, the synthetic
routes used in this work.

Copolymerizability of Tetrasubstituted Electron-Poor Olefins

Steric Factors

Dimethyl dicyanofumarate, dimethyl 1,1-dicyano-
ethylene-2,2-dicarboxylate, and dicarbomethoxymaleic
anhydride underwent 1:1 copolymerization with electron-rich
comonomers, while tetramethyl ethylenetetracarboxylate and
diisopropylidene ethylenetetracarboxylate failed completly
to show incorporation into copolymers, and trimethyl cyano-
ethylenetricarboxylate formed extremely low molecular weight
oligomers. Florianczyk and coworkers (1981) recently
reported that dimethylmaleic anhydride forms alternating
copolymers with styrenes.

X-ray crystal structure determinations have been performed on DDCF and TMET (Hall, Reineke et al. 1982). These results, summarized in Table 11 and Figures 2 and 3, showed that dimethyl dicyanofumarate is a largely planar molecule, with the carbonyl oxygens lying only 9° above and below the olefin framework. This leaves the olefin double bond relatively open for attack by the incoming radical. TMET, on the other hand, retains a high degree of steric hindrance to approach toward the olefin, as two of the carbonyl groups are forced 92° out of the olefin plane. Copolymerization can only occur where the cyano or ester groups are truly minimizing steric problems, a situation not seen in TMET.

That the cis ester groups provide significant steric interference had earlier been demonstrated by Lewis and Mayo (1948). They compared the reactivity of cis and trans diester, dichloro-, and dicyanoethylenes toward styrene. For the dichloro- and dicyanoethylenes, the less thermodynamic isomer was more the reactive, as expected if the intermediates for the two isomers are assumed to be similar. However, dimethyl fumarate, while being more stable, was also more reactive than dimethyl maleate. Again the intermediates formed should be similar, so it was concluded that the cis ester groups were retarding reaction through steric effects.

Table 11. Torsion angles for TMET and DDCF.

| TMET | | DDCF | |
Atoms	Torsion Angle	Atoms	Torsion Angle
C(3)-O(2)-C(2)-O(1)	5.7	C(3)-O(2)-C(2)-O(1)	4.3
C(3)-O(2)-C(2)-C(1)	-177.7	C(3)-O(2)-C(2)-C(1)	-175.5
C(5)-O(4)-C(4)-O(3)	-0.4	C(4)-C(1)-C(2)-O(1)	170.7
C(5)-O(4)-C(4)-C(1)	178.9	C(4)-C(1)-C(2)-O(2)	-9.5
C(4)-C(1)-C(2)-O(1)	84.3	C(1')-C(1)-C(2)-O(1)	-9.1
C(4)-C(1)-C(2)-O(2)	-92.4	C(1')-C(1)-C(2)-O(2)	170.7
C(1')-C(1)-C(2)-O(1)	-91.9	C(2)-C(1)-C(4)-N	2.2
C(1')-C(1)-C(2)-O(2)	91.3	C(1')-C(1)-C(4)-N	-178.0
C(2)-C(1)-C(4)-O(3)	-167.2	C(2)-C(1)-C(1')-C(2')	-180.0
C(2)-C(1)-C(4)-O(4)	13.5		
C(1')-C(1)-C(4)-O(3)	9.2		
C(1')-C(1)-C(4)-O(4)	-170.2		
C(2)-C(1)-C(1')-C(2')	180.0		

[a]The torsion angles for A-B-C-D are defined as positive for clockwise rotation of C-D toward A-B while looking along the B-C bond.

[b]Primed atoms are symmetry related atoms.

[c]Hall, Reineke, et al. (1982).
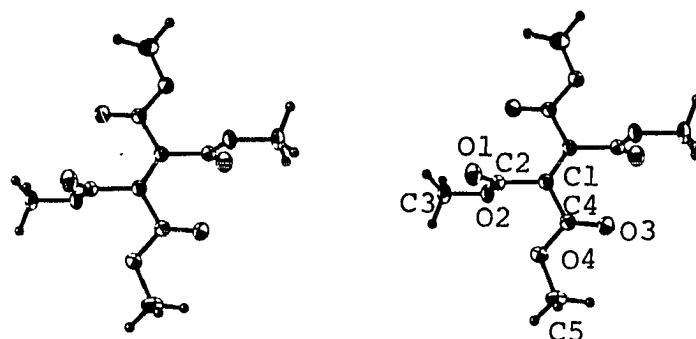
Figure 2. ORTEP stereoscopic view and numbering of TMET.

The hydrogen atoms have been assigned arbitrary thermal parameters. Ellipsoids enclose 30% of the probability distribution (Hall, Reineke et al. 1982).
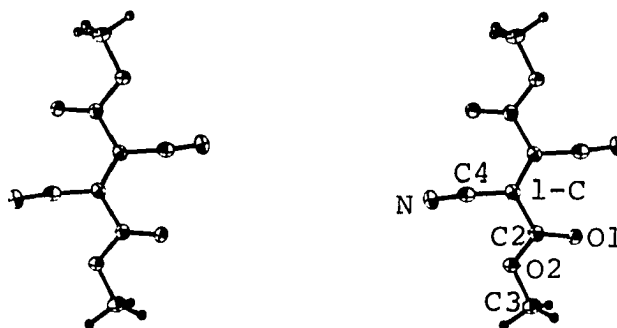
Figure 3. ORTEP stereoscopic view and numbering of DDCF.

The hydrogen atoms have been assigned arbitrary thermal parameters. Ellipsoids enclose 30% of the probability distribution (Hall, Reineke et al. 1982).

Formation of a maleic anhydride moiety evidently allows more freedom for the remainder of the substituents. In TMET and TCET the cis ester groups prevent polymerization, while DCMA, even with two remaining cis ester groups, can polymerize. It is doubtful that DCMA is planar, but it is probable that only one ester group is forced out of the plane and not as many steric problems are encountered by the incoming radical.

Steric problems are still high even in the systems that do form copolymers. This is manifested by low propagation rate constants, allowing termination and cyclization reactions to successfully compete. The low molecular weights are a direct result, as are the higher cycloadduct: copolymer ratios seen for the tetrasubstituted ethylenes versus trisubstituted analogues. In systems spontaneously copolymerizing, 50:50 ratios are the lowest obtainable for tetrasubstituted olefins; cycloadducts can only be isolated from trisubstituted olefins if inhibitors are added to prevent polymerization. Low ceiling temperatures are the result of the substantial steric congestion in the polymers after they have formed.

Orientation of DDED in Copolymers
with Electron-Rich Comonomers

Of the two possible orientations of DDED in its copolymer with styrene, orientation E has been tentatively

assigned, based on ^{13}C-NMR chemical shifts of the carbonyl and cyano carbons.
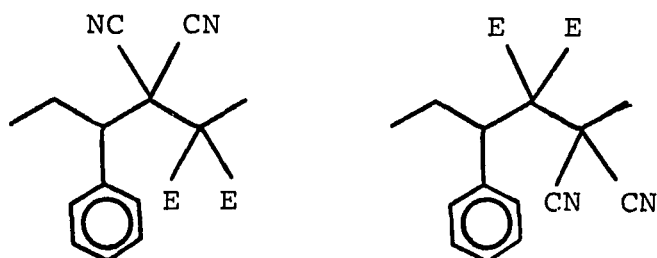
Orientation E is sterically favored, arising from attack of the secondary styryl radical at the less sterically congested dicyano carbon. Orientation F is electronically favored, the site β to the cyano groups being more electrophilic than that β to the esters. The assigned structure has the orientation in the copolymer determined by the steric considerations.

As already noted, steric factors are critical in determining whether propagation will proceed for tetrasubstituted olefins. Another example where steric factors are decisive is seen in the reactions of dimethyl dicyanofumarate and trimethyl ethylenetricarboxylate (Hall and Daly 1975). These trisubstituted olefins copolymerize with ethyl vinyl ether and styrene, but not with diethyl ketene acetal or α-methylstyrene. The latter are even more electron rich, but the increased steric effects are more than enough to overcome the favorable electronic effects and prevent polymerization.

Approach of the bulky styryl radical to the more electrophilic diester carbon of the olefin is sterically impeded and, as for TMET, will not occur. This forces propagation to proceed through attack at the dicyano site, where steric problems are lower.

