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I. SYNTHESIS AND POLYMERIZATION OF TWO NEW METHYLENECYCLOBUTENE ESTERS. II. MODEL COMPOUND SYNTHESIS FOR CARBON-13 NMR STRUCTURAL ELUCIDATION OF POLYBICYCLOBUTANE-1-CARBONITRILE

The University of Arizona PH.D. 1983

I. SYNTHESIS AND POLYMERIZATION OF TWO NEW METHYLENECYCLOBUTENE ESTERS; II. MODEL COMPOUND SYNTHESIS FOR ^{13}C NMR STRUCTURAL ELUCIDATION OF POLYBICYCLOBUTANE-1-CARBONITRILE

by

Larry Glen Snow

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 the dissertation prepared by Larry Glen Snow

entitled I. Synthesis and Polymerization of Two New Methylenecyclobutene Esters; II. Model Compound Synthesis for ^{13}C NMR Structural Elucidation of Polybicyclobutane-1-Carbonitrile

and recommend that it be accepted as fulfilling the dissertation requirement for the Degree of Doctor of Philosophy.

	7-19-82 Date
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	7-19-82 Date
H. K. Hall, Jr.	7/19/82 Date
	7/19/82 Date

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

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

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ACKNOWLEDGMENTS

The author wishes to thank Dr. H. K. Hall, Jr., for his guidance and many helpful discussions. I also thank Dr. M. Barfield and J. Kao with whom we have collaborated on the polybicyclobutane-1-carbonitrile project, and Dr. A. Deutschman, Jr., of The University of Arizona High Pressure Laboratory for doing the thermal cycloaddition reactions. The financial support given by the U.S. Army Research Office is also gratefully acknowledged.

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ABSTRACT

The two new compounds methyl 3-methylenecyclobutene-1-carboxylate and dimethyl 3-methylenecyclobutene-1,2-dicarboxylate were synthesized. The cycloadduct which forms between allene and acrylonitrile was used as the starting point for the synthesis of the former. This was chlorinated with phosphorus pentachloride, hydrolyzed with aqueous base, esterified with methanol and p-toluenesulfonic acid, and dehydrochlorinated with potassium hydride providing methyl 3-methylenecyclobutene-1-carboxylate. Chloromaleic anhydride was cycloadded to allene as the starting point for the synthesis of dimethyl 3-methylenecyclobutene-1,2-dicarboxylate. This cycloadduct was then hydrolyzed under basic conditions, esterified with diazomethane and dehydrochlorinated with 1,4-diazabicyclo[2.2.2]octane yielding dimethyl 3-methylenecyclobutene-1,2-dicarboxylate.

Each of these new methylenecyclobutenes was then polymerized. Free radical homopolymerization proceeded in a 1,5 manner in each case yielding film forming polymers. Copolymers were also prepared from each using representative comonomers in free radical systems.

Dimers of bicyclobutane-1-carbonitrile were prepared by the reaction of cyanocyclobutyl sodium with cyclobutane-

1-carbonitrile and then chlorinated with phosphorus pentachloride. The ^{13}C nmr spectra of the dimers and the chlorinated dimers were instrumental in showing that polybicyclobutane-1-carbonitrile obtained either radically or anionically is formed primarily by trans 1,3 incorporation of the cyclobutane rings.

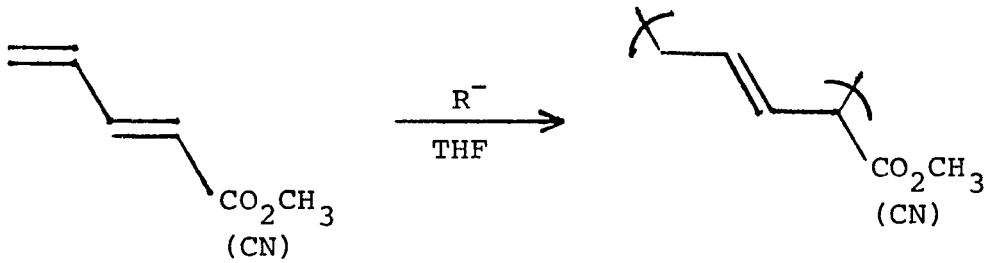
SYNTHESIS AND POLYMERIZATION OF TWO NEW METHYLENECYCLOBUTENE ESTERS

Introduction

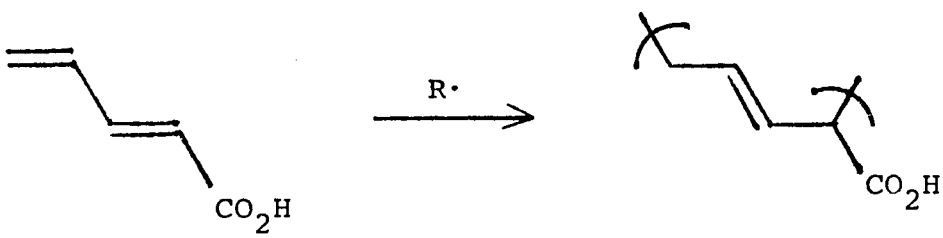
The search for new monomers which polymerize to useful materials has always been one of the primary goals of the organic polymer chemist. The incorporation of polar substituents into monomers often generates several advantages. Polar substituents will help stabilize an appropriate propagating intermediate, rendering such an intermediate more discriminating in the reactions it undergoes. This helps minimize side reactions so that high molecular weight polymer is obtained. The incorporation of polar substituents also leads to imporved mechanical properties in the resulting polymer by virtue of the increased secondary bonding interactions between polymer chains. Finally, the polar substituents often aid in the monomer synthesis as well by activating a certain position in the monomer precursor for reaction.

Polar substituents have been used extensively in olefin polymerization. One of the most industrially important polar substituents is the carbomethoxy group. Methyl acrylate and methyl methacrylate, the two simplest carbomethoxy containing monomers, are two of the most important monomers used industrially.

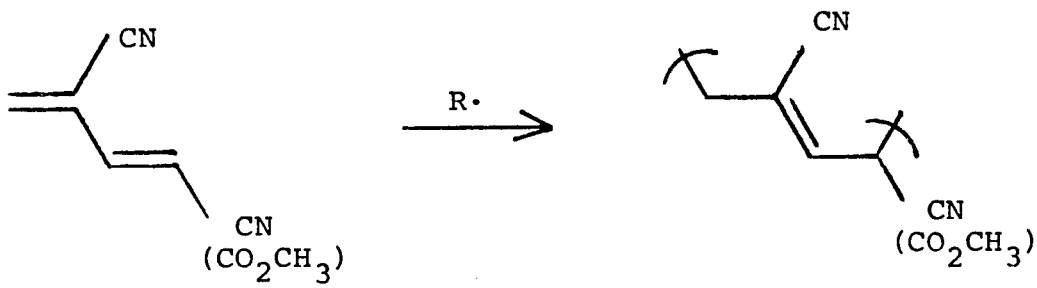
In recent years more attention has been devoted to diene monomers possessing polar substituents. Methyl butadiene-1-carboxylate and 1-cyanobutadiene each polymerize anionically giving predominantly trans 1,4 linkages (Worley and Young, 1972).



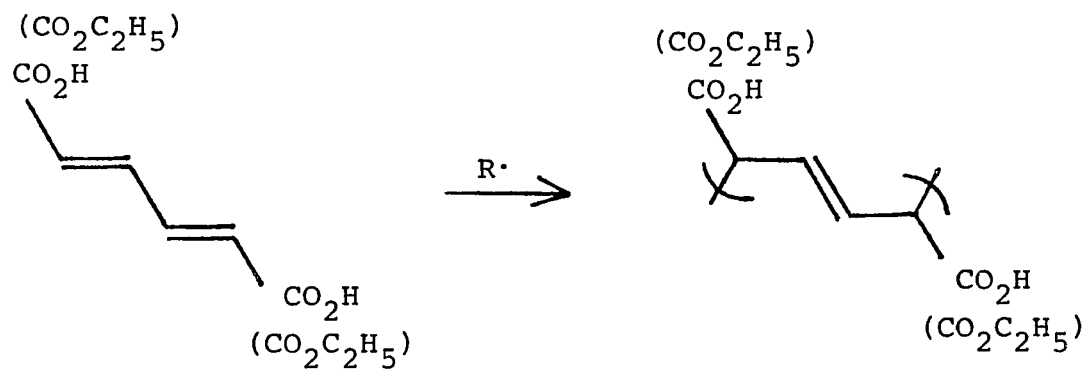
Butadiene-1-carboxylic acid has been shown to polymerize radically to the trans 1,4 structure (Bando and Minoura, 1976).



Several disubstituted butadienes have been examined as potential monomers as well. Polymerization of 1,3-dicyanobutadiene and methyl 3-cyanobutadiene-1-carboxylate in free radical systems gives trans 1,4 enchainment (Ahn and Hall, 1981).

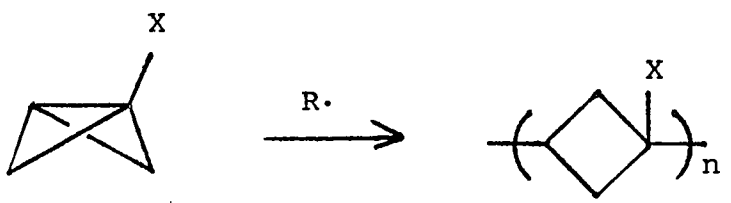


Muconic acid and ethyl muconate also give 1,4-trans polymer in free radical systems and, in the case of ethyl muconate, anionic systems also (Bando, Dodow, and Minoura, 1977).



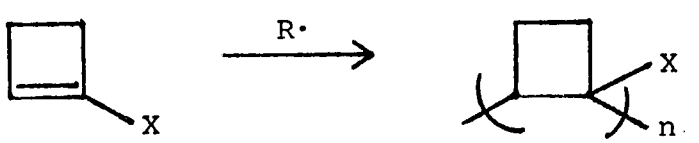
The incorporation of rings into polymer backbones may also result in desirable physical properties. The rigidity of the ring will stiffen the polymer backbone increasing Tg and Tm. In recent years several different methods have been developed for the incorporation of cyclobutane rings into a polymer backbone. One of these methods is the use of bicyclobutane compounds in addition polymerizations (Hall et al., 1971a, 1971b). These interesting

compounds, although formally saturated, behave much like olefins in free radical polymerizations. When substituted at at least one bridgehead with a potential stabilizing group, these compounds undergo facile free radical polymerization by opening the 1,3 bridge bond. This yields a polymer whose backbone is composed entirely of 1,3 cyclobutane units.



X = CO_2CH_3, CN, CO_2H, $CONH_2$, $COCH_3$

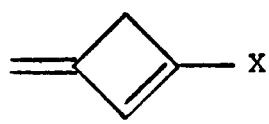
Cyclobutene compounds are another closely related class of compounds which have been examined as potential monomers (Gale et al., 1974). Here as well, when a potential stabilizing group is present facile free radical polymerization occurs. Methyl cyclobutene-1-carboxylate and cyclobutene-1-carbonitrile have given the best results yielding high molecular weight linear polymer by addition through the double bond.



X = CO_2CH_3, CN

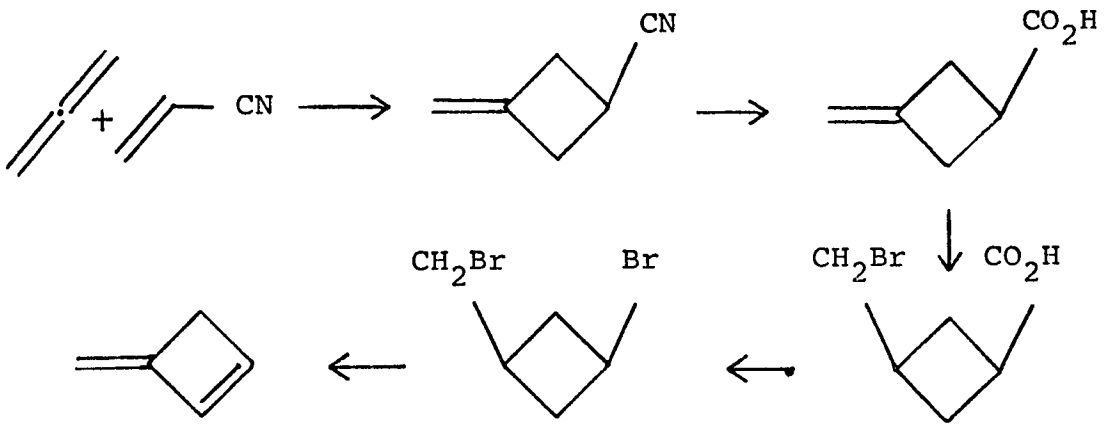
The polymers derived from both bicyclobutane and cyclobutene monomers show very good thermal stability and mechanical strength.

Another method which has been examined for incorporating four membered carbocyclic rings into a polymer backbone is the use of methylene cyclobutene compounds. When appropriately substituted with polar substituents, these compounds combine the high reactivity of a polarized diene with the advantages of ring containing monomers.

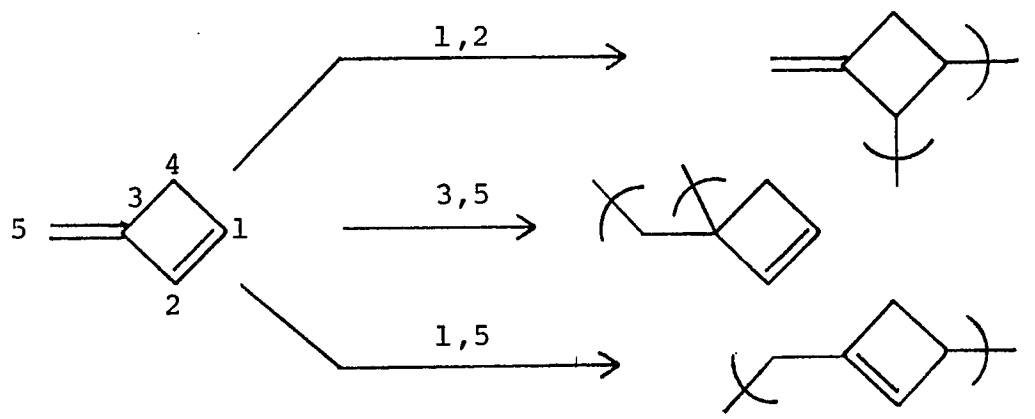


In comparison to acyclic dienes, ring containing dienes have been examined much less.

Two syntheses of the parent hydrocarbon first appeared in 1956 (Howton and Buchman, 1956; Applequist and Roberts, 1956). Each of these syntheses involved pyrolysis of a (methylenecyclobutyl)trimethylammonium salt which was available only by a laborious synthesis in low yield. The discovery of the cycloaddition reaction which occurs between allene and a variety of olefins (Cripps, Williams, and Sharkey, 1959) led to a more recent synthesis of this compound (Kiefer and Roberts, 1961; Wu and Lenz, 1972a). This cycloaddition reaction has since frequently been used in the synthesis of various methylenecyclobutenes.