Charge-Transfer Complexation

These electron-poor tetrasubstituted olefins, like the trisubstituted ethylenes studied earlier, form colored charge-transfer complexes with styrenes and vinyl ethers. These complexes are probably involved in the propagation. The discussion above concerning the orientation of DDED is an oversimplification, the results arising from rearrangement of the complex, not approach of free monomer to a reacting radical. The factors governing the direction of the rearrangement would remain essentially the same.

Summary

Tetrasubstituted electron-poor olefins can undergo copolymerization with electron-rich comonomers only if steric hindrance in the transition state has been largely removed. This occurs only if the carbonyl group can become essentially coplanar with the olefin framework, a situation not generally possible for most maleate species. Cyclization of tetraester to dicarbomethoxymaleic anhydride allows at least one of the ester groups to be coplanar, allowing

this olefin to copolymerize even though it still contains a pair of cis carbomethoxy groups.

The orientation of DDED in the copolymerization reaction is governed by steric factors. Reaction of the bulky styryl radical occurs at the sterically free dicyano site, allowing the sterically demanding diester to interact with the totally unhindered site of the styrene or vinyl ether.

Spontaneous Reactions of Electron-Poor and Electron-Rich Olefins

The results of these experiments are more consistent with tetramethylene intermediate theory than ion-radical formation and will be discussed in these terms.

Ionic versus Biradical Tetramethylenes

The spontaneous reactions observed from a given electron-poor/electron-rich olefin pair reflect the nature of the initially formed tetramethylene intermediate. Only biradical intermediates can initiate copolymerization, while zwitterionic intermediates cyclize or initiate homopolymerization of the electron-rich component.

The nature of the intermediate is determined by the nature of the substituents on both termini of the butane moeity, but especially on the electron-rich portion. No cases of spontaneous copolymerization have been reported for vinyl ethers, implying that their tetramethylenes are highly

zwitterionic. For styrene, being much less electron rich, biradical character is more favorable, and many electron-poor olefins spontaneously copolymerize with styrene. p-Methoxystyrene is intermediate in its electron-donating ability; the nature of the tetramethylenes is determined by the electron-acceptor at the other terminus.

The identity of the electron-withdrawing groups is also important, but less so than that of the electron-acceptor. Cyano groups tend to favor ionic intermediates, but biradical species ending with a dicyano terminus are not uncommon. Stille and Chung have demonstrated that the electron-rich comonomer determines the nature of the tetramethylene intermediates for vinylidene cyanide, with its dicyano groups favoring ionic species. The intermediates with vinyl ethers are indeed ionic, but that with styrene is a biradical. Replacing a cyano group with an ester will make biradical formation still less unfavorable, ionic intermediates occurring only with extremely electron-rich comonomers like vinyl ethers. Dimethyl cyanofumarate spontaneously copolymerizes with p-methoxystyrene; this tetramethylene remains a biradical.

β Substituent Effects

The nature of the tetramethylene intermediate is not a function exclusively of the substituents at the terminal carbons, but is also influenced by groups in the β position.

The spontaneous reactions of TCNE, DDED, MDA, and tricyano-
ethylene illustrate this point. All have a dicyano terminus,
yet tetramethylenes formed during reaction with styrenes
range from entirely ionic for TCNE and tricyanoethylene to
entirely biradical for MDA. DDED falls somewhere in between,
forming a biradical intermediate with styrene and an ionic
intermediate with p-methoxystyrene.

$$\begin{array}{c}
\text{CN} \\
X \diagdown \quad | \quad * \\
\diagup \quad \diagdown \text{CN} \\
Y \diagdown \\
\quad * \\
\text{Ar}
\end{array}$$
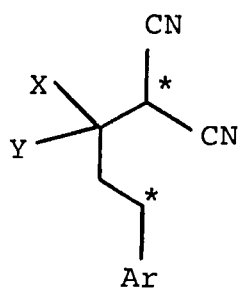
X = CN; Y = H,CN   X = COOCH$_3$; Y = H   X = Y = COOCH$_3$
Ar = C$_6$H$_5$,C$_6$H$_4$OCH$_3$ Ar = C$_6$H$_5$,C$_6$H$_4$OCH$_3$ Ar = C$_6$H$_5$
* = +/−   * = ↑/↓   * = ↑/↓

X = Y = COOCH$_3$
Ar = C$_6$H$_4$OCH$_3$
* = +/−

Another example of structural changes away from the
termini affecting the nature of the intermediates is pro-
vided by a comparison of the trimethylene and tetramethylene
intermediates possessing a styryl and an α cyano carbo-
methoxy termini. The tetramethylene species is best
described as a biradical (Rasoul 1981), while the analogous
trimethylene intermediate is Cram's classic zwitterionic
intermediate (Chmurny and Cram 1973).

COOCH
CN

COOCH
CN
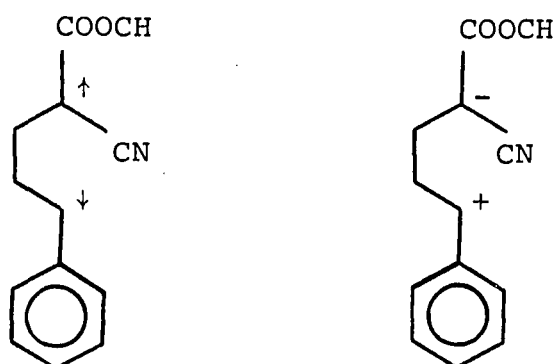
Spontaneous Polymerizations

Biradical tetramethylene intermediates commonly initiate radical copolymer propagation, while only one example, p-methoxystyrene/DDED, of ionic polymerization by zwitterionic intermediates was observed. These results can be understood by a consideration of the conformational mobility of the intermediate.

As described in the introduction, 1,4-zwitterions exist predominantly as self-solvating ion pairs. The butane nucleus is locked into a cisoid conformation, with the dipolar termini in close proximity to each other. Such a species interacts only slightly with the comparatively non-polar free monomer, and closes to cyclobutane before it can be trapped by reaction with monomer. Spontaneous ionic polymerization can only occur if the reaction medium, either solvent or monomer, can solvate the zwitterion well enough to enable it to leave the cisoid conformation and allow reaction with monomer to proceed.

1,4-Biradicals, on the other hand, are relatively free to adopt any conformation. There is a fairly high amount of transoid butane present, which can interact with monomer to initiate polymerization. The intermediate is not locked in an unreactive conformation, as is the case for highly ionic intermediates.
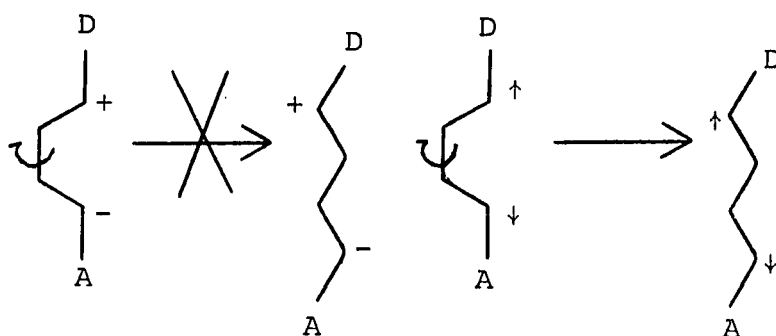
Orientation of Tetramethylenes of
Dimethyl 1,1-Dicyanoethylene-
2,2-dicarboxylate

The structure of the cyclobutane isolated gives a direct insight into the structure of the initially formed tetramethylene intermediate. Isomer C, arising from tetramethylene H below, has been proven to be the only cyclo-adduct produced from reactions of DDED, meaning tetramethylene formation proceeds to form the electronically favored intermediate. H is more stable because of increased resonance with the two cyano groups of the zwitterionic form of the tetramethylene, while I is sterically favored with initial bond formation occurring at the less sterically

CN · · · · E · · · · E
E · · · · * · · · · NC · · · · *
E—· · CN · · · · NC—· · E
· · * · · · · · · · *
· · | · · H · · I · · |
· · R · · · · · · · · R
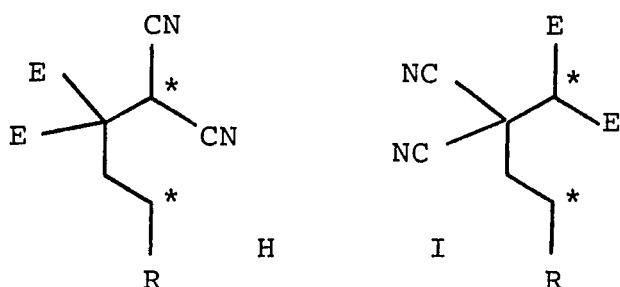
congested dicyano site. Electronic factors are more impor-
tant in determining the tetramethylene structure.