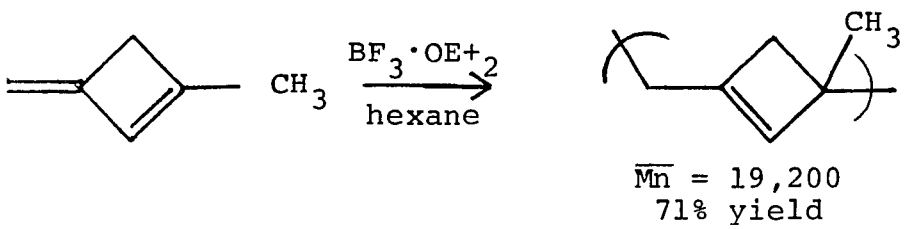


Methylenecyclobutene itself has been polymerized cationically, anionically, and free radically. Cationic polymerization leads to 1,5 enchainment while anionic polymerization gives 1,2 addition (Wu and Lenz, 1972a). Free radical polymerization was reported to give a mixture of 1,2; 1,5 and 3,5 additions (Applequist and Roberts, 1956). Doubt has been cast on the 3,5 free radical enchainment (Wu and Lenz, 1972b).

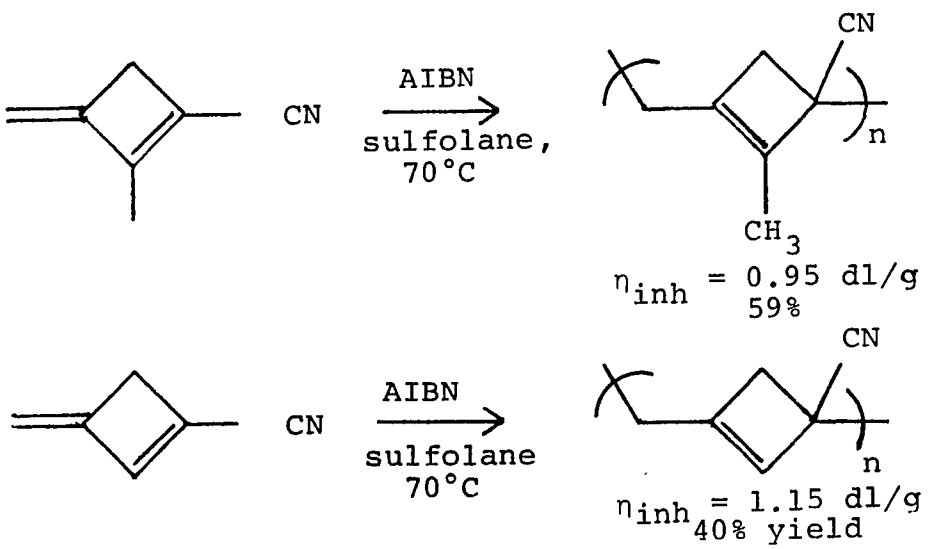


These polymers were typically of rather low molecular weight (≤4000) and formed only in low to moderate conversion (≤40%).

Methylenecyclobutenes possessing a 1-substituent have proved to be superior to the parent hydrocarbon in polymerizability. 1-Methyl-3-methylenecyclobutene gives exceptionally high molecular weight polymer for a diene monomer by cationic initiation with boron trifluoride diethyletherate (Wu and Lenz, 1972a).

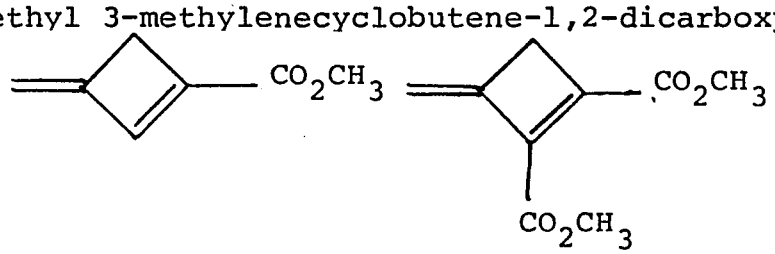


Both 3-methylenecyclobutene-1-carbonitrile and 2-methyl-3-methylenecyclobutene-1-carbonitrile react with free radicals giving high molecular weight polymer by 1,5 addition (Hall and Snider, 1979).

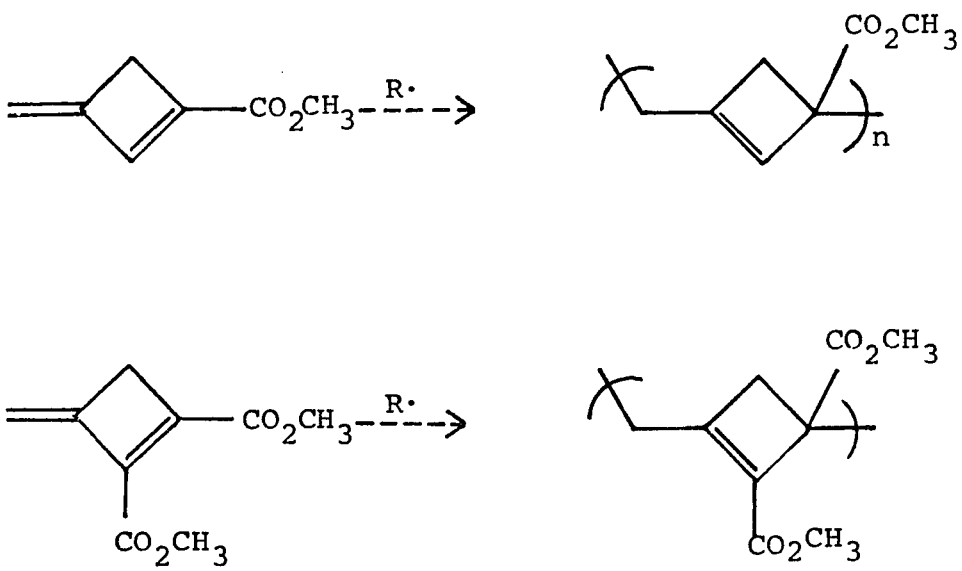


These four methylenecyclobutenes are the only ones which have been examined as potential monomers.

One of the objectives of this work was to synthesize and polymerize methyl-3-methylenecyclobutene-1-carboxylate and dimethyl 3-methylenecyclobutene-1,2-dicarboxylate.



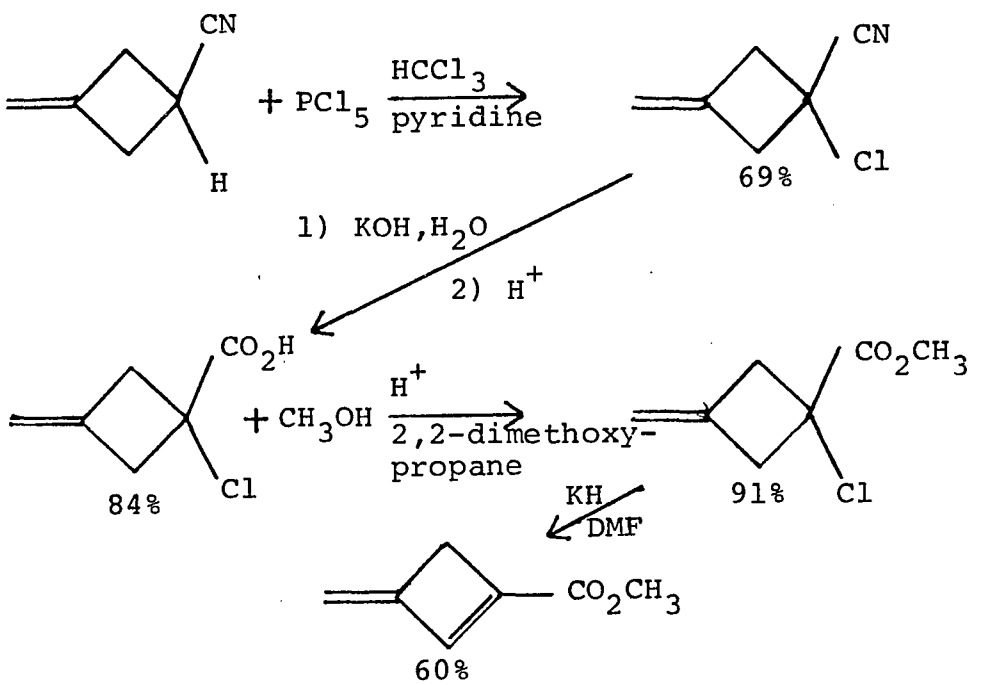
By analogy with 3-methylenecyclobutene-1-carbonitrile and 2-methyl-3-methylenecyclobutene-1-carbonitrile these compounds would be expected to be highly reactive in free radical polymerization. Their incorporation in a 1,5 sense would yield a polymer possessing polar-substituted cyclobutene rings flanked by adjacent methylene units.



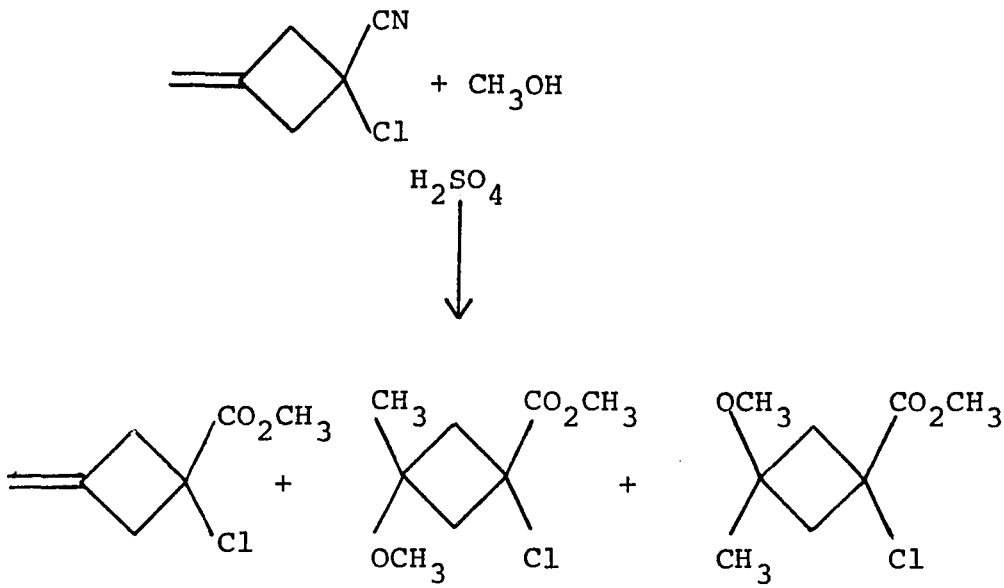
Results

Synthesis of Methyl 3-Methylene-cyclobutene-1-carboxylate

The following four step reaction sequence was used for the synthesis of methyl 3-methylenecyclobutene-1-carboxylate:



The allene acrylonitrile cycloadduct (Cripps, Williams, and Sharkey, 1959) was used as the starting point for this synthesis. The introduction of a potential leaving group for the formation of the endocyclic double bond was performed using phosphorus pentachloride in chloroform (Hall and Snider, 1979). Direct esterification of this chloro-nitrile with methanol and sulfuric acid produced a mixture of products:

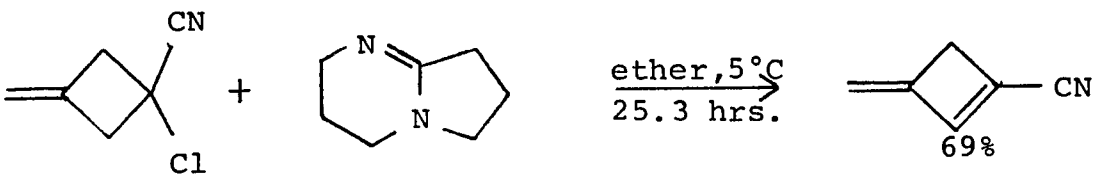


Because of the sensitivity of the exocyclic double bond to the acidic conditions necessary for the solvolysis of the nitrile group, an alternative was sought. Basic hydrolysis to the carboxylic acid avoided the problem of competitive reaction at the double bond. Also, the solubility of the carboxylic acid in dilute base allowed for simple and efficient purification using extraction followed by distillation.

The resulting carboxylic acid could then be esterified under milder conditions with a catalytic amount of p-toluenesulfonic acid in methanol and 2,2-dimethoxypropane. Dimethoxypropane is used here to react with the water formed upon esterification thus driving the reaction to completion (Radin, Hajra, and Akahori, 1960).

The dehydrochlorination of 1-chloro-3-methylene-cyclobutene-1-carbonitrile had been accomplished using

1,5-diazabicyclo[4.3.0]non-5-ene (DBN) in ether at 5°C (Hall and Snider, 1979).



In our case, the corresponding ester reacted much more sluggishly with this base.

Attempts were made to effect this elimination with DBN in ether (0-25°C) and in tetrahydrofuran (25-65°C). GC analysis of the volatile products showed that after 50 hours in ether at 25°C a 50:50 mixture of elimination product and starting material was present. After 65 hours no volatile products remained. In refluxing tetrahydrofuran, an 80:20 mixture of elimination product and starting material was present after 26.5 hours. In this system also however, eventually only tars are obtained and starting material is observable throughout the reaction.

It was desirable to find a system in which the elimination would proceed more rapidly, completely consuming the starting material. This simplifies the purification of the delicate diene monomer. Since monomer purity is very important to successful polymerization, a more powerful non-nucleophilic base was sought which would completely consume the starting material before significant monomer decomposition had occurred.

Several attempts were made using potassium hydride in ether. These early heterogeneous reactions produced erratic results. Working between temperatures of -20 and 25°C, some reactions proceeded vigorously at first and then stopped short of completion while others did not start at all. Somewhat better results were obtained by using tetrahydrofuran as solvent but here again often the reaction would stop short of completion.

Since the evolution of hydrogen was quite vigorous at times, it appeared that the hydride reagent was sufficiently reactive to induce the desired dehydrochlorination. One possible explanation for the observed inconsistencies is that the surface of the potassium hydride becomes occluded by some species in the reaction mixture such as potassium chloride or hydroxide and the reactants merely cannot get together in this heterogeneous mixture. In one particular attempt in tetrahydrofuran which had stopped short of completion, addition of wet tetrahydrofuran caused the evolution of hydrogen to resume. GC analysis of aliquots showed that the elimination reaction had proceeded further. Upon workup, it was discovered that a side product was generated as well. This was 3-methylenecyclobutene-1-carboxylic acid, suggesting that saponification had occurred:

This was a welcome side product, as it could be easily removed from the desired ester by extraction into dilute aqueous base and provided an additional member of the methylenecyclobutene series.

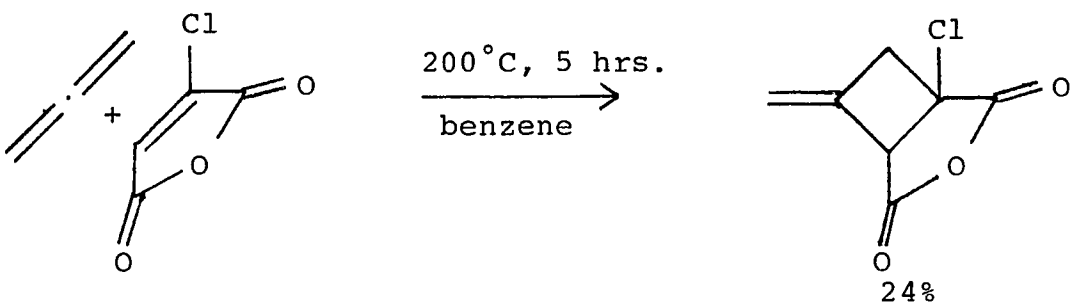
Later it was found that by working in dimethylformamide as solvent at -10°C the reaction would consistently go to completion in 20-40 minutes. Even in these reactions however a small amount of carboxylic acid was formed. It is likely that this forms when the reaction is quenched by pouring into a mechanically stirred slush of ether and ice containing small quantities of HCl and 3-t-butyl-4-hydroxy-5-methylphenyl sulfide free radical inhibitor as all attempts to keep the reaction mixture rigorously dry did not prevent its formation. Also on one occasion use of AR bulk ether in the quenching led to formation of substantial quantities of the ethyl ester presumably from ethanol in the ether.