There are two significant differences between tetra-
methylene formation, which is electronically controlled, and
propagation, in which the orientation was said to be con-
trolled by steric factors:

1) Propagation involves interaction of the bulky
styryl radical with DDED, while tetramethylene formation
involves the unhindered CH_2 group of the electron-rich
olefin. The steric problems encountered during the approach
of the styryl radical between the two ester groups would be
much larger than in approach by the relatively small methyl-
ene (see structures below). While steric hindrance prevents
reaction of the styryl radical at the dicarbomethoxy site,
forcing it to react at the less electronically favorable
dicyano carbon, no such problem exists for the methylene
and reaction can occur where electronically favored.

2) Tetramethylenes possess more zwitterionic charac-
ter than propagating radicals and resonance stabilization
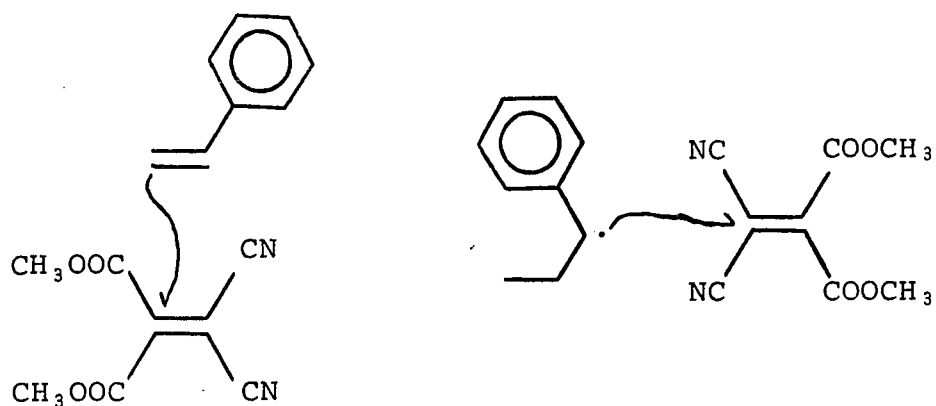
should be more important in determining the stability of
the transition states during their formation. Intermediates
from vinyl ethers are "pure" zwitterions, and even those
from styrene will have some ionic character, so the dipolar
nature of the transition state is rather large. Resonance
factors are important in stabilizing these real charges, as
opposed to their role in radical propagation where they are
more dipole/dipole interactions.

Cycloadduct Formation

DDED, TMET, and MDA react with electron-rich olefins
to form, in addition to any copolymer, cyclobutanes as the
only cycloadduct. Cyclobutanes can arise from formation of
both biradical and ionic tetramethylenes and provide little
information about the intermediate.

Cyclohexanes were not produced in any of these
reactions.

TCET and DDCF react with electron-rich olefins to form 6-alkoxy-3,4-dihydro-2H-pyrans. DCMA produces similar products with vinyl ethers and styrene. This reaction has been shown to be quite general for acrylates bearing an α electron-withdrawing group (Hall, Rasoul et al. 1982). The pyrans are unstable, undergoing ring opening followed by oligomerization or hydrogen transfer to form the more stable 1-butene. Pyrans of the tetrasubstituted olefins are, however, more stable than those from trisubstituted analogues, being isolable and stable at 25°C for several days. The pyran from the reaction of DDCF and isobutyl vinyl ether remained intact for several weeks at this temperature.

The mechanism of pyran formation has not been demonstrated, but preliminary results suggest a stepwise process involving a biradical tetramethylene intermediate. Ring opening of isolated pyrans leads to 1-butenes or oligomerization, no starting materials ever being isolated. Hall and Gillard (1981) trapped a biradical intermediate with $CBrCl_3$ during the ring opening of a pyran adduct. It is possible a rapid, reversible concerted reaction is responsible for pyran formation, but such a pathway fails to explain why only products of a stepwise process are isolated by the reverse reactions.
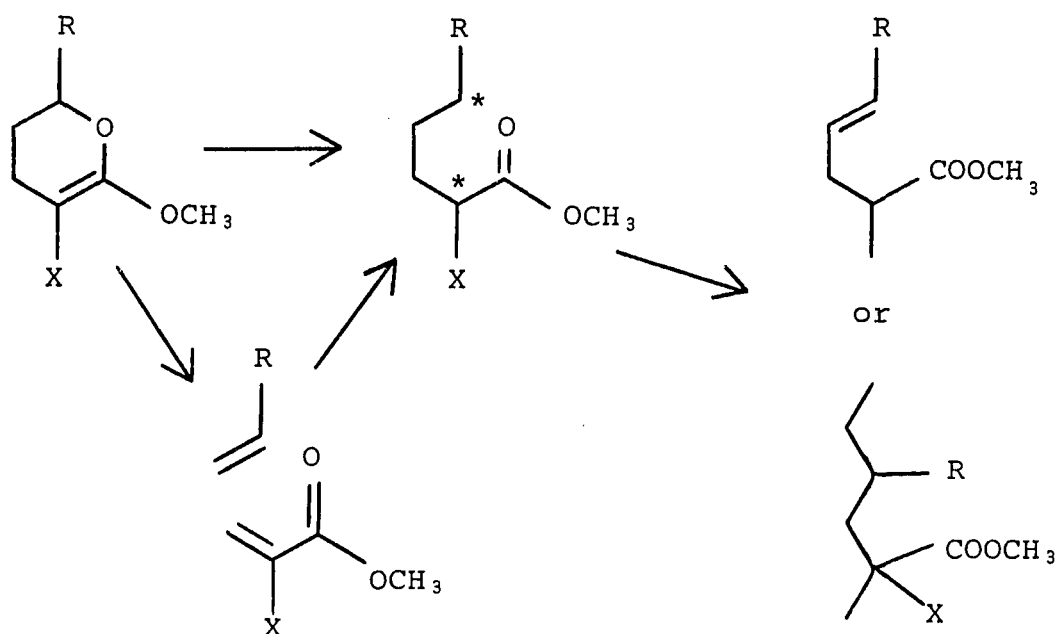
With more electron-rich styrenes, DCMA forms 2:1
Diels-Alder adducts, the so-called Wagner-Jauregg adducts
(Wagner-Jauregg 1981). Small changes in the structure of
the styrene cause a major shift in the course of the reac-
tion. That more electron-rich styrenes prefer the Wagner-
Jauregg pathway is clear, but the reasons behind this
preference are not.

Another situation where very slight structural
changes lead to a drastic change in reaction pathway was
reported by Shirota et al. (1977) for the reaction of TCNE
with 1-vinylnaphthalene, indene, and acenaphthalene. The
latter two undergo a 2+2 stepwise cycloaddition to cyclo-
butane, while 1-vinylnaphthalene adds in a concerted 2+4
fashion across the styrene-like vinyl diene to form a

cyclohexane, as in the first step of Wagner-Jauregg adduct formation. As with DCMA, small changes in the identity of the electron-rich olefin cause a shift from a stepwise to concerted process.
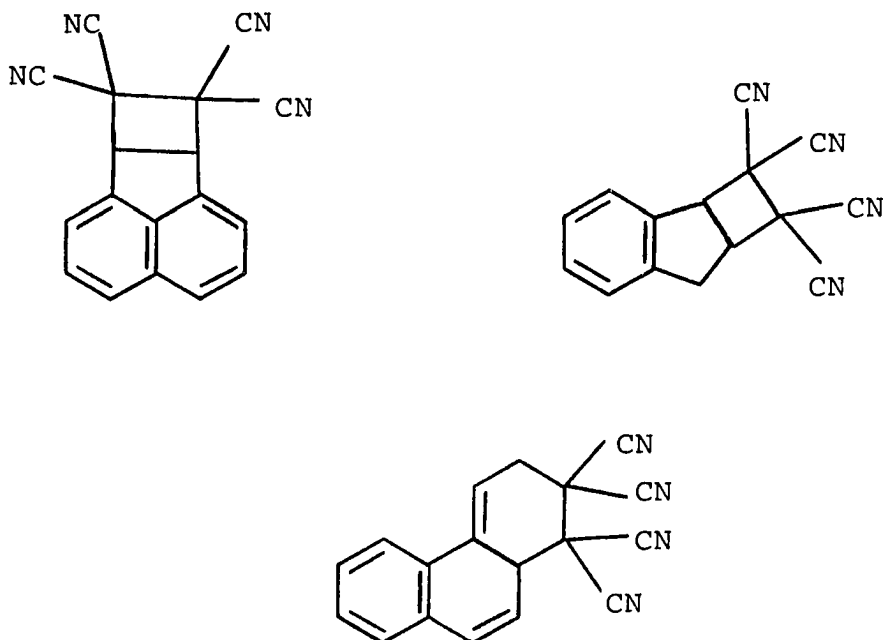
Notes on Syntheses

Dimethyl Ketomalonate

The procedure used was a modification of that developed by Pardo and Salomon (1981), itself a derivative of the method of Faust and Mayer (1976). The original method called for flash distillation at 300°C, a procedure requiring a large Wood's metal bath. Attempts to substitute passage through a heated pyrolysis tube gave only low yields of the desired ketoester.

The present procedure works well. There are,
however, several aspects which should be noted. Since trace
amounts of hydrogen bromide inhibit the acetylation which
follows, all traces of HBr must be rigorously removed by
passage of dry nitrogen through the molten dibromomalonate.
As HBr is apparently quite soluble in $CBr_2(COOCH_3)_2$, this
takes about six hours (heating overnight at 90°, with stir-
ring, failed to remove the HBr). Secondly, the addition of
the first aliquot of potassium acetate must be done extremely
slowly. Too rapid an addition will cause an excessive
frothing and a rapid pressure buildup.

Methyl Cyanoglyoxylate

Tetracyanoethylene oxide reacts with nucleophiles
by undergoing carbon-carbon bond cleavage (Linn et al. 1965).
This leads to a convenient synthetic approach to carbonyl
cyanide. This reaction is possible because the two geminal
groups increase the susceptibility of the carbons to nucleo-
philes and allows the formation of stable anions. This
reaction failed for dicyanofumarate oxide, which apparently
undergoes normal carbon-oxygen ring opening. The ester
groups are not electron-withdrawing enough to activate the
carbons for this unusual reaction.

Knoevangel Condensations

In the synthesis of the tetrasubstituted olefins,
it was necessary to use an excess of ketomalonate in order

to isolate the desired olefin. These ethylenes are very electrophilic and would add another molecule of malononitrile under the reaction conditions if 1:1 stoiciometry were used. The 2:1 adduct is probably a propane derivative, as identified by Corson, Hazen, and Thomas (1928). Similar reactions have been reported for TCNE under both acidic and basic catalysis (Ciganek, Linn, and Webster 1970).
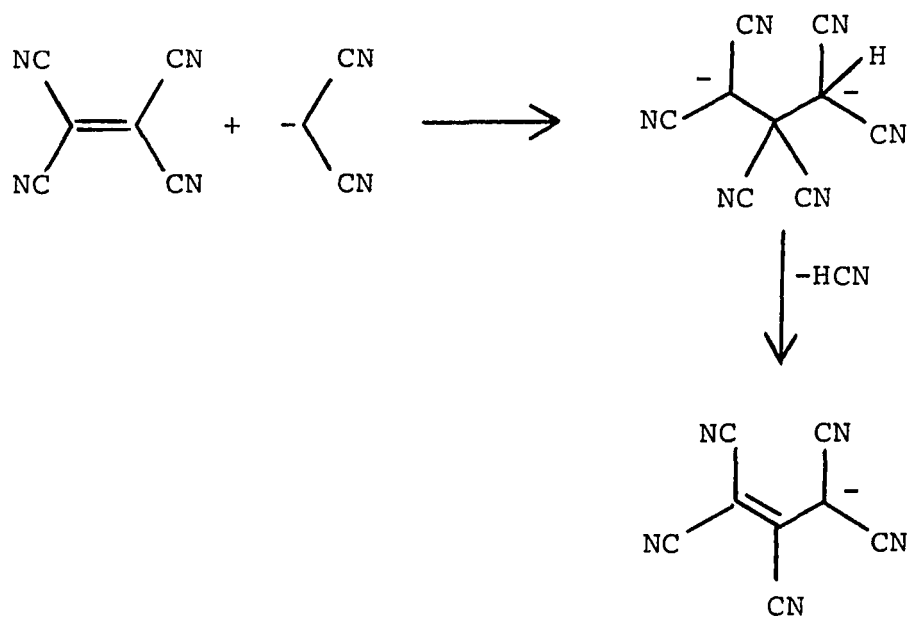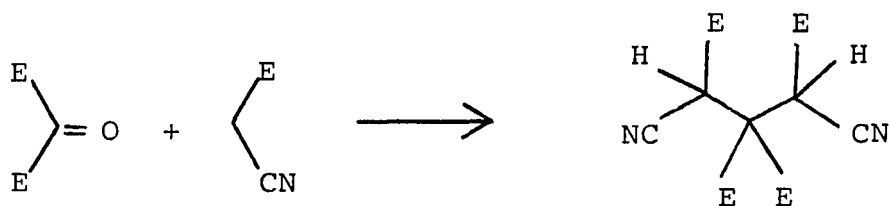
CHAPTER 4

SUMMARY AND CONCLUSIONS

Tetrasubstituted electron-poor olefins can copolymerize with electron-rich comonomers if the steric hindrance to approach of the bulky secondary radical can be alleviated. This is possible for olefins that do not contain cis carbomethoxy groups, and for maleic anhydrides in which the olefin carbon atoms are left comparatively unhindered.

While copolymerization is a function of steric factors, the spontaneous reactions are under the control of electronic factors. The tetramethylene intially forms by bond formation to the sterically undemanding methylene of the electron-rich olefin and steric factors are much less important than they are for reactions involving the relatively large propagating radicals.

The nature of the tetramethylene is determined principally by the electron-rich comonomer. Vinyl ethers form zwitterionic intermediates; the biradical character increases as the electron-richness of the comonomer decreases. The electron-withdrawing groups at the other terminus have an influence on the nature of the tetramethylene in borderline cases, as do substituents in the β position.

81

Zwitterionic tetramethylene intermediates do not initiate ionic polymerization well because they are locked in cisoid conformations. Biradicals, on the other hand, are free to rotate to the more efficient trans conformation, and are very good at initiating radical copolymerization.

Zwitterionic intermediates can collapse to cyclobutanes, as can biradical intermediates. Pyrans are often the major product of reactions of acrylates with α electron-withdrawing substituents, but the reaction path can be diverted to a concerted reaction route by changes in the electron-rich monomer.

CHAPTER 5

EXPERIMENTAL

Instrumentation

All boiling points and melting points are uncorrected. Capillary melting points were determined on a Thomas-Hoover melting point apparatus. Inherent viscosities were determined with an Ostwald-Fenske Viscometer. Number average molecular weights were measured with a Hewlett-Packard 5930A vapor pressure osmometer.

Proton nuclear magnetic resonance spectra were obtained on Varian EM360 or T60 spectrometers. ^{13}C nuclear magnetic resonance spectra were obtained on a Brucker WH-90.

Mass spectra were obtained on a Varian 311A mass spectrometer with data acquisition done by a Varian SS200. Infrared spectra were taken on Perkin-Elmer 337 spectrophotometers.

Elemental analyses were performed by the University Analytical Center, Department of Chemistry, University of Arizona and by Micanal, Tucson, Arizona.

Electron-Rich Olefins

Electron-rich olefins were purchased from Aldrich. They were distilled from calcium hydride and stored under argon at -10°C before use.

83

Solvents

Solvents were all commercially available reagent grade. Acetonitrile was distilled from calcium hydride immediately before use. Anhydrous diethyl ether was bought from Mallinkrodt and used as received.

NMR solvents were from Norell and all shifts are relative to TMS, expressed in Δ.

Reagents and Chemicals

All chemicals used were reagent grade and commercially available. They were used as received except where noted before.