This series of reactions provides a direct four step synthesis of the new monomer methyl 3-methylenecyclobutene-1-carboxylate in 32% yield overall from the allene-acrylonitrile cycloadduct.

Synthesis of Dimethyl 3-Methylenecyclobutene-1,2-dicarboxylate

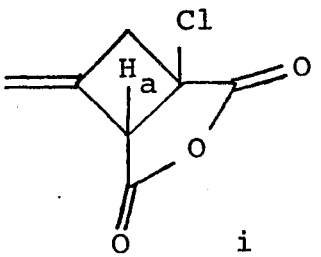
The synthesis of dimethyl 3-methylenecyclobutene-1,2-dicarboxylate was accomplished using another allene-olefin cycloadduct. In this case, chloromaleic anhydride was cycloadded to allene forming the methylenecyclobutane

skeleton (Cripps, Williams, and Sharkey, 1959). A modified version of the literature method was used. Use of one equivalent of chloromaleic anhydride made more efficient use of the anhydride, and an equal volume of benzene was used to moderate the reaction. Chloromaleic anhydride is commercially available however only in a technical grade. Pure chloromaleic anhydride was obtained through chlorination of maleic anhydride followed by pyrolytic elimination of HCl at 180°C. The use of chloromaleic anhydride in the cycloaddition reaction avoided the necessity of placing a potential leaving group on the ring later.

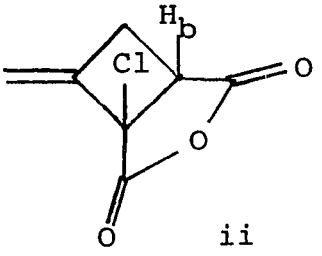


This cycloadduct is reported in the literature (Cripps, Williams, and Sharkey, 1959) as a liquid (b.p. 136°C at 25 mm Hg). The chlorine atom is reported to be in either the 1 or 2 position. In our hands, this cycloadduct crystallized upon storage at -10°C. The white crystalline material showed a melting point of 59-60°C. The nmr spectrum and GC behavior of the white solid were indistinguishable from those of fresh liquid distillate,

and each was consistent with the formation of only one isomer, i or ii:



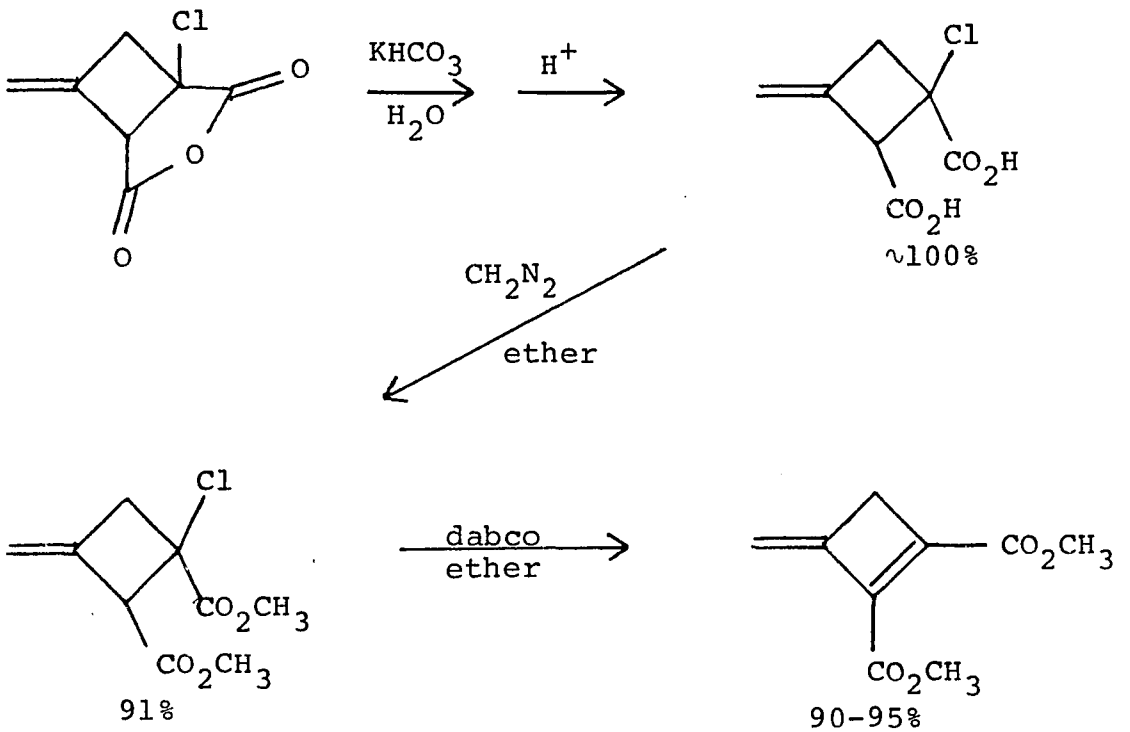
i



ii

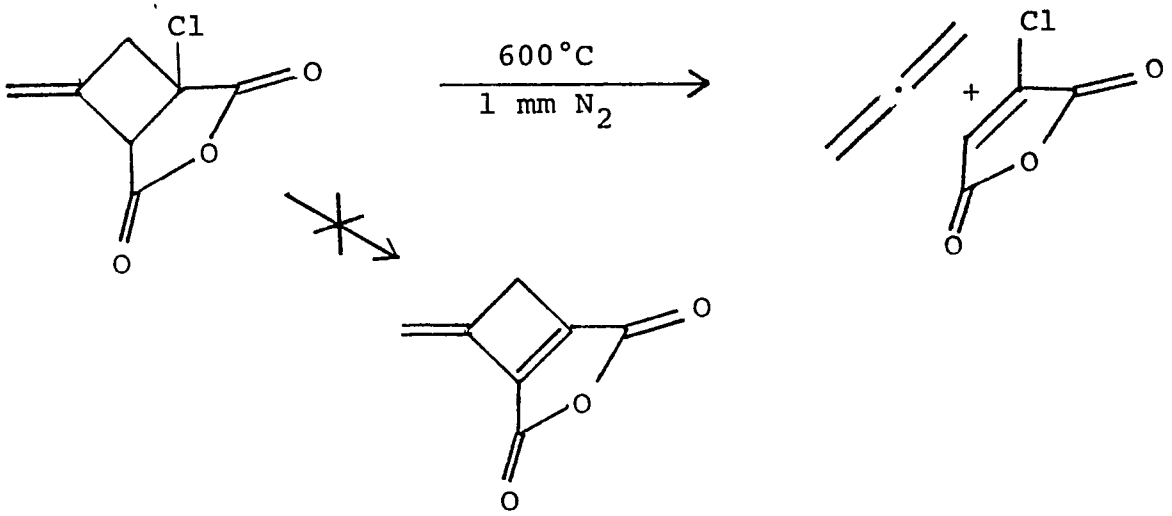
The nmr spectrum ($DCCl_3$) shows a multiplet centered at δ4.25 which integrates for one proton. This multiplet contains at least ten lines and is $\sim$ 11 Hz wide. It would be surprising for H_a and H_b to fall at precisely the same chemical shift since each is in different proximity to the double bond and ring methylene unit. Furthermore, if only one type of proton is present in this multiplet, it must be H_a as H_b would only be expected to experience coupling with the cyclobutane methylene unit generating a maximum of four lines. Hence structure i is assigned.

The anhydride adduct was then opened to the diacid in virtually quantitative yield by stirring with aqueous potassium bicarbonate solution. The diacid did not esterify well using methanol and acid catalyst but did undergo esterification in very good yield with diazomethane. Diazomethane was generated according to a literature procedure (Stanley, 1966). Once formed, the chlorodiester underwent dehydrochlorination using much milder conditions than were necessary for the monoester.

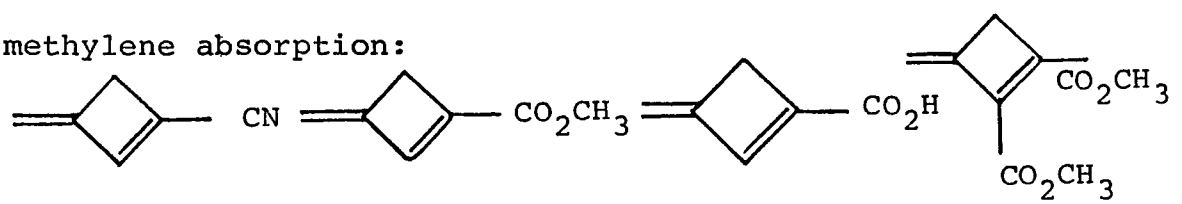


Attempted Synthesis of 3-Methylene-cyclobutene-1,2-dicarboxylic Anhydride

Two different approaches were used in attempting to dehydrochlorinate the chloromaleic anhydride-allene cyclo-adduct. Pyrolysis in a quartz column packed with quartz chips at 1 mm N_2 pressure produced no reaction between temperatures of 400°and 550°C. At 600°C cycloreversion to allene and chloromaleic anhydride began to occur.



Attempts to use a variety of bases also failed. When working with a room temperature solution of the chloromaleic anhydride-allene cycloadduct in diethyl ether, potassium t-butoxide, 1,5-diazabicyclo[4.3.0]non-5-ene (DBN), 1,4 diazabicyclo[2.2.2]octane (DABCO), triethylamine and 1,8 bisdimethylaminonaphthalene (proton sponge) all produced an instant reaction when added. The solution darkened and clumpy dark solids formed. GC of the ether soluble portion showed partial consumption of the starting material but no new volatile products. The solids were largely soluble in D_2O and showed new resonances in the vinyl region (δ4.90 and 5.60; 1:1). This is in the same general region that other substituted exomethylenecyclobutenes show the exomethylene absorption:



δ4.90 & 5.14 δ4.85 & 5.05 δ4.90 & 5.15 δ5.05 & 5.45

It would appear that the anhydride ring opened along with partial dehydrochlorination. This was not too surprising in light of the resistance to pyrolytic dehydrochlorination and no further attempts were made to obtain 3-methylenecyclobutene-1,2-dicarboxylic anhydride.

Other Attempted Cycloadditions

It was originally thought that since allene underwent cycloaddition with a wide variety of olefins, this reaction could be used to better advantage in the synthesis of methyl 3-methylenecyclobutene-1-carboxylate by incorporating a carbomethoxy group and a potential leaving group in the olefin compound.

Attempts to cycloadd methyl α-chloracrylate to allene gave tars; however, no cyclobutane adducts were detected. Methyl acrylate itself will undergo this cycloaddition. Attempts to place halogens in the ring with N-bromosuccinimide, N-chlorosuccinimide or phosphorus pentachloride all failed. Attempts were also made to cycloadd α-chloroacrylonitrile to allene. Here again tars are produced. No cyclobutanes could be detected.

Owing to these difficulties and the fact that acrylonitrile undergoes cycloaddition with allene especially well (62%) giving a cyclobutane adduct which may be readily chlorinated with phosphorus pentachloride in chloroform, no further attempts were made to find alternative

cycloadducts for synthesis of methyl 3-methylenecyclobutene-1-carboxylate.

One attempt was made to shorten the synthesis of dimethyl 3-methylenecyclobutene-1,2-dicarboxylate by cycloaddition of dimethyl acetylenedicarboxylate to allene. In this case no reaction was observed by progressively heating a sealed nmr tube from 25 to 190°C over a 67 hour period.

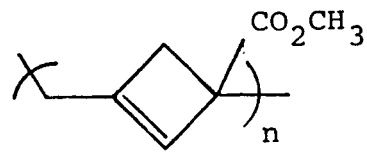
Homopolymerization of Methyl 3-Methylenecyclobutene-1-carboxylate

The title monomer was polymerized with azobisisobutyronitrile in dimethylsulfoxide and in bulk at 70°C or by irradiation with UV light in dimethylsulfoxide solution at 38°C. Polymerization in bulk at 70°C produced cross-linked polymer insoluble in chloroform, acetone and dimethylformamide. Methyl 3-methylenecyclobutene-1-carboxylate also polymerized when left at room temperature in air to insoluble polymer. Solution polymerization in toluene at 70°C gave both soluble and insoluble fractions.

All polymerizations at 38°C using UV light with azobisisobutyronitrile produced linear chloroform-soluble polymers. Typically yields of $\sim$ 40% were obtained in 10% dimethylsulfoxide solution after 20 hours with 1% azobisisobutyronitrile. Gas chromatograms of methanol-soluble portions from polymerization showed unreacted monomer and dimethylsulfoxide as principal components.

Polymer prepared in dimethylsulfoxide solution using UV light showed η_{inh} = 0.44 dl/g. Polymers prepared at 70°C were slightly yellow while those prepared using UV light at 38°C gave white powders. All homopolymers yellowed rapidly when heated.

Films were cast from chloroform. The structure of the polymer arises predominantly from 1,5 addition through the diene moiety.

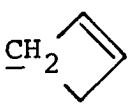
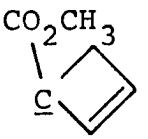
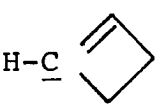
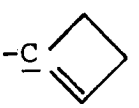


This structure is consistent with a new vinyl proton in the nmr at δ5.90 which integrates for 0.90 proton relative to carbomethoxy absorption at δ3.65. Also consistent with this structure is the C=C stretching band at 1630 cm^{-1} in the ir spectrum. The proton nmr spectrum also shows multiplet absorption between δ2.0 and 3.0 which integrates for 4.1 protons relative to carbomethoxy protons and a small multiplet at δ4.90 which is ∿ 6% as intense as the other vinyl absorption. Broad band and proton decoupled cmr spectra also support this structure (Table 1).

Homopolymerization of Dimethyl 3-Methylene-cyclobutene-1,2-dicarboxylate

Unexpectedly, this monomer also underwent crosslinking when polymerized in bulk at 70°C with azobisisobutyronitrile. Under these conditions, a hard clear glossy plug

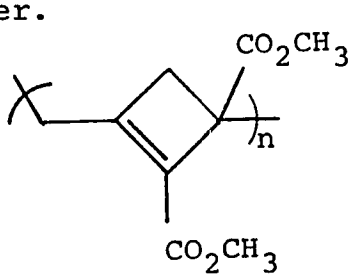
Table 1. CMR of Poly (Methyl 3-Methylenecyclobutene-1-carboxylate) in Deuterochloroform.

Absorption	Shift (δ)	Number of Hydrogens	Assignment
1	37.81	2	$-\underline{C}H_2-$
2	41.61	2	
3	50.59	-	
4	51.75	3	$-CO_2\underline{C}H_3$
5	132.21	1	
6	148.22	-	
7	174.88	-	$-\underline{C}O_2CH_3$

was produced in less than two minutes which was insoluble in chloroform, acetone and dimethylformamide. Free radical polymerization at 70°C in dimethylsulfoxide solution for one hour produced a nearly quantitative yield of chloroform soluble polymer (η_{inh} = 1.24 dl/g).

Polymerization in dimethylsulfoxide solution using azobisisobutyronitrile and UV light at 38°C produced chloroform soluble polymers in all cases. Polymerization of this monomer also occurred when left at room temperature in air. These polymers were also chloroform soluble. Films could be cast from chloroform. Both the yields and molecular weights were higher with this monomer than with methyl 3-methylenecyclobutene-1-carboxylate. Yields of greater than 90% were obtained in 24 hours using 1 mole percent AIBN in 10% dimethylsulfoxide solution (η_{inh} = 1.35 dl/g). No unreacted monomer was visible by gas chromatography with this procedure. These polymers yellow rapidly when heated in air. The air oxidation of methylenecyclobutene polymers has been shown to be facile (Wu and Lenz, 1972b).

As was the case with methyl 3-methylenecyclobutene, these polymers also arise from 1,5 addition to the diene moiety of the monomer.

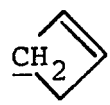
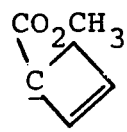
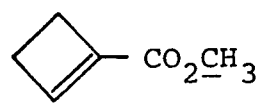
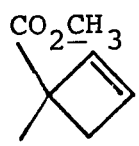
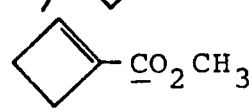
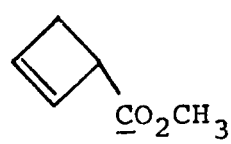


Several pieces of spectroscopic evidence support this structure. The proton nmr shows complete absence of vinyl protons indicating addition to the exomethylene unit. The carbonyl region of the ir spectrum is broadened showing a shoulder at $\sim$ 1740 cm^{-1} and a maximum at 1720 cm^{-1}. The shoulder at 1740 cm^{-1} compares well to the carboxyl stretch at 1743 cm^{-1} in methyl 1-chloro-3-methylenecyclobutane-1-carboxylate and that at 1720 cm^{-1} is what would be expected for the carbonyl group which is still conjugated to a double bond. (Methyl 3-methylenecyclobutene-1-carboxylate shows absorption at 1719 cm^{-1}.) The carbon-carbon double bond stretching frequency has shifted from 1690 cm^{-1} in the monomer to 1660 cm^{-1} in the polymer. This again compares well to the C=C stretching frequency for methyl 3-methylenecyclobutene-1-carboxylate at 1663 cm^{-1}. Although the quatenary carbons are not all easily discernible, the CMR spectrum again supports the 1,5 structure (Table 2).

Copolymerization of Methyl 3-Methylenecyclobutene-1-carboxylate and Dimethyl 3-Methylenecyclobutene-1,2-dicarboxylate

Each of the new methylenecyclobutene monomers underwent copolymerization with styrene, p-methoxystyrene and methyl methacrylate when exposed to UV light in the presence of azobisisobutyronitrile in dimethylsulfoxide solution. Unreacted methyl 3-methylenecyclobutene-1-carboxylate was present at 18-20 hours reaction time, while copolymerization

Table 2. CMR of Poly (Dimethyl 3-Methylenecyclobutene-1,2-dicarboxylate) in Deuterochloroform.

Absorption	Shift (δ)	Number of Hydrogens	Assignment
1	32.91	2	$-CH_2-$
2	40.02	2	
3	49.94	-	
4	51.00	3	
5	52.15	3	
6	161.56	-	
7	173.09	-	

of dimethyl 3-methylenecyclobutene-1,2-dicarboxylate had to be stopped after two hours reaction time to avoid complete consumption. The results are summarized in Table 3. The polymer composition was determined by nmr and/or elemental analysis. Unreacted methylenecyclobutene monomers and co-monomers were detected in methanol soluble products in each case. Every polymer was rich in the methylenecyclobutene monomer. The incorporation of the methylenecyclobutene monomers in a 1,5 sense is consistent with both the nmr and ir spectra in all cases.

Discussion

Monomer Synthesis

The cycloaddition reactions which occur between allene and a variety of olefins under heat and pressure (Cripps, Williams and Sharkey, 1959) provide a direct means for synthesizing substituted methylenecyclobutane compounds. While this reaction has been known for more than twenty years, its mechanism is still a subject of debate. Whether this reaction involves biradical intermediates in a two step process or a concerted mechanism is not entirely clear. Whatever the case, when allene itself is cycloadded to olefins, the regiochemistry of the products is that which would be predicted based upon the most stable biradical intermediate.

Table 3. Copolymerization of Methyl 3-Methylenecyclobutene-1-carboxylate and Dimethyl 3-Methylenecyclobutene-1,2-dicarboxylate.

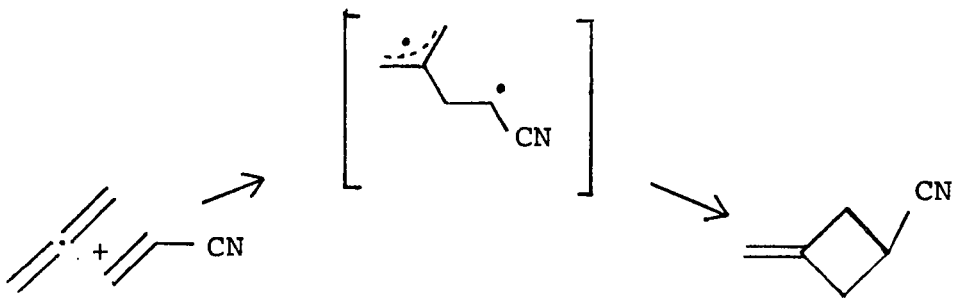
MCB[a]	Comonomer	Feed Ratio[b]	Rx Time (hr)	Yield[c] (%)	MCB (%)	η_{inh}[d] (dl/g)
MCB-ME	styrene	0.989/1	19.2	40	79	0.26
MCB-ME	p-methoxy-styrene	1.08/1	19.2	18	78	0.32
MCB-ME	methyl methacrylate	0.054/1	18	26	71	0.30
MCB-DE	styrene	1.00/1	2	64	83	0.58
MCB-DE	p-methoxy-styrene	0.89/1	2	29	88	0.35
MCB-DE	methyl methacrylate	0.88/1	2	7	88	-

[a] MCB-ME = methyl 3-methylenecyclobutene-1-carboxylate; MCB-DE = dimethyl 3-methylenecyclobutene-1,2-dicarboxylate

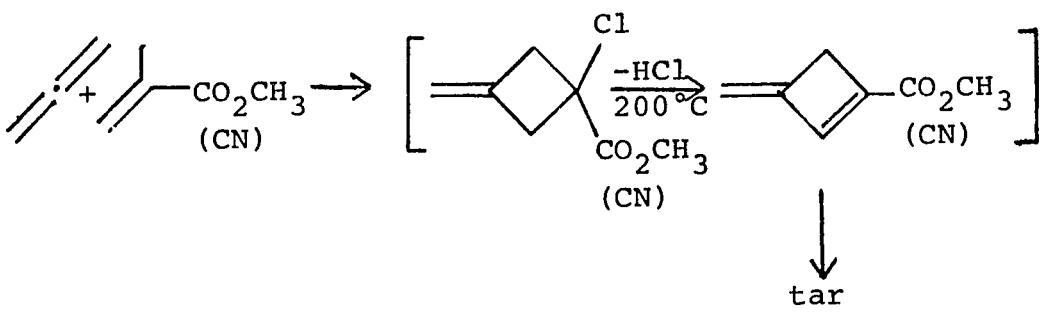
[b] Moles MCB/Moles Comonomer

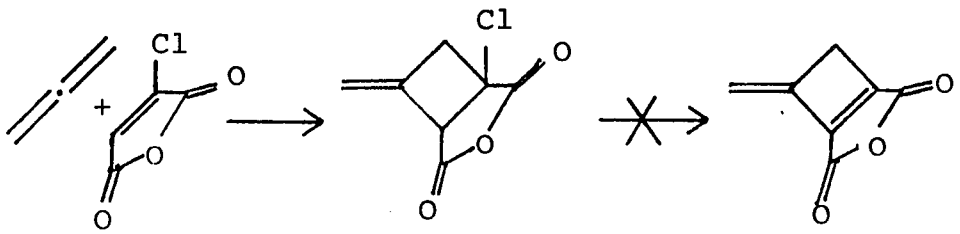
[c] Based on conversion MCB

[d] 0.1g/100 ml $HCCl_3$, 30°C

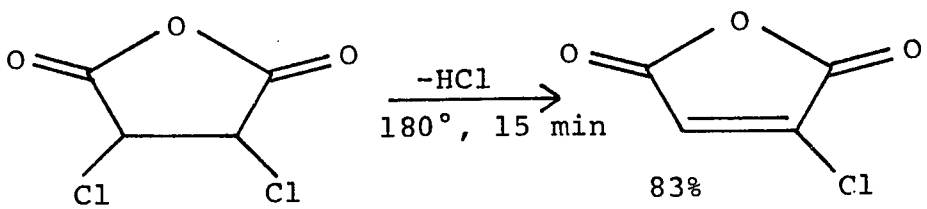


While the synthesis of both new methylenecyclobutene monomers utilized an allene-olefin cycloaddition reaction, it is interesting to note that only in the synthesis of dimethyl 3-methylenecyclobutene-1,2-dicarboxylate could a chlorine atom be included at this stage for the subsequent elimination reaction. It is not immediately obvious why chloromaleic anhydride will give cyclobutane adducts with allene while methyl α-chloroacrylate and α-chloroacrylonitrile each give only tars. A possible explanation for this difference may be that the acyclic olefins pyrolytically lose HCl after forming cyclobutane adducts and resinify under the reaction conditions. The cyclobutane adduct derived from chloromaleic anhydride possesses a bicyclic structure which would experience considerable ring strain upon loss of HCl.

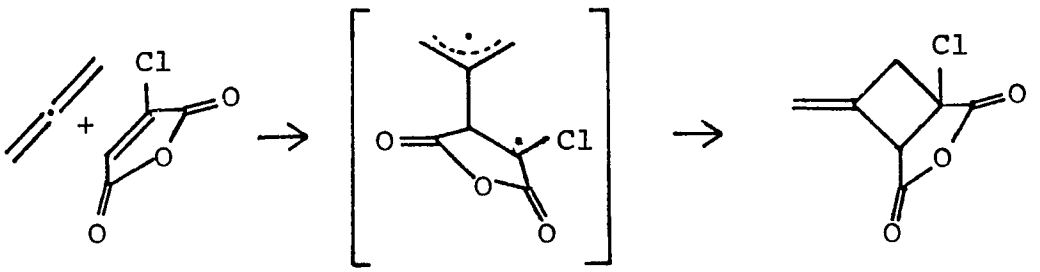




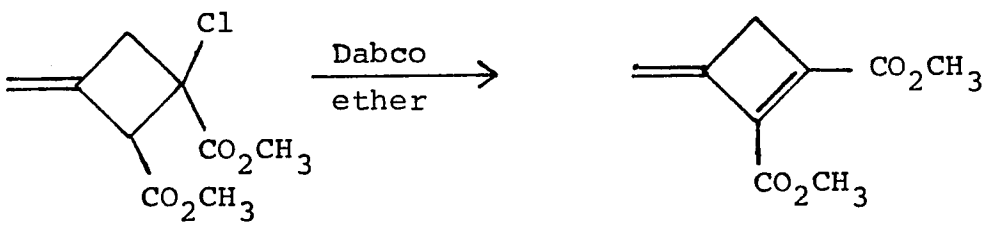
This explanation is consistent with the observations that attempted cycloadditions of methyl α-chloroacrylate and α-chloroacrylonitrile consume most of the starting olefin and smell strongly of HCl when the reactions are removed from the reactor. Also consistent with this explanation is that attempts to deliberately dehydrochlorinate 1-chloro-3-methylenecyclobutene-1,2-dicarboxylic anhydride pyrolytically produce no reaction up to 550°C while dichlorosuccinic anhydride pyrolyzes cleanly at 180°C.



It is also of interest that only one cyclobutane adduct appears to form with chloromaleic anhydride. The isomer which forms is the one that would be expected from both steric and electronic arguments. Assuming a biradical process, the first bond would be expected to form to the least sterically congested position since this also leads to the more stable radical.

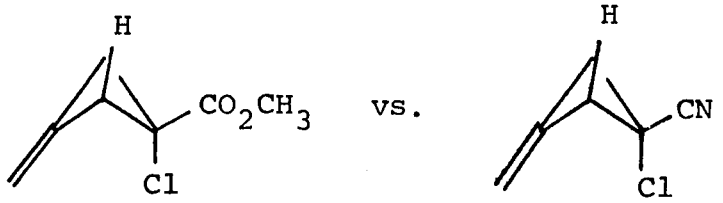


While this cycloaddition reaction only gives a 24% yield, all of the subsequent transformations are very clean, high yield reactions. The dehydrochlorination step is especially facile in this series owing to the acidity of the proton activated by a carbomethoxy substituent:



The dehydrochlorination of methyl 1-chloro-3-methylenecyclobutane-1-carboxylate was much more difficult. In this case, the proton which must be removed is only activated by a carbon-carbon double bond so it is not surprising that more vigorous conditions were necessary. What is surprising is that this compound is substantially more resistant to elimination than the corresponding nitrile (Hall and Snider, 1979). Since both the carbomethoxy and nitrile substituents are β to the proton to be removed, differences in reactivity are not likely due to electronic effects. A possible explanation is that the carbomethoxy

group being bulkier than a nitrile substituent sterically interferes with the base's approach to the acidic protons.

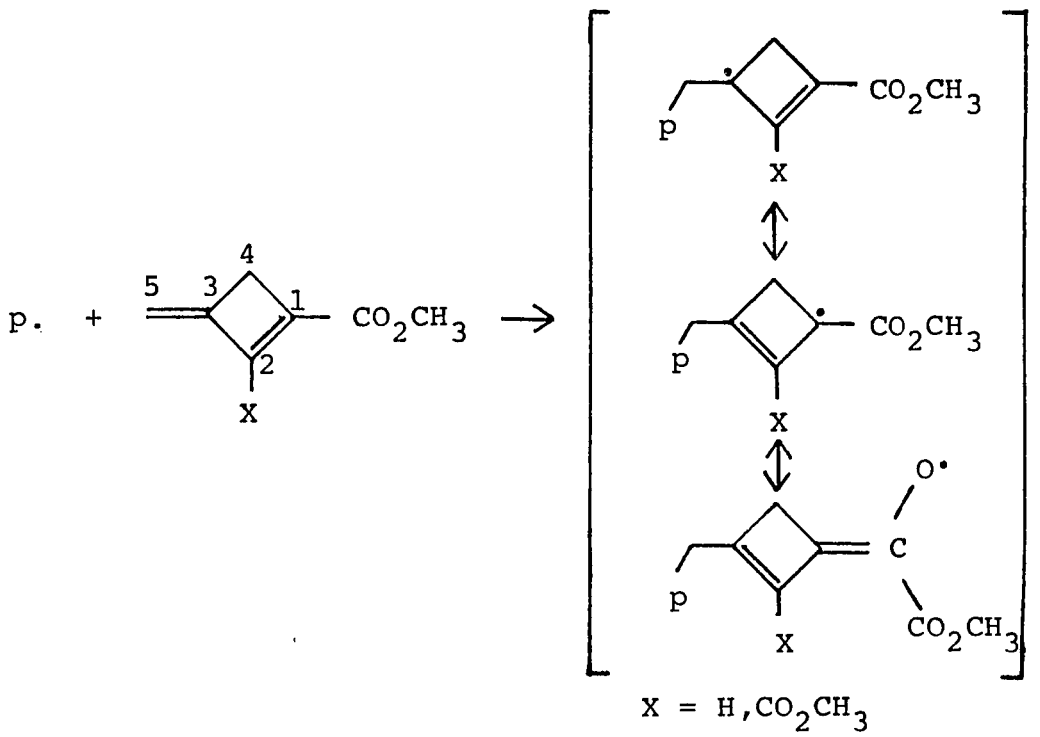


In any event, the use of potassium hydride in dimethylformamide provided the desired monomer in reasonable yield.