Methyl glyoxylate methyl hemiacetal was provided by Monsanto Company. Malononitrile, from Aldrich, was distilled and stored at -10°C in a brown bottle.

Synthesis of Electron-Poor Olefins

Tetramethyl Ethylenetetracarboxylate

TMET was synthesized by the method of Hall and Daly (1975). 132.12 g (1 mole) dimethyl malonate was dissolved in 150 ml CCl_4 and brominated with 53 ml Br_2 under UV light. The solvent was removed and the reaction mixture distilled to give 201 g dimethyl bromomalonate (bp 62°C, 0.20 torr). This intermediate was stirred overnight at 25°C with a slurry of 171 g K_2CO_3 and 500 ml DMF. The mixture was filtered, and the DMF removed under aspirator vacuum.

Recrystallization from ethyl acetate gave 36.6 g (56%) pure TMET (mp = 118.5-119.5°C).

Diethyl and Dimethyl Dicyanofumarate

Diethyl dicyanofumarate was prepared by the method of Ireland et al. (1976). Tetrahydrofuran (10 ml) was added to thionyl chloride (12 ml, 0.168 mole, redistilled from triphenyl phophite) followed by dropwise addition of ethyl cyanoacetate (10 ml, 0.1 mole). The reaction mixture was then refluxed with stirring for 3 hours and left at room temperature for 18 hours. The solid diethyl dicyanofumarate was collected and purified by repeated recrystallization from ethanol. Yield 52%, mp 116-117°C.

Dimethyl dicyanofumarate was prepared analogously. Yield 55% after recrystallization from absolute methanol, mp 175-176°C, NMR (CD$_3$CN): 3.97 (s); IR (KBr): 2950, 1740, 1440, 1380 cm^{-1}; anal. calc'd for C$_8$H$_6$O$_4$N$_2$: C, 57.13; H, 6.17; N, 9.52, found: C, 57.88; H, 6.14; N, 9.70.

Dimethyl 1,1-Dicyanoethylene-
2,2-dicarboxylate and Trimethyl
Cyanoethylenetricarboxylate

Dimethyl ketomalonate. In a modification of Pardo and Salomon (1981), 330.3 g (2.5 mol) dimethyl malonate was placed in a 3L 3-neck flask with mechanical stirrer, reflux condenser, and dropping funnel. Bromine (850 g, 5 mole) was added dropwise rapidly, then heated to 60° for

60 minutes, 88° for 60 minutes, and cooled to 55°. Dry

argon was bubbled through the reaction slurry overnight.

The reaction was diluted with 500 ml anhydrous

methanol. Five aliquots of dry potassium acetate, the first

52 g in 150 ml methanol, 2 through 5 50 g in 100 ml methanol

were added over a four hour period, then refluxed overnight.

After filtration to remove KBr, the methanol was removed

under aspirator vacuum. Vacuum distillation (45-47°C,

0.05 torr) of the impure acetyl bromomalonate gave 3.7 g

(87%) dimethyl ketomalonate. NMR (CDCl$_3$): 4.0 (s).

Dimethyl 1,1-dicyanoethylene-2,2-dicarboxylate.

Dimethyl ketomalonate (46.8 g, 0.32 mol), 5.28 g (0.08 mol)

malononitrile, 3.00 g glacial acetic acid, 0.72 g β-alanine,

and 70 ml toluene were refluxed using a Dean-Stark trap for

24 hours. The toluene was removed under aspirator vacuum

and the remaining solution vacuum distilled.

Unreacted ketomalonate was collected as the first

fraction, 60% being recovered.

DDED was collected at 75-76°C (0.05 torr). The pale

green liquid was redistilled to give (0.07 mol, 88%) pure

product. ^{1}H-NMR(CDCl$_3$): 3.9 (s). ^{13}C-NMR(DMSO-d$_6$): 159.5

(CO), 109.4 (CN), 97.5, 93.8 (C=C), 54.5 (OCH$_3$). IR(neat,

NaCl): 2995, 2230, 1740, 1610 cm^{-1}. Anal. calc'd. for

C$_8$H$_6$O$_4$N$_2$: C, 50.01; H, 2.10; N, 14.58. Found: C, 49.57;

H, 2.07; N, 14.45.

<u>Trimethyl cyanoethylenetricarboxylate</u>. 16.23 g

(0.11 mole) dimethyl ketomalonate and 10.00 g (0.10 mole)

methyl cyanoacetate were refluxed 24 hours in 30 ml benzene

using a Dean-Stark trap to remove H_2O and 0.24 g β-alanine

with 1.0 g acetic acid catalyst. Chilling the reaction

mixture at -10°C leads to crystallization of crude TCET.

Recrystallization from acetonitrile gave 10.5 g (80%) pure

TCET. mp = 77-78°C. NMR(CDCl$_3$) 3.9 (s). Anal. calc'd.

for $C_9H_9NO_6$: C, 47.58; H, 3.99; N, 6.17. Found: C, 47.35;

H, 4.01; N, 6.16.

Dicarbomethoxymaleic Anhydride

Tetramethyl ethylenetetracarboxylate (15.0 g) and

10 g of phosphorous pentoxide were mixed in a closed flask

and heated to 160°C for 24 hours. The solid black residue

was allowed to cool and then vacuum distilled. bp 105-110°C

(0.05 torr). The crude DCMA was recrystallized from diethyl

ether. mp 75-76 C. Yield: 3.4 g (27%). NMR(CDCl$_3$): 4.0

(s). IR(KBr): 1860, 1790, 1720, 1660 cm^{-1}. Anal. calc'd.

for $C_8H_6O_7$: C, 45.0; H, 2.84. Found: C, 45.2; H, 2.9.

Diisopropylidene Ethylenetetracarboxylate

This olefin was made by the method of Snyder and

Kruse (1968). 14.4 g (0.1 mole) isopropylidene malonate

was dissolved in 100 ml 2N NaOH at 0°C. 10.3 ml (0.2 mole)

Br$_2$ was added dropwise with stirring, forming a brownish

solid. This was washed with H_2O twice, extracted into

benzene, and the benzene removed under aspirator vacuum.
11 g (36%) isopropylidene dibromomalonate was produced.
(mp = 74-75°C; lit. 75-76°.)

10.0 g (0.03 mole) isopropylidene dibromomalonate
was dissolved in 100 ml DMF and left stirring at 25° for
24 hours. Filtration gave crude product (9%), which was
used without further purification. Decomposed about 200-
210°C (lit: d, 215-225). NMR(acetone-6): 1.4 (s).

Methyl 3,3-Dicyanoacrylate

To methyl glyoxylate methyl hemiacetal (12.00 g,
0.1 mole) 5.68 g (0.04 moles) P_2O_5 was added in five por-
tions and stirred for 30 minutes. Distillation through a
30 cm fractionating column under aspirator vacuum yielded
pure methyl glyoxylate, 42-54°.

Methyl glyoxylate (8.8 g, 0.1 mole), 3.3 g (0.05
mole) malononitrile, 20 ml benzene, 0.20 g β-alanine, and
0.80 g glacial acetic acid were refluxed 18 hrs in a Dean-
Stark apparatus. Benzene and unreacted glyoxylate were
removed under aspirator vacuum and the remaining liquid
distilled under vacuum through a 30 cm fractionating column.
MDA was collected at 53-55°C (0.05 torr). Yield: 3.24 g
(38%). NMR (CDCl$_3$): 7.2 (s,1H); 3.9 (s,3H). IR (NaCl,
neat): 2224, 1740, 1600 cm^{-1}. Anal. calc'd. for $C_7H_7O_4N$:
C, 4971; H, 4.17; N, 8.28. Found: C, 49.56; H, 4.14;
N, 8.30.

Trisubstituted Electron-Poor Olefins

Trimethyl ethylenetricaboxylate and dimethyl cyano-
fumarate were prepared by the method of Hall and Daly (1975).

Dimethyl 2-cyanoethylene-1,1-dicarboxylate was
available in the lab.