Homopolymerizations

Both methyl 3-methylenecyclobutene-1-carboxylate and dimethyl 3-methylenecyclobutene-1,2-dicarboxylate undergo free radical polymerization by 1,5 addition. This is the expected mode of addition. The exomethylene unit offers a sterically accessible point of reaction leading to a highly resonance stabilized intermediate free radical.

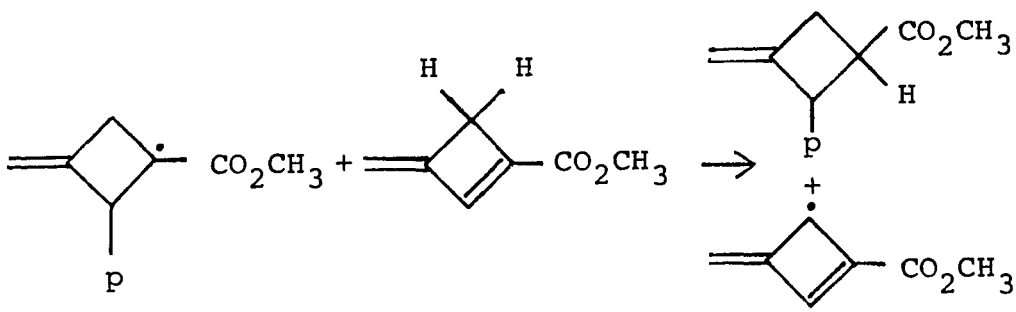
As the resonance structures show, attack at the exo-methylene unit might also lead to 3,5 addition. This would appear less favorable on steric grounds however because of the bulkiness of the polymer chain. One would also expect that the most important resonance form is that one in which the radical is placed α to the carbomethoxy group.



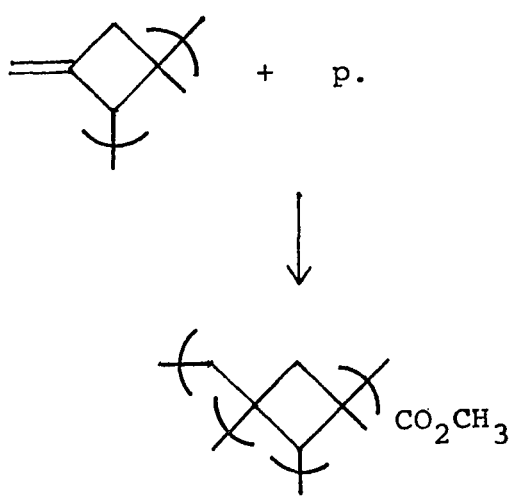
Some evidence of 1,2 addition can be seen in the spectra of the homopolymer from methyl 3-methylenecyclobutene-1-carboxylate. The nmr spectrum shows only 0.90 protons for the new vinyl ring proton relative to the methyl group of the ester and there is a small multiplet in the region expected for a cyclobutane exomethylene unit (δ5.0).

The occurrence of 1,2 addition in the homopolymerization of methyl 3-methylenecyclobutene-1-carboxylate offers a possible explanation for the smaller molecular weights obtained with this monomer relative to dimethyl 3-methylenecyclobutene-1,2-dicarboxylate (η_{inh} = 0.44 dl/g vs. 1.35 dl/g).

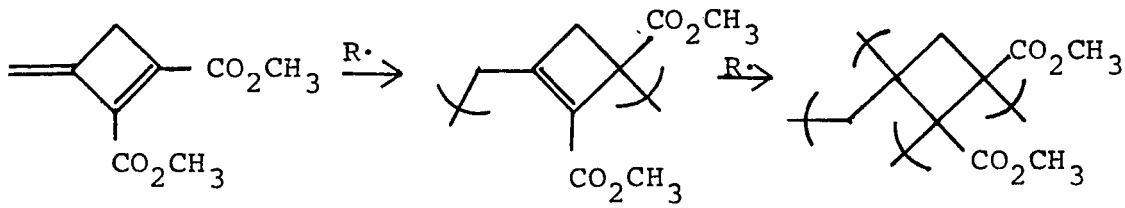
The intermediate radical which results from 1,2 addition would be of higher energy and consequently should be more likely to undergo chain transfer reactions to monomer or polymer.

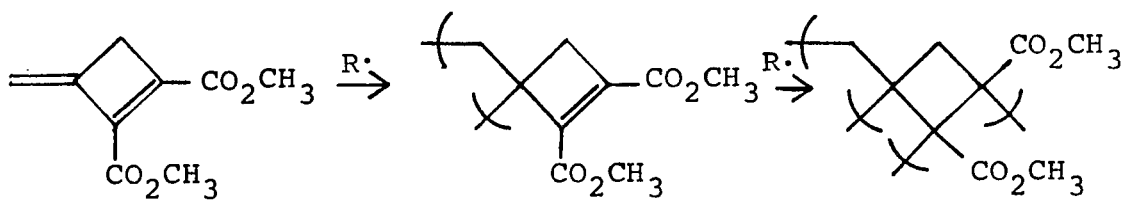


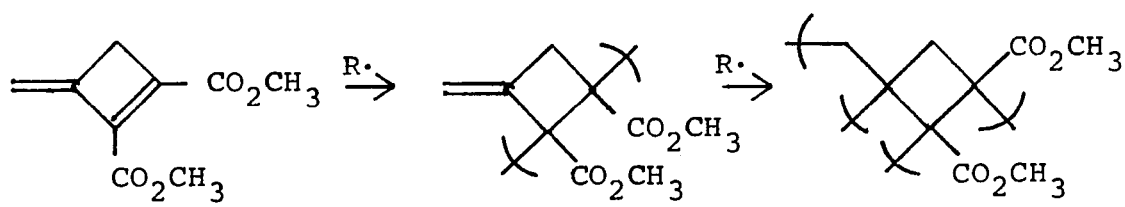
A small amount of 1,2 addition could also explain the crosslinking which occurs with this monomer at 70°C in bulk or solution. Addition through the cyclobutene portion of the molecule would leave the exomethylene unit intact which could react with another growing chain to produce crosslinks.



It is more difficult to explain the crossliking observed with dimethyl 3-methylenecyclobutene-1,2-dicarboxylate when polymerized in bulk at 70°C. In this case, conventional crosslinking mechanisms which may be imagined require addition through a tetrasubstituted double bond at some point.

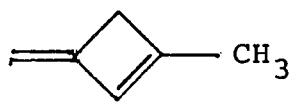




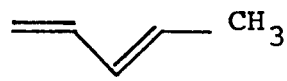


While none of these mechanisms are very attractive, any one of them could explain the observed crosslinking.

The heat of hydrogenation of 1-methyl-3-methylene-cyclobutene has been measured (Turner, 1959). The heat of hydrogenation of this compound can be seen to be little different from the acyclic analog 1,3-pentadiene (Conant and Kistiakowsky, 1937).



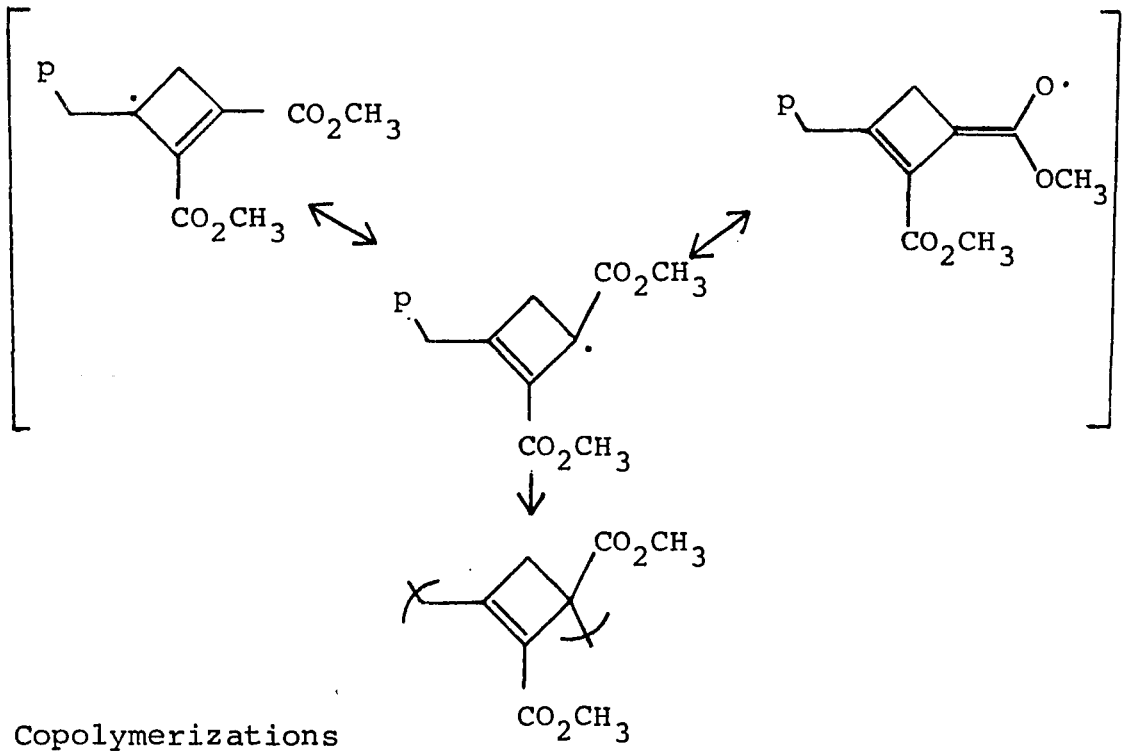
-55.0 Kcal/mole



-54.1 Kcal/mole

This suggests that little strain energy is relieved by removal of trigonal centers from a four-membered carbocyclic ring. The driving force for polymerization then must primarily be conversion of carbon-carbon Π-bonds to carbon-carbon σ-bonds in these systems.

If there is no special driving force operating here, then the high reactivity must be due to the highly delocalized nature of the intermediate radical. If this is the case, then it is interesting that dimethyl 3-methylenecyclobutene-1,2-dicarboxylate is qualitatively more reactive than methyl 3-methylenecyclobutene-1-carboxylate in free radical homopolymerization. Conventional resonance forms show no radical character at the two position so it is not obvious why substitution of a carbomethoxy substituent here should increase reactivity. One possible explanation for this is that the conjugation energy present in the product is reflected to some extent in a lower energy of activation.



Copolymerizations

The greater reactivity of dimethyl 3-methylenecyclobutene-1,2-dicarboxylate can also be seen in the results of copolymerization. Copolymerizations with this monomer had to be stopped after two hours in order to avoid complete consumption. Copolymerization of methyl 3-methylenecyclobutene-1-carboxylate with representative vinyl monomer could be run for 18-20 hours without complete consumption. In both cases the polymers are very rich in the methylenecyclobutene monomer showing the high reactivity of these monomers when compared to conventional vinyl monomers.

One surprising observation is that neither of these two electron-poor methylenecyclobutene monomers show any greater tendency to incorporate an electron-rich comonomer than an electron-poor comonomer. This absence of polar

effects suggests that the radicals derived from the methylenecyclobutene monomers are sufficiently stabilized by resonance that polar effects which would favor cross-propagation are unimportant. The incorporation of vinyl monomer which does occur would offer an explanation for the lower molecular weights which are observed in copolymerizations. As with 1,2 incorporation of methyl 3-methylenecyclobutene, the incorporation of vinyl monomer leads to a higher energy species more likely to undergo chain transfer reactions.

Summary

Syntheses were developed for the two new compounds methyl 3-methylenecyclobutene-1-carboxylate and dimethyl 3-methylenecyclobutene-1,2-dicarboxylate. The key step in these syntheses is the cycloaddition of allene to an olefin, providing a methylenecyclobutane skeleton. The generality of this reaction should enable the placement of a variety of substituents onto the cyclobutane ring through judicious choice of olefin in any future work.

Each of these new methylenecyclobutene esters was shown to be highly reactive in free radical polymerizations. In both cases, gel formation was a problem when polymerized in bulk at 70°C with AIBN. Linear polymers could be obtained however at 38°C in solution using UV light and AIBN for initiation. The ir, H-nmr and ^{13}C-nmr spectra of these

polymers is consistent with predominant 1,5 addition in all cases where gels were not formed.

Copolymers with representative vinyl monomers were prepared from each of the methylenecyclobutene esters. The high reactivity of these new compounds was again demonstrated as the polymers were always very rich in the methylenecyclobutene monomers. All of the linear homopolymers and copolymers were film forming.

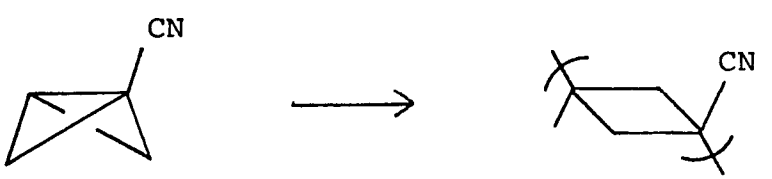
These new polymers suffer from a tendency to air oxidize. Each incorporated methylenecyclobutene unit possesses four secondary allylic hydrogen atoms. These are presumably the points at which oxydation takes place leading to yellowing and insolubility.

The high reactivity of these compounds combined with their tendency to crosslink at 70°C suggests an application as a crosslinking agent for most vinyl polymerizations. Another possible application might be as a thermosetting plastic as attempts to melt these polymers lead instead to extensive crosslinking. This is thought to occur by opening of the cyclobutene rings to butadiene segments which then undergo crosslinking through Diels Alder reactions.

MODEL COMPOUND SYNTHESIS FOR ^{13}C NMR STRUCTURAL ELUCIDATION OF POLYBICYCLOBUTANE-1-CARBONITRILE

Introduction

Until relatively recently, the synthesis of polymers containing only carbon in the backbone was largely limited to the use of vinyl and diene monomers. Bridgehead-substituted bicyclobutanes have been shown to provide a new class of highly reactive monomers yielding all carbon backbones upon polymerization (Hall et al., 1977a; 1977b). Bicyclobutane monomers have been reviewed (Hall and Ykman, 1976; Hall and Snow, 1982). These new monomers polymerize by opening the 1,3 bridge bond to yield polymers whose backbone is composed entirely of 1,3 cyclobutane rings. When carrying a bridgehead substituent capable of stabilizing the propagating intermediate, these compounds show remarkable reactivity for a carbon-carbon σ-bond giving very high molecular weight linear polymer in high yield.

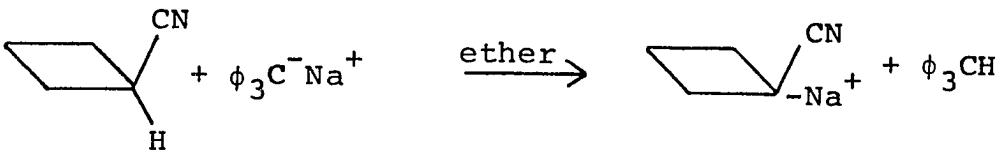


These monomers respond best to free radical conditions although anionic polymerization has been accomplished as well.