The precursor to tricyanoethylene, 1-bromo-1,1,2-
tricyanoethane, was available in the lab. 1.67 g of the
ethane was dissolved in 9 ml anhydrous diethyl ether and
chilled to -78°. Triethylamine (0.86 g) in 9 ml ether was
added with rapid stirring. Filtration and removal of sol-
vent produced a granular orange solid. Vacuum sublimation
(0.05 torr) of this solid gave white crystals of tricyano-
ethylene, mp 39-40°. This is a modification of the procedure
of Dickenson et al. (1960).

General Reaction Procedures

General Procedure for Bulk Reactions

The electron-poor comonomer (1 mmol) was weighed
into a 10 ml Pyrex reaction tube and frozen at -78°. The
electron-rich comonomer was added by syringe, and the system
placed under vacuum for three minutes. The Pyrex tube was
then sealed, the reaction mixture allowed to thaw, and
stirred overnight at the desired temperature.

The reaction products were dissolved in chloroform
and polymers precipitated with diethyl ether. After

filtration, the polymers were redissolved in chloroform, and reprecipitated with anhydrous methanol.

The ether from the original precipitation was removed by rotoevaporation. Any nonvolatile residue was dissolved in deuterated chloroform. If the NMR spectrum indicated small molecules other than starting materials to be present, the solution was placed under 0.5 torr vacuum for several hours to remove unreacted styrene (or vinyl ether) and the production characterized by NMR.

General Procedure for Solution Reactions

The procedure followed was essentially as above except 2 ml dry acetonitrile or benzene was added and frozen between addition of the electron-poor and electron-rich olefins. AIBN was also added at this time, where appropriate. Workup was as above.

Copolymers

Yields and viscosities of the copolymers of tetra-substituted electron-poor olefins (as well as those of MDA) are presented in Tables 3, 4, 5, and 10. The ^{13}C NMR spectrum for the copolymer of DDED and styrene is given in Table 7, and those of model copolymers from trisubstituted olefins in Table 8.

Analyses of these copolymers are presented as Tables 12 and 13.

Table 12. Analyses of copolymers of tetrasubstituted electron-poor olefins.

Electron-Poor Olefin	Electron-Rich Olefin	Analysis Calculated	Found
TCEI for $C_{17}H_{17}O_6N$	Styrene	C, 61.63 H, 5.17 N, 4.23	C, H, N,
DDCE for $C_{16}H_{14}O_4N_2$	Styrene	C, 64.43 H, 4.70 N, 9.40	C, 64.93 H, 4.92 N, 9.20
DDCE for $C_{17}H_{16}O_4N_2$	p-Methylstyrene	C, 65.37 H, 5.16 N, 8.97	C, 65.02 H, 4.99 N, 8.63
DDCE for $C_{17}H_{16}O_5N_2$	p-Methoxystyrene	C, 62.19 H, 4.91 N, 8.53	C, 61.89 H, 4.97 N, 8.42
DDCE for $C_{12}H_{14}O_5N_2$	Ethyl vinyl ether	C, 54.13 H, 5.30 N, 10.52	C, 54.75 H, 5.50 N, 9.89
DDED for $C_{16}H_{14}O_4N_2$	Styrene	C, 64.43 H, 4.70 N, 9.40	C, 64.98 H, 4.67 N, 9.14
DDED for $C_{16}H_{14}O_4N_2$ (1:2 monomer feed ratio)	Styrene	C, 64.43 H, 4.70 N, 9.40	C, 65.60 H, 5.08 N, 9.22
DDED for $C_{17}H_{16}O_4N_2$	p-Methylstyrene	C, 65.37 H, 5.16 N, 8.97	C, 65.59 H, 5.28 N, 9.14
DDED for $C_{17}H_{16}O_5N_2$	p-Methoxystyrene	C, 62.19 H, 4.91 N, 8.53	C, 61.87 H, 5.31 N, 8.64
DDED for $C_{12}H_{14}O_5N_2$	Ethyl vinyl ether	C, 54.13 H, 5.30 N, 10.52	C, 53.65 H, 5.17 N, 9.98
DCMA for $C_{16}H_{14}O_7$	Styrene	C, 60.38 H, 4.43	C, 59.56 H, 4.45

Table 13. Analyses of copolymers of trisubstituted electron-poor olefins.

Electron-Poor Olefin	Electron-Rich Olefin	Analysis Calculated	Found
MDA for $C_{14}H_{12}O_2N_2$	Styrene	C,69.99 H, 5.03 N,11.66	C,69.71 H, 4.64 N,11.31
MDA for $C_{15}H_{14}O_3N_2$	p-Methoxystyrene	C,66.65 H, 5.22 N,10.37	C,66.42 H, 5.26 N,10.04
MDA for $C_{10}H_{12}O_3N_2$	Ethyl vinyl ether	C,57.68 H, 5.81 N,13.46	C,57.43 H, 5.75 N,13.34
Trimethyl ethylene-tricarboxylate for $C_{16}H_{18}O_6$	Styrene	C,62.74 H, 5.92	C,62.92 H, 5.20
Dimethyl 2-cyanoethylene-1,1-dicarboxylate for $C_{15}H_{15}O_4N$	Styrene	C,65.92 H, 5.53 N, 5.13	C,66.54 H, 5.72 N, 5.02
Tricyanoethylene for $C_{13}H_9N_3$	Styrene	C,75.34 H, 4.38 N,20.28	C,76.76[a] H, 3.98 N,19.26

[a]Hall and Daly (1975).

Cyclobutanes

Tetramethyl 3-Ethoxycyclobutane-1,1,2,2-tetracarboxylate

A mixture of 0.52 g (2 mmol) TMET and 0.25 ml (0.4 mmol) ethyl vinyl ether was sealed in a reaction tube and heated to 116° for 24 hours. Unreacted TMET was removed by recrystallization from diethyl ether. The second crop of crystals was the desired cyclobutane. It was recrystallized again from ether to give 0.174 g (26.2%) cyclobutane, mp 110-112°C. NMR (CDCl$_3$): 1.3 (t, 3H), 2.6 (m, 2H), 3.7-4.0 (4s, 12H), 4.4 (m, 1H). Anal. calc'd. for C$_{14}$H$_{20}$O$_9$): C, 50.60; H, 6.07. Found: C, 50.42; H, 5.86.

Tetramethyl 3-(p-Methoxyphenyl)-cyclobutane-1,1,2,2-tetracarboxylate

A mixture of 0.27 g (2 mmol) of p-methoxystyrene and 0.52 g (2 mmol) TMET was heated in a pressure tube in bulk at 116° for 65 hours. The mixture was dissolved in 20 ml ether to remove unreacted TMET. The solvent and styrene were removed under vacuum (0.1 torr) and the cyclobutane recrystallized from ether to yield 0.07 g (9%) product, mp 136-137°C (lit. 136-137).

Dimethyl 3-Ethoxy-2,2-dicyano-cyclobutane-1,1-dicarboxylate

A mixture of 0.194 (1 mmol) DDED and 0.06 ml (1 mmol) ethyl vinyl ether was degassed. After stirring for 18 hours at 25°C, the reaction mixture was dissolved in CDCl$_3$,

transferred to 25 ml diethyl ether, and placed at -60° for 3 hours. Filtration isolated 0.305 g (97%) cycloadduct, mp 63-64°. NMR (CDCl$_3$): 1.3 (t, 8 Hz, 3H), 2.8 (d, 8 Hz, 1H), 3.3-4.0 (m, 3H), 3.9 (s, 6H), 4.4-4.8 (dd, 8.18 Hz, 1H), mass spectrum: 266, 207, 179, 151, 147, 122, 113, 93, 72 (BP). Anal. calc'd. for C$_{12}$H$_{14}$O$_5$N$_2$: C, 54.13; H, 5.30; N, 10.52. Found: C, 53.69; H, 5.19; N, 10.54.

Dimethyl 3-Isobutoxy-2,2-dicyano-
cyclobutane-1,1-dicarboxylate

A mixture of 0.194 g (1 mmol) DDED and 0.14 ml (1 mmol) isobutyl vinyl ether was stirred in bulk at 25° over-night. Recrystallization from diethyl ether gave 98% (0.29 g) cyclobutane. mp 38-39°C. NMR (CDCl$_3$): 0.8-1.0 (d, 6 Hz, 6H), 1.5-2.2 (m, 1H), 2.7-2.9 (d, 8 Hz, 1H), 3.1-3.7 (m, 3H), 3.9 (s, 6H), 4.5-4.8 (dd, 8, 8 Hz, 1H). ^{13}C NMR (CDCl$_3$): 166.9 (s), 166.0 (s), 112.6 (s), 110.8 (s), 78.9 (d), 77.4 (t), 54.7 (q), 54.0 (q), 52.9 (s), 41.7 (s), 35.9 (t), 28.7 (d), 19.3 (q). Mass spectrum: 294, 238, 179, 150, 145, 113, 57 (BP). Anal. calc'd. for C$_{14}$H$_{18}$O$_5$N$_2$: C, 57.13; H, 6.17; N, 9.52. Found: C, 56.89; H, 5.95; N, 9.61.