The geometry of the cyclobutane ring generates the possibility of 1,3 cis enchainment or 1,3 trans enchainment during polymerization. Little is known of the structures present in these polymers. One attempt has been made to prepare stereoregular polybicyclobutane-1-carbonitrile using dialkylmagnesium and magnesium dialkylamide initiators (Hall et al., 1977). These initiators were chosen because of their successful stereoregular polymerization of methacrylonitrile (Joh et al., 1967; 1970). The ^{13}C spectra (Barfield et al., 1982) of these polymers however are indistinguishable from those of the radically initiated ones. Both show two envelopes of absorption (DMSO, δ121.7 and 123.1) attributable to nitrile carbon atoms. The resonance occurring at higher field predominates (∿3:1). The occurrence of two types of nitrile groups suggests that both cis and trans incorporation occur.

In order to gain some insight into the structure of these polymers, the task of synthesizing dimers of bicylobutane-1-carbonitrile was undertaken. The assignment of absolute structure in the dimers was hoped to enable assignment of structure in the polymers.

The anion of cyanocyclobutane was already known (Hall et al., 1977). It had been prepared by reaction of cyanocyclobutane with triphenylmethyl sodium in ether.

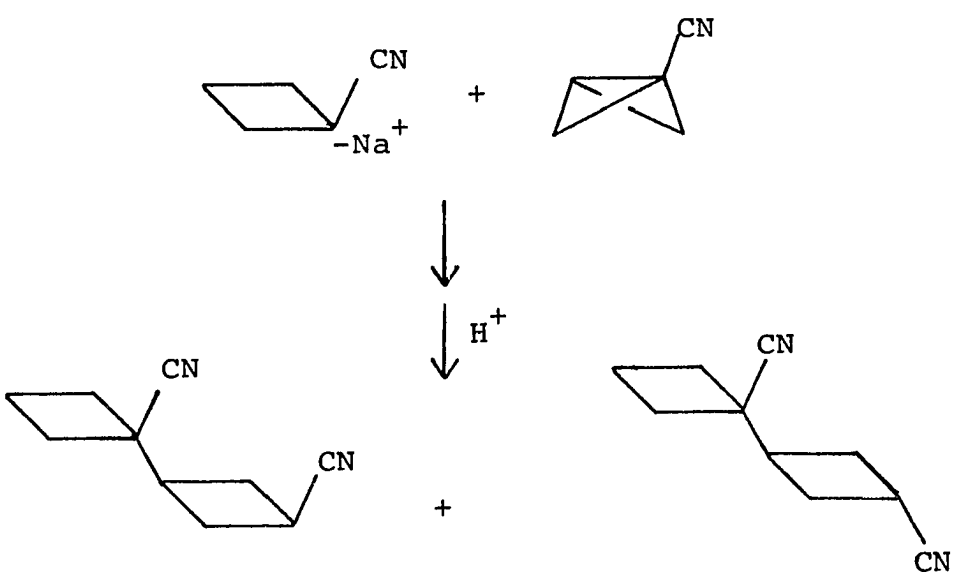


Since bicyclobutane-1-carbonitrile was known to polymerize anionically we expected to be able to synthesize dimers by reacting an excess of sodiocycanocyclobutane with bicyclobutane-1-carbonitrile followed by a proton source.

Results

Synthesis of cis- and trans-3-(1'-Cyclobutyl-1'-carbonitrile)-cyclobutane-1-carbonitrile

The synthesis of dimers of bicyclobutane-1-carbonitrile was accomplished by reaction of an excess of the anion of cyanocyclobutane with bicyclobutane-1-carbonitrile followed by a proton source.



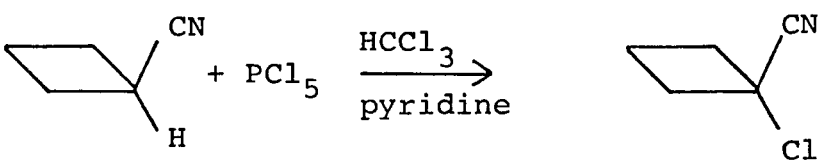
Rapid addtion of a bicyclobutane-1-carbonitrile solution in tetrahydrofuran to the anion solution followed immediately by propionic acid produced a mixture of products. After vacuum distillation, GC peak heights indicate the dimers are formed in 16 - 21% yields (based on starting bicyclobutane-1-carbonitrile). One of the dimers formed in approximately 2:1 preference over the other.

This procedure is the culmination of some trial and error. The key features appear to be use of a chilled dilute bicyclobutane-1-carbonitrile solution and a short reaction time. Addition of bicyclobutane-1-carbonitrile neat at room temperature to the anion solution produced homopolymer of bicyclobutane-1-carbonitrile. Addition of a chilled dilute solution of bicyclobutane-1-carbonitrile dropwise to the anion solution avoids polymerization but a complex mixture of nonvolatile products results. These mixtures show a ketone carbonyl stretch in the ir at 1720 cm^{-1}.

The dimers were isolated in small quantities by preparative GC for characterization and ^{13}C nmr spectra. Each of the two compounds demonstrated spectral characteristics which were consistent with dimer structures.

Chlorination of cis- and trans-3-(1'-Cyclobutyl-1'-carbonitrile)-cyclobutane-1-carbonitrile

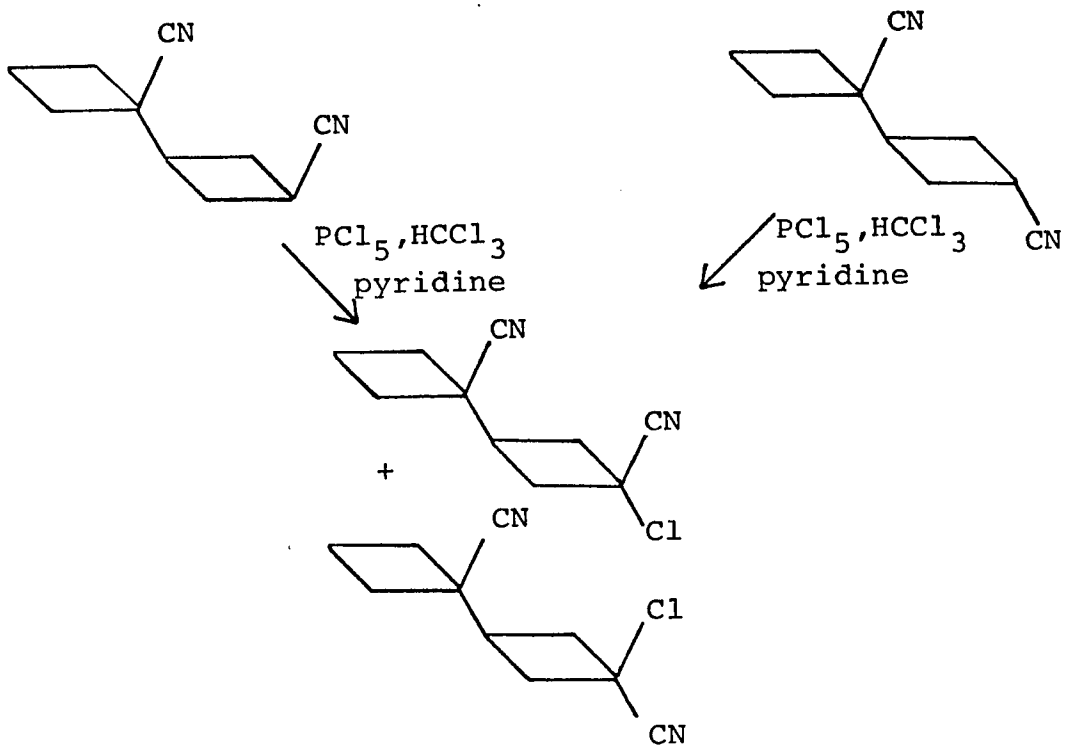
The two dimers each showed two ^{13}C resonances in the region expected for nitrile groups (least volatile isomer: $\delta(DCCl_3)$ 122.70 and 120.95; more volatile isomer: $\delta(DCCl_3)$ 122.77 and 122.51). In order to establish which nitrile corresponded to each resonance it became desirable to place a substituent α to the terminal nitrile which would affect the chemical shift of that nitrile carbon atom without significantly influencing the other. Toward this end, cyanocyclobutane was chlorinated with phosphorus pentachloride in chloroform and pyridine to establish the influence of an alpha chlorine on a nitrile chemical shift and to establish optimal reaction conditions:



The substitution of chlorine for hydrogen proceeded readily, giving a product whose nitrile absorbence was shifted 2.76 ppm to higher field.

Each of the dimers was then chlorinated using the same procedure. This produced identical mixtures of both possible isomers regardless of which dimer was used as starting material. Here as well, the formation of one isomer predominates in approximately a 2:1 ratio. The ^{13}C spectra of the mixture showed three resonances in the

nitrile region, $\delta(DCCl_3)$ 118.03; 119.65; 122.09, occurring in a 2:1:3 ratio, respectively.



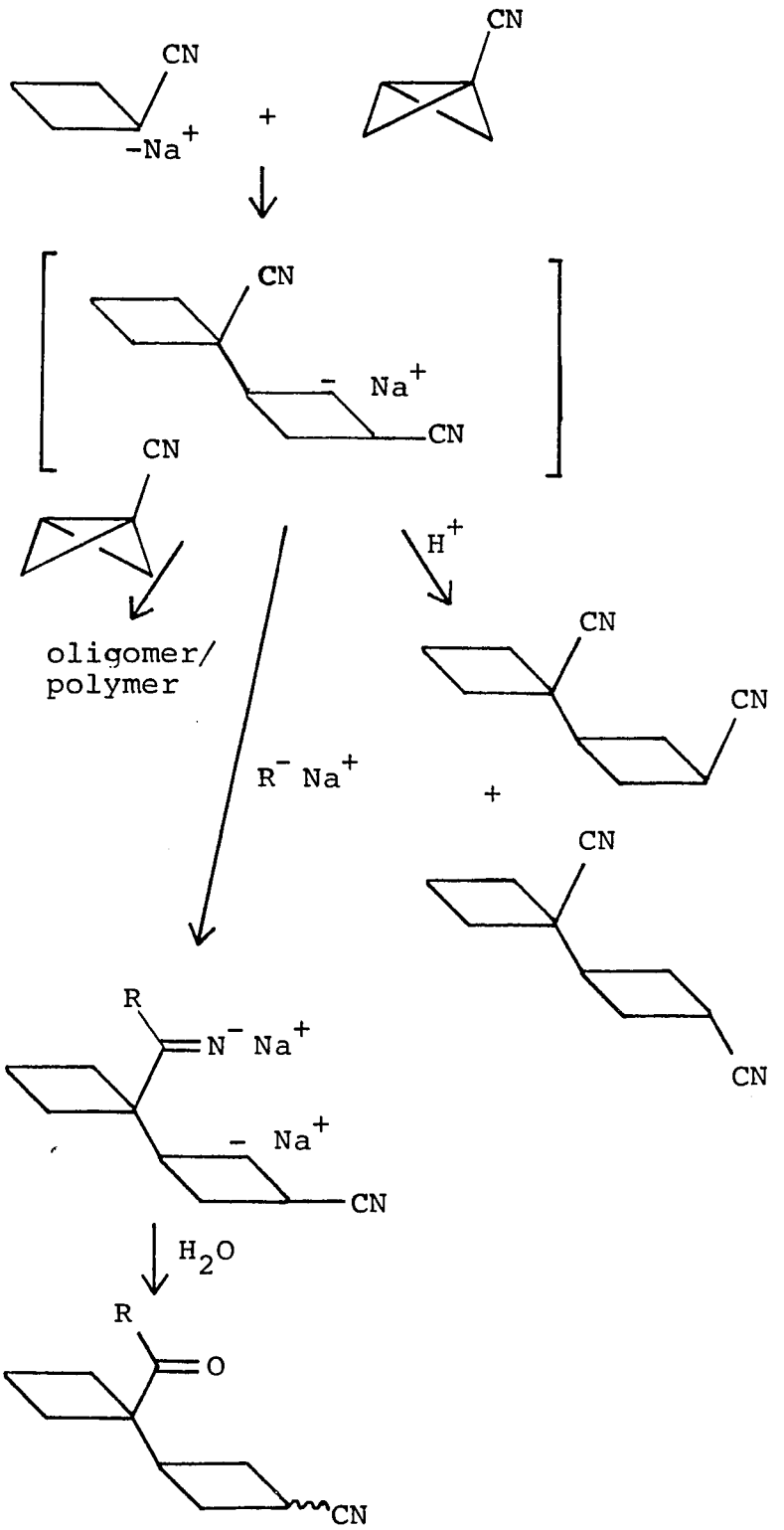
Discussion

Synthesis of cis- and trans-3-(1'-Cyclobutyl-1'-carbonitrile)-cyclobutane-1-carbonitrile

The difficulties we experienced in our early dimer synthesis experiments suggest that two competing side reactions complicate the formation of dimers. The first problem is that bicyclobutane-1-carbonitrile is so reactive that addition of it neat at room temperature leads to polymerization faster than mixing can occur. This problem may be avoided by chilling and diluting the bicyclobutane and then adding this solution dropwise. This approach however made

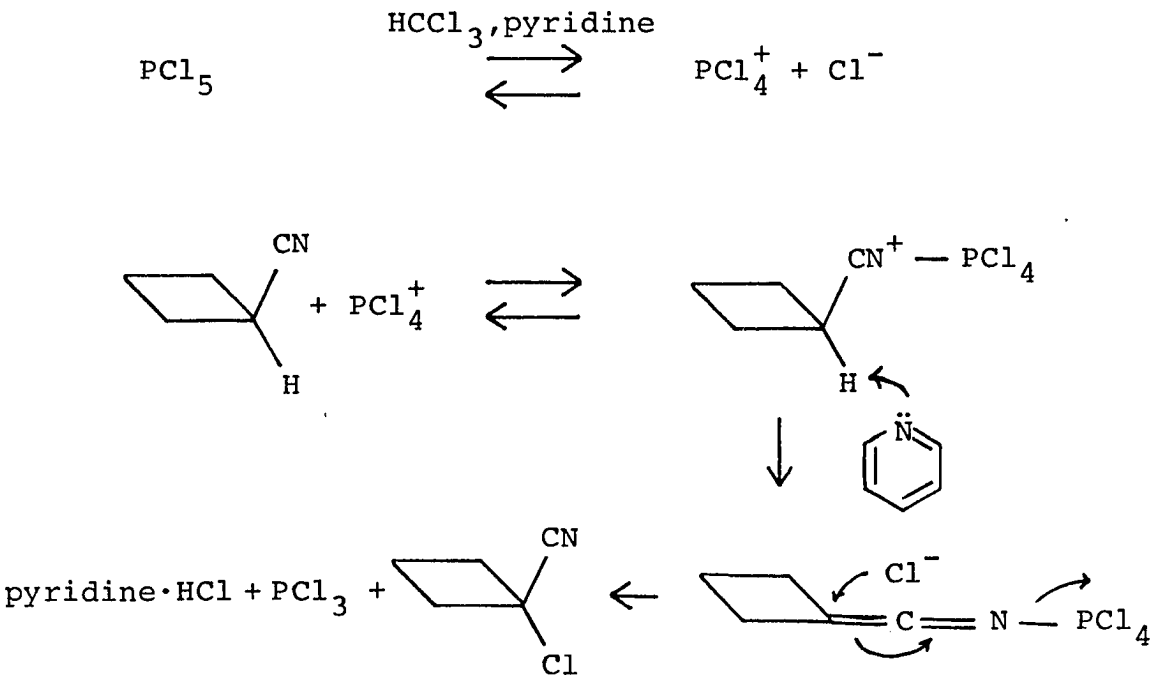
the second problem apparent. Once the anion of cyanocyclobutane adds to bicyclobutane-1-carbonitrile then there exist nitrile groups in the solution which are no longer involved in charge delocalization. These nitrile groups are then susceptible to Thorpe-Ziegler condensations with carbanions in the solution. These reactions produce ketone carbonyl groups under aqueous workup. No good way to prevent this reaction from occurring was found; however, minimizing the reaction time did allow for the formation of the dimers in combined 21% yield. Preparation of the dimers by this method gave a 2:1 ratio of products with the dimer of less volatility predominating. While 21% yield is not particularly satisfying, this method provided sufficient quantities of the desired dimers for our purpose.