Dimethyl 3-Phenyl-2,2-dicyano-
cyclobutane-1,1-dicarboxylate

An equimolar mixture of 1 mmol DDED (0.194 g) and styrene (0.12 ml) was reacted in 2 ml acetonitrile at 25° for 18 hours. After removal of solvent and excess styrene under vacuum, recrystallization from ether/pentane gave

0.10 g (33%) cyclobutane, mp 41-43. NMR ($CDCl_3$): 7.2 (Ar, 5H), 4.7 (m, 1H), 3.8 (2s, 6H), 3.5-3.2 (m, 2H). Mass spectrum: 298, 178, 154, 104 (BP), 72. Anal. calc'd. for $C_{16}H_{14}O_4N_2$: C, 64.42; H, 4.73; N, 9.39. Found: C, 64.27; H, 4.71; N, 9.30.

Dimethyl 3-(p-Methylphenyl)-2,2-
dicyanocyclobutane-1,1-dicarboxylate

A mixture of 0.194 g DDED and 0.13 ml p-methyl styrene (1 mmol each) was stirred in acetonitrile for 18 hours at 25°. Removal of solvent left an orange oil, to which vacuum was applied to remove excess styrene. Yield: 0.17 g (54%). NMR ($CDCl_3$): 7.2-6.9 (m, 4H), 4.8-4.4 (m, 1H), 3.9 (2s, 6H), 3.6-3.0 (m, 3H). Anal. calc'd. for $C_{17}H_{16}O_4N_2$: C, 65.37; H, 5.16; N, 8.97. Found: C, 66.17; H, 5.14; N, 9.02.

Dimethyl 3-(p-Methoxyphenyl)-2,2-
dicyanocyclobutane-1,1-dicarboxylate

A mixture of 0.194 g (1 mmol) DDED and 0.14 ml (1 mmol) p-methoxystyrene was stirred overnight at 25°. Recrystallization from ether/pentane produced 0.12 g (39%) cyclobutane, mp 56-48°. NMR ($CDCl_3$): 7.4-6.8 (dd, 4H), 4.7-4.3 (dd, 8, 11 Hz, 1H), 3.9, 3.85, 3.8 (3s, 9H), 3.4-2.5 (m, 2H). Mass spectrum: 328, 208, 134 (BP), 119, 113. Anal. calc'd. for $C_{17}H_{16}O_5N_2$: C, 62.19; H, 4.91; N, 8.53. Found: C, 62.06; H, 4.86; N, 8.53.

Methyl 1-Ethoxy-2,2-dicyano-
cyclobutane-3-carboxylate

The bulk reaction mixture of 1 mmol (0.136 g) MDA
and 0.06 ml ethyl vinyl ether was, after 18 hours at 25°C,
dissolved in 25 ml diethyl ether. Recrystallization at
-60° gave an almost quantitative yield of fibrous yellow
cyclobutane, as a mixture of isomers. mp = 60-64°C.
NMR (CDCl$_3$): 4.8-4.2 (m, 1H), 3.8 (s, 3H), 3.3-4.0 (m, 3H),
2.8 (m, 2H), 1.3 (t, 3H). ^{13}C NMR (CDCl$_3$): 166.7 (s),
165.7 (s), 112.3 (s), 110.7 (s), 75.4 (d), 66.7 (t), 53.8
(q), 52.4 (d), 41.8 (s), 35.7 (t), 14.9 (q). Anal. calc'd.
for C$_{10}$H$_{12}$O$_3$N$_2$: C, 57.68; H, 5.81; N, 13.46. Found:
C, 57.39; H, 5.66; N, 13.74.

Methyl 1-Isobutoxy-2,2-dicyano-
cyclobutane-3-carboxylate

An equimolar mixture (1 mmol) of 0.136 g MDA and
0.14 ml isobutyl vinyl ether was stirred at 25° for 18
hours. Removal of solvent and unreacted vinyl ether under
vacuum left an orange oil, which proved to be nearly pure
cis and trans cyclobutane. NMR (CDCl$_3$): 4.8-4.1 (m, 1H),
4.1-3.7 (m, 1H), 3.8 (s, 3H), 3.7-3.0 (m, 3H), 2.8-2.4 (m,
1H), 2.1-1.4 (m, 1H), 0.9 (d, 6H). ^{13}C NMR (CDCl$_3$):
169.2 (s), 167.7 (s), 114.9 (s), 112.6 (s), 112.4 (s),
78.4 (d), 76.3 (d), 65.8 (t), 53.4 (q), 40.6 (d), 38.3 (s),
31.1 (t), 14.9 (q). Anal. calc'd. for C$_{12}$H$_{16}$O$_3$N$_2$: C, 61.00;
H, 6.83; N, 11.86. Found: C, 59.83; H, 6.79; N, 11.83.

Methyl 1-Phenyl-2,2-dicyano-cyclobutane-3-carboxylate

A mixture of 0.136 g (1 mmol) MDA and 0.12 ml (1 mmol) styrene in 2 ml acetonitrile was stirred overnight at 25°C. Polymeric products were precipitated with diethyl ether, separated by filtration, and the solvent removed. The residue was dissolved in 10 ml ether. Addition of pentane and cooling to -60° caused an orange glass to solidify beneath the liquid phase. This glass was isolated by decantation of this system while still cold, allowed to thaw, and placed under vacuum to remove any entrapped solvent. This oil was a mixture of cis and trans cyclobutane. Yield: 0.103 g (43%). NMR (CDCl): 7.3 (Ar, 5H), 4.4-4.1 (m, 1H), 3.8 (s, 3H), 3.8-3.0 (m, 1H), 3.1-2.5 (m, 2H). Anal. calc'd. for $C_{14}H_{12}O_2N_2$: C, 69.99; H, 5.03; N, 11.66. Found: C, 70.14; H, 5.15; N, 11.52).

Methyl 1-(p-Methoxyphenyl)-2,2-dicyanocyclobutane-3-carboxylate

A mixture of 1 mmol (0.136 g) MDA and 1 mmol (0.14 ml) p-methoxystyrene in 2 ml acetonitrile was left at 25° for 18 hours. The reaction mixture was dissolved in chloroform, and mixed with 100 ml diethyl ether. After filtration the solvent was removed under vacuum. Attempted recrystallization from ether/pentane at -60° produced an orange glass, from which the liquid was decanted. The glass melted upon warming, but solidified after standing for several weeks at

-10° to give an orange granular solid, mp 30-38°C. The isolated cyclobutanes, a mixture of cis and trans isomers, amounted to 0.12 g (43%). NMR (CDCl$_3$): 7.4-6.7 (Ar, 4H), 4.7-3.9 (m, 1H), 3.8 (2s, 6H), 3.7-3.2 (m, 1H), 3.1-2.5 (m, 2H). Anal. calc'd. for C$_{16}$H$_{14}$O$_3$N$_2$: C, 66.65; H, 5.22; N, 10.37. Found: C, 66.51; H, 5.15; N, 10.45.

6-Methoxy-3,4-dihydro-2H-pyrans

2-Phenyl-4-methoxycarbonyl-6-
methoxy-3,4-dihydro-2H-pyran-
4,5-dicarboxylic Anhydride

A mixture of 0.214 g (1 mmol) DCMA and 0.12 ml (1 mmol) styrene was heated for 18 hours at 60° in bulk. The reaction residue was dissolved in chloroform and recrystallized from diethyl ether. 0.15 g (47%) white crystals were isolated. NMR (CDCl$_3$): 7.5 (Ar, 5H), 5.8 (dd, 3, 12 Hz, 1H), 3.9 (s, 3H), 3.8 (s, 3H), 2.9 (dd, 3, 14 Hz, 1H), 1.9 (dd, 12, 14 Hz, 1H). IR (KBr): 1830, 1765, 1740, 1600 cm^{-1}. Anal. calc'd. for C H O: C, 60.38; H, 4.43. Found: C, 60.59; H, 4.34.