This Thorpe-Ziegler condensation was shown to be the mode of termination in the anionic polymerization. In the polymerization however monomer concentration is high and carbanion concentration is low so that this is not as much of a problem. As a suggestion for future work, the use of ether as solvent should render the carbanions insoluble and thus should help prevent this type of condensation. Bicyclobutane-1-carbonitrile is sufficiently reactive to react in a heterogeneous system. Heterogeneous systems were noted to give higher molecular weights in the anionic polymerization of bicyclobutane-1-carbonitrile.


CN
-Na+
+
CN
CN
- Na+
CN
CN
oligomer/
polymer
H+
CN
CN
R- Na+
+
CN
CN
R
N- Na+
- Na+
CN
H2O
R
O
CN

Chlorination of cis- and trans-3-(1'-Cyclobutyl-1'-carbonitrile)-cyclobutane-1-carbonitrile

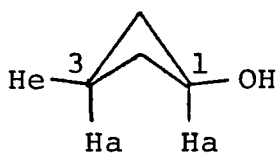
A likely mechanism for the alpha chlorination of cyanocyclobutane is shown below:

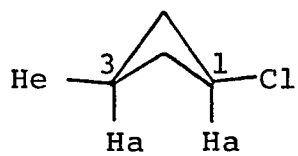


An important aspect of this mechanism is that the carbon atom which ultimately obtains the chlorine atom passes through a planar species. This can be attacked by chloride ion from either of the two faces. This mechanism then predicts the observation that chlorination of each of the dimers produces identical mixtures regardless of the configuration of the starting dimer. This also predicts that the relative amounts of the two possible products will be determined by steric interactions.

Assignment of Structure of cis- and trans-3-(1'-Cyclobutyl-1'-carbonitrile)-cyclobutane-1-carbonitrile

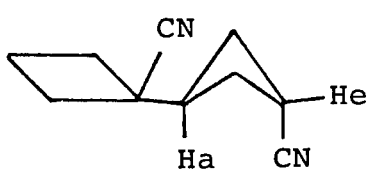
The assignment of structure of the two dimers rests primarily on nmr evidence. Consider the following compounds:

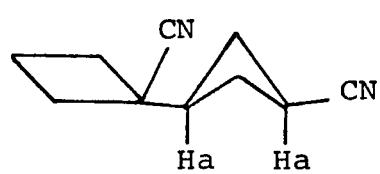




$^4J_{1a3a}$	-0.01	0.11
$^4J_{1a3e}$	-1.07	-0.90

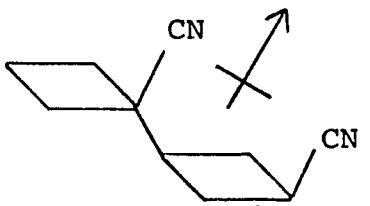
The important feature here is that a large four-bond coupling constant is observed between the 1 axial position and the 3 equatorial position while the coupling constant is small between the 1 axial and the 3 axial positions. Examination of possible dimer structures reveals that only one should show this large four-bond coupling.



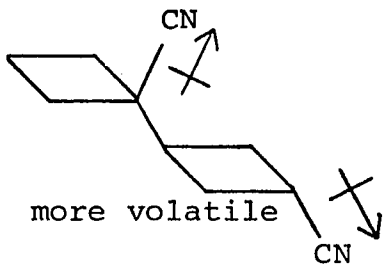


The 250 MHz proton nmr spectrum of the more volatile isomer shows this large four-bond coupling ($J = 1.27$ Hz) while the other isomer does not ($J < 0.3$ Hz). This suggests that the

more volatile isomer is the trans isomer. It is pleasing to note that this is the same assignment which would have been reached by assuming that the isomer which possesses the larger dipole moment should be less volatile.

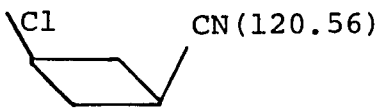


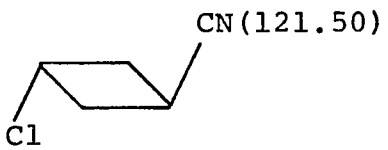
less volatile

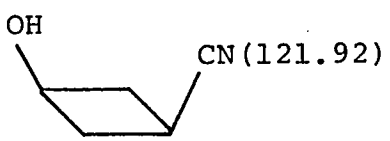


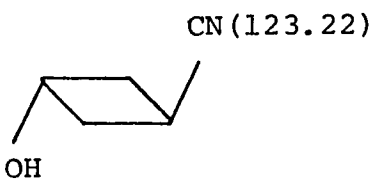
more volatile

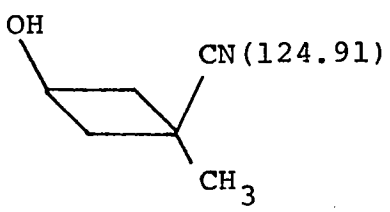
Further evidence for this assignment comes from a comparison of the ^{13}C nitrile carbon resonances with nitrile resonances in other cyclobutanes. Consider the following series of isomeric pairs. (Numbers indicate ^{13}C chemical shift (δ) of nitrile carbon atom in deuterochloroform.)

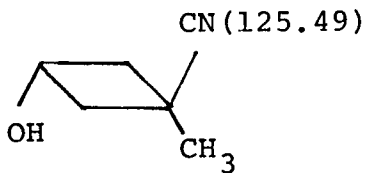






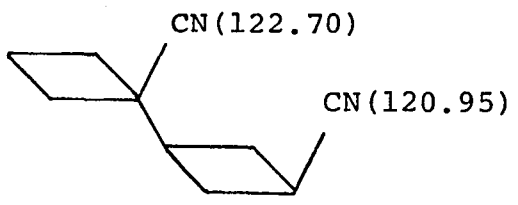


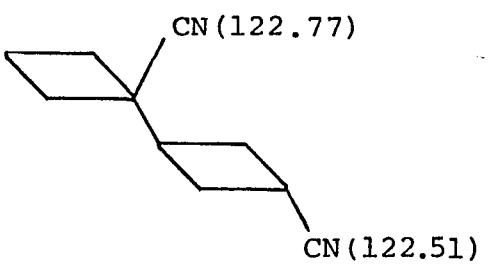




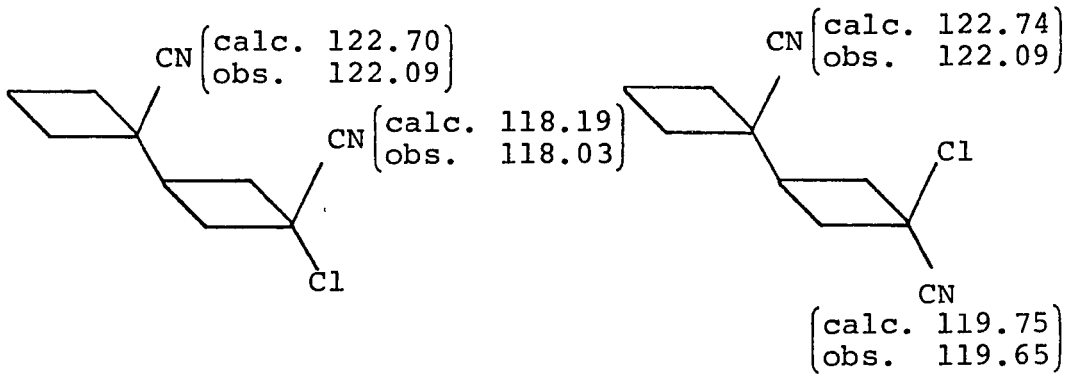
In each case, the nitrile group which is cis to the 3 substituent resonates at a higher field strength than does the trans isomer. In the case of the dimers, only the cis isomer possesses a nitrile group which is cis to the

3 substituent across the ring. The dimer of less volatility shows ^{13}C nitrile carbon resonances at δ122.70 and 120.95 ($DCCl_3$) while the other shows resonances at δ122.51 and 122.77 ($DCCl_3$). Of these four resonances only the one at δ120.95 is substantially different and it is shifted to higher field than the remaining three. This again supports the conclusion that the less volatile isomer is the cis isomer and the more volatile isomer is the trans isomer. This analysis also allows for the assignment of the other nitrile resonance in the cis isomer. This same assignment in the trans isomer is more difficult since they are much more similar. Consideration of the influence exerted by an α methyl group in the two 3-hydroxycyanocyclobutanes suggests that an α alkyl group will shift the nitrile carbon resonance to lower field. If one assumes that the cyanocyclobutane group constitutes an alkyl fragment, the nitrile carbon resonance in the trans isomer which occurs at lower field may be assigned to the nitrile group which is attached to a tertiary carbon. This leads to the following assignments:



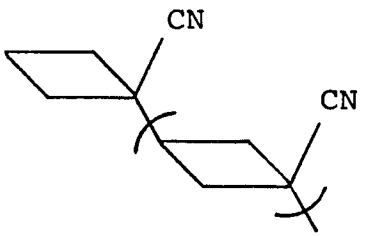


The nitrile resonances observed in the chlorinated dimers are also consistent with the above assignments. If one assumes that a shift of 2.76 ppm to higher field will occur here as it did with cyanocyclobutane and that the nitrile resonances removed from the chlorine atom are unresolved, good agreement is obtained between calculated and observed values:

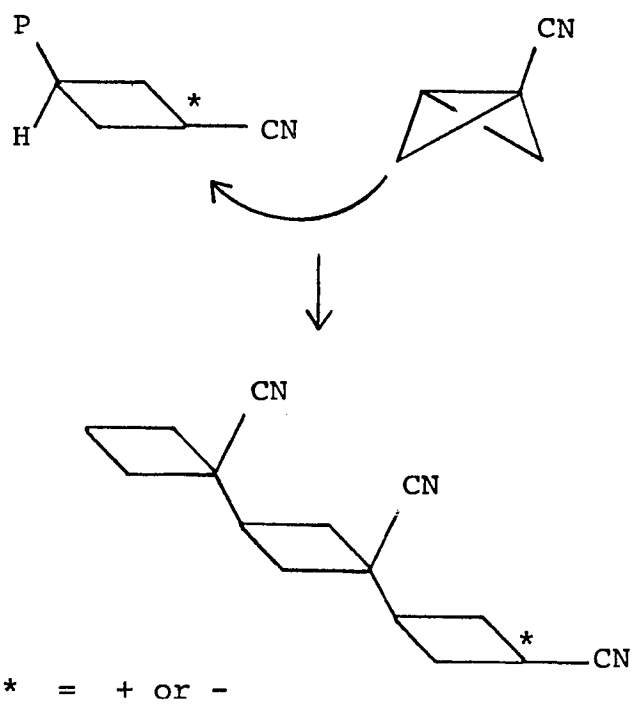


Assignment of Structure in Polybicyclobutane-1-carbonitrile

The assignemtn of the polymer structure in polybicyclobutane-1-carbonitrile follows from the arguments made for the dimers. The nitrile resonances which occur at higher field (DMSO, δ123.1) then must by extension be assigned to nitrile groups which are trans to the 3 substituent. The fact that the high field resonance predominates shows that the monomers are incorporated to give predominately 1,3 trans units.

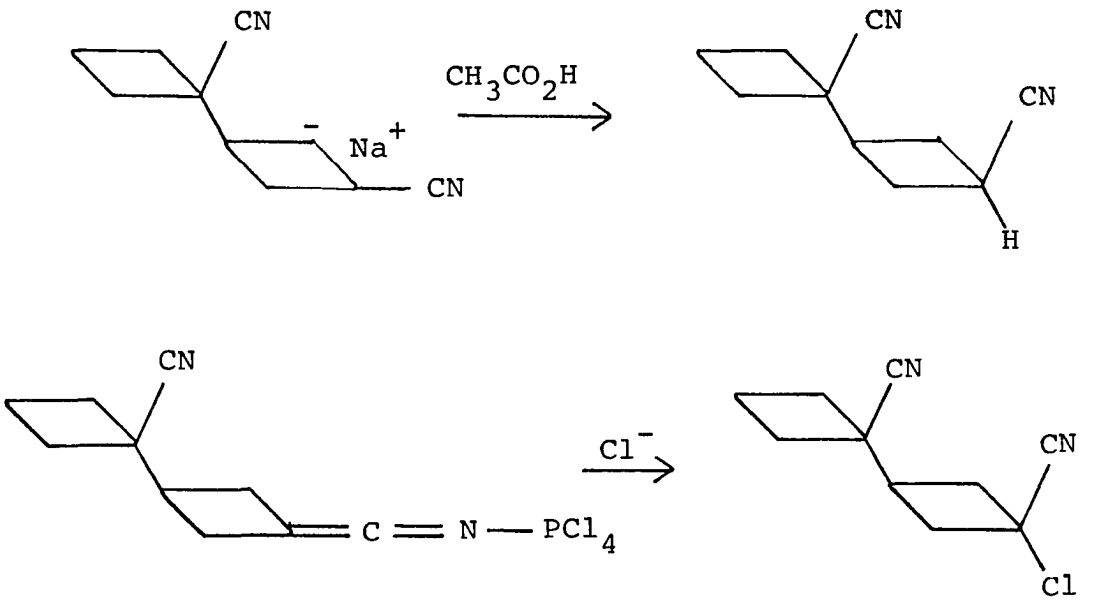


The most obvious explanation for this is that the propagating intermediate is planer (or nearly so) and that monomer addition is governed by steric interactions:



The polymer chain is the bulkiest substituent so that monomer is directed to the opposite face.

Consistent with this interpretation is the fact that both the synthesis of the dimers and the chlorination of the dimers yielded the isomer expected on steric grounds in greater abundance than the other isomer.



EXPERIMENTAL

Instrumentation

All boiling points and melting points are uncorrected. Melting points were determined on a Thomas-Hoover melting point apparatus. Infrared spectra were taken on a Perkin Elmer 337 spectrophotometer in potassium bromide, between sodium chloride plates or as a film. Nmr spectra were obtained on a Varian T-60 spectrometer and ^{13}C-nmr spectra were obtained on a Bruker WH-90 spectrometer. Mass spectra data were collected on a Varian Mat 311A mass spectrometer. Preparative and analytical gas-liquid chromatography was done on a Varian Aerograph 1700 instrument. Elemental analyses were performed by Mic Anal Inc., Tucson, AZ.