2-Isobutoxy-4-methoxycarbonyl-
6-methoxy-3,4-dihydro-2H-pyran-
4,5-dicarboxylic Anhydride

Equimolar amounts of DCMA (0.107 g, 0.5 mmol) and isobutyl vinyl ether (0.07 ml) were mixed with 2 ml aceto-nitrile. After 18 hours at 25°, the solvent was removed under vacuum. The oily residue was dissolved in diethyl

ether and separated into two layers by addition of petroleum ether. The oil was dried under vacuum. Both cis and trans isomers were present. Yield: 0.06 g (40%). NMR (acetone-d_6): 5.85 (m, 1H), 4.10-4.45 (m, 2H), 3.80 (m, 6H), 3.30 (m, 2H), 2.5-2.8 (m, 1H), 1.4 (2d, 6H). IR (NaCl, CDCl$_3$): 1850, 1780, 1745. Anal. calc'd. for $C_{14}H_{18}O_8$: C, 53.50; H, 5.77. Found: C, 53.37; H, 5.92.

Dimethyl 2-Phenyl-5-cyano-
6-methoxy-3,4-dihydro-2H-
pyran-4,4-dicarboxylate

TCET (0.227 g, 1 mmol) and 0.12 ml (1 mmol) styrene were mixed and heated, in bulk, to 60°C. After 3 hours, the mixture had become glassy. It was dissolved in chloroform, polymer precipitated in ether, and removed. The solution was concentrated and placed at -60° for 18 hours. 0.12 g (36%) pyran, mp = 117-119°C, was isolated. NMR (CDCl$_3$): 7.4 (Ar, 5H), 5.2 (dd, 1H), 3.9 (s, 6H), 3.8 (s, 3H), 2.1 (m, 2H). Anal. calc'd. for $C_{17}H_{17}O_6N$: C, 61.63; H, 5.17; N, 4.23. Found: C, 61.83; H, 5.20; N, 4.00.

Methyl 2-Isobutoxy-4,5-dicyano-
6-methoxy-3,4-dihydro-2H-pyran-
4-carboxylate

A mixture of 0.194 g (1 mmol) DDCF and 0.14 ml (1 mmol) isobutyl vinyl ether was prepared in 2 ml acetonitrile and heated at 70° for 18 hours. After removal of solvent under vacuum, recrystalization from ether gave

0.10 g (34%) pyran, mp = 115-121°, as a mixture of isomers.

NMR (CDCl$_3$): 5.5 (m, 1H0, 3.9 (s, 6H), 3.5 (m, 2H), 2.5

(m, 2H), 1.9 (m, 1H), 0.9 (m, 6H). Anal. calc'd. for

C$_{14}$H$_{18}$O$_5$N$_2$: C, 57.13; H, 6.17; N, 9.52. Found: C, 57.33;

H, 6.25; N, 9.45.

Methyl 2-Phenyl-4,5-dicyano-6-methoxy-3,4-dihydro-2H-pyran-4-carboxylates

A mixture of 0.194 g (1 mmol) DDCF and 0.12 ml

(1 mmol) styrene were mixed and heated in 3 ml acetonitrile

to 100° for 2.5 hours. The reaction products were dissolved

in CHCl$_3$ poured in 50 ml diethyl ether. Addition of pentane

and chilling to -78° caused separation into two phases. The

lower glassy phase was separated, melted, and vacuum applied

for 24 hours. Yield: 30%. NMR (CDCl$_3$): 7.45 (Ar, 5H),

5.4 (m, 1H),3.8 (s, 6H), 2.7-2.4 (m, 2H). Anal. calc'd. for

C$_{16}$H$_{14}$O$_4$N$_2$: C, 64.42; H, 4.73; N, 9.39. Found: C, 64.62;

H, 4.96; N, 9.24.

Methyl 2-Aryl-4,5-dicyano-6-methoxy-3,4-dihydro-2H-pyran-4-carboxylates

Pyrans were also formed during the reaction of DDCF

and p-methyl- and p-methoxy-styrene. These pyrans were

unstable and were not purified for analysis, but were iden-

tified from their NMR spectra, taken in CDCl$_3$.

2-(p-methylphenyl)-pyran: 7.6-7.2 (Ar, 4H), 5.35 (m, 1H), 3.9 (s, 6H), 2.85-2.55 (m, 2H), 2.35 (m, 3H).

2-(p-methoxyphenyl)-pyran: 7.6-7.2 (Ar, 4H), 5.3 (m, 1H), 3.9 (s, 6H), 3.85 (s, 3H), 2.8-2.3 (m, 2H).

Other Adducts

2:1 Adduct of DCMA and p-Methoxystyrene

Equimolar amounts of DCMA and p-methoxystyrene were reacted in bulk at 60° for 18 hours and the product was recrystallized from ether at -50°. NMR (CDCl$_3$): 2.7 (m, 2H), 3.0-3.5 (m, 3H), 3.6 (s, 3H), 3.8, 3.9, 3.95, 4.0 (4s, 12H), 5.2 (m, 1H), 6.1 (m, 1H). Anal. calc'd for C$_{25}$H$_{22}$O$_{15}$: C, 53.58; H, 3.94. Found: C, 53.07; H, 3.76.

2:1 Adduct of DCMA and Divinylbenzene

Equimolar amounts of 0.25 mmole) of DCMA and divinyl-benzene were mixed with 4 ml of ether and left at room temperature for 2 days. Yield: 10%. NMR (acetone-d$_6$): 2.95 (m, 4H), 3.1-3.6 (m, 2H), 3.8-4.0 (4s, 12H), 6.0-6.4 (m, 4H). IR (KBr): 1855, 1780 (anhydride), 1760, 1720 (ester carbonyl), 1630 (C=C) cm^{-1}. Anal. calc'd. for C$_{26}$H$_{22}$O$_{14}$: C, 55.9; H, 3.9. Found: C, 56.0; H, 4.0.

2:1 Adduct of DCMA and Anethole

Equimolar amounts (0.25 mmole) of DCMA and anethole were mixed with 1 ml ether. After 3 days at room temperature, white crystals were obtained. Yield: 20%. NMR

(acetone-d_6): 1.55 (d, 7 Hz, 3H), 2.95 (m, 2H), 3.5 (s, 3H), 3.8-4.2 (m + 4s, 14H), 5.25 (dd, 1H), 5.9 (m, 1H). IR (KBr): 1860, 1785, 1765, 1750, 1730, 1635 cm^{-1}. Anal. calc'd. for $C_{26}H_{24}O_{15}$: C, 54.2; H, 4.2. Found: C, 54.1; H, 4.1.

2:1 Adduct of DCMA and Diphenylethylene

Equimolar amounts (0.5 mmole) of DCMA and diphenyl-ethylene were mixed with 3 ml ether. After 4 weeks at room temperature, crystals formed. Yield: 15%. NMR (acetone-d_6): 3.0-3.6 (m, 3H), 3.7, 3.8, 3.85, 4.07 (4s, 12H), 4.2-4.5 (m, 2H), 6.4-7.0 (m, 3H), 7.2-7.7 (m, 5H). IR (KBr): 1865, 1795, 1760, 1740, 1730 cm^{-1}. Anal. calc'd. for $C_{30}H_{24}O_{14}$: C, 59.2; H, 4.0. Found: C, 59.4; H, 4.1.

1-Methyl-4,5-di(methoxycarbonyl)-cyclohex-1-ene-4,5-dicarboxylic Anhydride

Equimolar amounts (0.25 mmole) of 54 g DCMA and 25 µl isoprene in 1 ml chloroform were allowed to react for 24 hours. The solvent was removed and the product recrystallized from diethyl ether. Yield: 32 mg, 44%. mp = 64-65°C. NMR (CDCl$_3$): 1.8 (m, 3H), 2.75 (m, 4H0, 3.8 (s, 6H), 5.6 (m, 1H). Anal. calc'd. for $C_{13}H_{14}O_7$: C, 55.32; H, 5.00. Found: C, 55.13; H, 5.01.

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