Monomer Synthesis

1-Chloro-3-methylenecyclobutane-1-carboxylic Acid

Potassium hydroxide (42.2 g, 0.752 moles) was dissolved in 750 ml water in a two liter Erlenmeyer flask with magnetic stirring. After cooling to room temperature, freshly distilled 1-chloro-3-methylenecyclobutane-1-carbonitrile (48.0 g, 0.376 moles, prepared by the method

of Hall and Snider, 1979) was added. This heterogeneous mixture was stirred at room temperature until it had become homogeneous (∿ 2 hours). At this time the aqueous solution was transferred to a separatory funnel and washed with two portions of diethyl ether. These washings were discarded. The aqueous layer was then acidified with 37% HCl and again extracted with two portions of diethyl ether. These extracts were saved. The aqueous layer was further acidified with 37% HCl and extracted with two more portions of diethyl ether. These ether extracts were combined with previous extracts from acidic aqueous phase and dried over magnesium sulfate. After filtering, the ether was removed on a rotary evaporator. The crude concentrated organic product was then subjected to vacuum distillation. The fraction boiling 58-59°C/0.2 mm Hg was taken as an 84% yield (46.3 g, 0.316 moles) of 1-chloro-3-methylenecyclobutane-1-carboxylic acid.

nmr ($DCCl_3$) δ: 12.0 (s,1H); 5.0 (m,2H); 3.4 (m,4H)

ir (neat): O-H, 3690-2150 cm^{-1}, max. ∿ 3065 cm^{-1}, s; C=O, 1716 cm^{-1}, s; C=C, 1680 cm^{-1}, m

Mass spectra (70 eV) m/e: 146 (P, 23.7%); 148 (P + 2, 7.7%); 111 (base)

Anal. Calc'd for $C_6H_7O_2Cl$: C, 49.17; H, 4.81

Found: C, 49.14; H, 4.89

Methyl 1-Chloro-3-methylene-
cyclobutane-1-carboxylate

A 500 ml three neck, roundbottom flask was equipped with a reflux condenser topped with a drying tube, magnetic stir bar and a dropping funnel. This was degassed by alternatively evacuating and filling with nitrogen. Into this vessel was added 126.3 ml (12.3 g, 0.386 moles) AR methanol and 0.49 g (2.57×10^{-3} moles) p-toulenesulfonic acid. With stirring, 1-chloro-3-methylenecyclobutane-1-carboxylic acid (37.72 g, 0.257 moles) was added dropwise through the dropping funnel. After the addition was complete, heating was begun and then reflux maintained for 14 hours. At this time, the entire reaction mixture was poured into 700 ml saturated sodium bicarbonate solution. The phases were separated and the aqueous washed twice with water. The organics were then combined and washed twice with saturated potassium chloride solution. The organics were then dried over magnesium sulfate, filtered and concentrated on a rotary evaporator. Short path distillation yielded 38.24 g (91.2%) of the desired ester (b.p. 39-40°C/ 2.0 mm Hg). This product was contaminated with a small amount of impurity which showed a slightly shorter retention time on 6' x 1/4" Carbowax 6000 column at 135°C. Pure fractions of the desired ester were obtained by careful spinning band column distillation (b.p. 60-61°C/7.0 mm Hg).

nmr ($DCCl_3$) δ: 4.95 (m,2H); 3.80 (s,3H); 3.4 (m, 4H)

ir (neat): C-H, 3080, 2985, 2952, and 2845 cm^{-1}, m,s,s,m; C=O, 1743 cm^{-1}; C=C, 1686 cm^{-1}, s,m

Mass spectra (70 eV) m/e: 160 (P, 3.5%); 162 (P+2, 2.1%); 125 (base)

Anal. Calc'd for $C_7H_9O_2Cl$: C, 52.35; H, 5.65

Found: C, 52.36; H, 5.67

Methyl 3-Methylenecyclobutane-1-carboxylate

A dry 500 ml three neck, roundbottom flask was equipped with a magnetic stirring bar, a vacuum adapter and sealed with septums. This apparatus was degassed by alternatively evacuating and filling with nitrogen. Into this vessel was introduced, with vigorous nitrogen flow, 4.90 g of a dispersion of potassium hydride in oil (24.6% KH, 1.2 g KH, 0.030 moles). The vessel was resealed and then the contents rinsed with 3 x 10 ml portions of dry hexane. The remaining greyish-white solid was then covered with 60 ml dry dimethylformamide to which a small spatula of 3-t-butyl-4-hydroxy-5-methylphenyl sulfide free radical inhibitor had been added. With vigorous nitrogen flow the apparatus was rearranged for mechanical stirring and equipped with a septum sealed dropping funnel. The dropping funnel was then charged with 1.78 g (0.0111 mole) methyl 1-chloro-3-methylenecyclobutane-1-carboxylate. The reaction vessel

was chilled to -10°C in an ice/methanol bath and stirring begun. The chloroester was then added dropwise at a sufficient rate to maintain a steady evolution of hydrogen. After all of the chloroester had been added, the dropping funnel was rinsed with 2 ml of dry dimethylformamide. Stirring was continued until the evolution of hydrogen had ceased (20-30 minutes). At this time, the entire reaction mixture was poured into a mechanically stirred mixture of ∿ 500 g ice, 500 ml ether, 10 ml 37% HCl and a spatula tip of 3-t-butyl-4-hydroxy-5-methylphenyl sulfide free radical inhibitor. After melting was complete, the layers were separated and the aqueous was washed twice with ether. These extracts were combined with other organics and washed with three portions of a 5% sodium bicarbonate solution. The organics were then washed with two portions of saturated potassium chloride solution, dried over magnesium sulfate and filtered. These organics were then concentrated on a rotary evaporator and vacuum distilled at room temperature. Distillate was collected in a Dry Ice chilled receiver containing 3-t-butyl-4-hydroxy-5-methylphenyl sulfide. Methyl 3-methylenecyclobutene-1-carboxylate (0.85 g, 60.5%) was collected between 10 mm Hg and 0.1 mm Hg at 25°C. This material was pure by nmr and GC.

nmr ($DCCl_3$)δ: 6.80 (s,1H); 5.05 (m,1H); 4.85 (m,1H); 3.80 (s,3H); 3.10 (m,2H)

ir (neat): C-H, 3085, 2958, 2925 and 2832 cm^{-1}, m,s,s,m; C=O, 1719 cm^{-1}, s; C=C, 1663, 1562 cm^{-1}, m,m

Mass spectra (70 eV) m/e: 124 (P, 36.5%); 125 (P+2, 2.78%); 66 (base)

Anal. Calc'd for $C_7H_8O_2$: C, 67.73; H, 6.50

Found: C, 67.53; H, 6.55

The sodium bicarbonate extracts were acidified with 37% HCl and extracted with two portions of ether containing 3-t-butyl-4-hydroxy-5-methylphenyl sulfide. These extracts were washed with saturated potassium chloride solution twice, dried over magnesium sulfate, filtered and concentrated on a rotary evaporator. This material was then kugelrohr-distilled from a preheated oven at 40-45°C/0.1 mm Hg into a Dry Ice chilled receiver containing 3-t-butyl-4-hydroxy-5-methylphenyl sulfide. 3-Methylenecyclobutene-1-carboxylic acid (0.30 g, 23.7%) was isolated in this way.

nmr ($DCCl_3$)δ: 11.4 (s,1H); 6.95 (s,1H); 5.15 (m,1H); 4.90 (m,1H); 3.10 (s,2H)

ir (neat): O-H, 3500-2950 cm^{-1}, s; C=O, 1690 cm^{-1}, s; C=C, 1670, 1575 cm^{-1}, m,m

Mass spectra (70 eV) m/e: 110 (P, base); 111 (P+1, 7.0%); 82 (42%); 68 (40%)

Chloromaleic Anhydride

A two liter three neck, roundbottom flask was equipped with a large condenser and a magnetic stir bar. The apparatus was degassed and filled with nitrogen. Carbon tetrachloride (1300 ml) was added and stirring and heating begun. At reflux was added 153 g (2.07 moles) maleic anhydride. At this time the apparatus was equipped with a chlorine bubbler and a scrubbing apparatus. A slow flow of chlorine gas into the reaction was maintained for 43.5 hours. The vessel was exposed to a 250 watt white lightbulb during this time. The mixture was then cooled to 0°C and filtered. The crude product was then recrystallized from chloroform to yield 90 g (0.621 moles, 30%) dichlorosuccinic anhydride (clean by nmr).

This material was not further purified. A 500 ml one neck, roundbottom flask was equipped with a reflux condenser fitted with a vacuum adapter and a magnetic stir bar. The vacuum adapter was connected to a bubbler and the condenser turned on. The flask was then immersed in a preheated 190°C oil bath and stirring begun. HCl evolved for ∿ 15 minutes. When gas evolution ceased, the flask was removed from the oil bath and allowed to cool to room temperature. This black liquid was then vacuum distilled to give 58.3 g (83%) chloromaleic anhydride (b.p. 44-45°C/ 1 mm Hg). This material crystallized in the receiver and was solid at room temperature (lit. m.p. 32°C).

1-Chloro-3-methylenecyclobutane-
1,2-dicarboxylic Anhydride

The cycloaddition reaction used was a modified version of the literature method (Cripps, Williams and Sharkey, 1959). A stainless steel rocker bomb was charged with chloromaleic anhydride (58.3 g, 0.44 mole), allene (18 g, 0.45 moles), benzene (60 ml as diluent) and 3-t-butyl-4-hydroxy-5-methylphenyl sulfide (1.57 g, 0.0044 mole). The contents were freeze degassed and then heated at 200°C with agitation for five hours. At the end of this period the black sludge was poured into a large volume of ether to precipitate the oligomeric products. This was filtered and the filtrate reconcentrated and reprecipitated into ether again. This was again concentrated and vacuum distilled. Unreacted chloromaleic anhydride was removed (25-45°C/1 mm Hg) and then 18.22 g (0.106 mole, 24%) 1-chloro-3-methylene-cyclobutane-1,2-dicarboxylic anhydride was collected (75-76°C/1.0 mm Hg). This material crystallized upon storage at -10°C.

nmr ($DCCl_3$) δ: 5.4 (m,2H); 4.25 (m,1H); 3.55 (m,2H)

ir (neat): C-H, 3100, 2990, 2945 cm^{-1}, m,s,m;
C=O, 1865, 1790 cm^{-1}, s,s; C=C, 1682 cm^{-1}

Mass spectra (70 eV) m/e: 172 (P, 20%); 174 (P + 2, 7%); 155 (base); 137 (61%)

Anal. Calc'd for $C_7H_5O_3Cl$: C, 48.73; H, 2.92
Found: C, 48.75; H, 2.91

1-Chloro-3-methylenecyclobutane-
1,2-dicarboxylic Acid

A solution of 60 g (0.60 mole) of potassium bicarbonate in 800 ml of water was prepared. To this was added 13.25 g (0.077 mole) crystalline 1-chloro-3-methylenecyclobutane-1,2-dicarboxylic anhydride. This was stirred magnetically until all of the solid had dissolved (four hours). At this time the solution was transferred to a separatory funnel and washed twice with ether while still basic. These washings were discarded and then the aqueous phase was acidified with 37% HCl. This was again extracted with two portions of ether. These ether extracts were washed with saturated potassium chloride solution and then dried over magnesium sulfate. This was concentrated on a rotary evaporator and then pumped on at 0.1 mm Hg for one hour. The crude yield at this point was 13.88 g (0.073 mole, 95%). This compound was normally not further purified but used immediately in the subsequent esterification with diazomethane. It showed a melting point of 128-130°C in this state of purity.

nmr ($DCCl_3$) δ: 10.7 (s,2H); 5.40 (m,1H); 5.15 (m,1H); 4.35 (m,1H); 3.40 (m,2H)

ir (neat): O-H, 3650-2750 cm^{-1}, max. $\sim$ 3000 cm^{-1}, s; C-H, 2960, 2900 cm^{-1}, s,m; C=O & C=C, 1680-1720 cm^{-1}, s

Mass spectra (70 eV) m/e: 190 (P, 0.51%); 155 (base); 137 (54%)

Dimethyl 1-Chloro-3-methylene-cyclobutane-1,2-dicarboxylate

A solution of diazomethane in ether was generated by the reaction of N-methyl-N-nitro-N-nitroso-guanidine in ether with aqueous potassium hydroxide according to the literature procedure (Stanley, 1966). The just prepared diacid (5.05 g, 0.0265 mole) was dissolved in 50 ml anhydrous ether in a 500 ml Erlenmeyer flask. With magnetic stirring the diazomethane solution was added in portions until the yellow color persisted (no ground glass joints). The excess diazomethane was then decomposed by the addition of glacial acetic acid. This solution was washed twice with 10% potassium bicarbonate solution and then twice with saturated potassium chloride solution. After drying over magnesium sulfate and filtering, the crude organic product was concentrated on a rotary evaporator. Vacuum distillation yielded 5.22 g (0.0239 mole, 90.2%) dimethyl 1-chloro-3-methylenecyclobutane-1,2-dicarboxylate (b.p. 76-77°C/1.0 mm Hg).

nmr ($DCCl_3$) δ: 5.35 (m,1H); 5.10 (m,1H); 4.30 (m,1H), 3.80 (s,3H), 3.75 (s,3H); 3.55 and 3.20 and 3.00 (m,2H)

ir (neat): C-H, 3085, 3000, 2955, 2845 cm^{-1}, w,m, m,w; C=O, 1740, 1715 cm^{-1}, s,m; C=C, 1685 cm^{-1}, m

Mass spectra (70 eV) m/e: 218 (P, 15%); 220 (P+2, 4%); 183 (base)

Anal. Calc'd for $C_9H_{11}O_4Cl$: C, 49.44; H, 5.07

Found: C, 49.41; H, 5.15

Dimethyl 3-Methylenecyclobutene-1,2-dicarboxylate

A 250 ml two neck, roundbottom flask was equipped with a reflux condenser, a magnetic stir bar, a dropping funnel, a small spatula tip of 3-t-butyl-4-hydroxy-5-methylphenyl sulfide and sealed with septums. This was degassed by alternately evacuating and filling with nitrogen. While maintaining positive nitrogen pressure, a solution of 3.0 g (0.014 mole) dimethyl 1-chloro-3-methylenecyclobutane-1,2-dicarboxylate in 60 ml absolute ether was introduced via syringe. At room temperature with stirring a solution of 1.80 g (0.016 mole) 1,4-diazabicyclo[2.2.2]octane (Dabco) in 100 ml anhydrous ether was added dropwise over thirty minutes through the dropping funnel. This caused an instant precipitate to form and gently refluxed the ether. The flask was placed in a room temperature water bath to moderate the heat generated by the reaction. After addition was complete the reaction mixture was filtered through a coarse sintered glass filter. No new precipitate formed so the solution was transferred to a separatory funnel and washed with two portions of 10% HCl solution followed by two portions of saturated potassium chloride solution. This was

then dried over magnesium sulfate, filtered and concentrated on a rotary evaporator. The crude product was then further concentrated by pumping at 0.1 mm Hg at room temperature for thirty minutes. At this time, the crude product was introduced into a preheated kugelrohr oven and distilled. The new diester monomer was collected at an oven temperature of 50-55°C/0.1 mm Hg, yielding 2.42 g (0.013 mole, 95%).

nmr ($DCCl_3$) δ: 5.45 (m,1H); 5.05 (m,1H); 3.85 (s,6H); 3.15 (m,2H)

ir (neat): C-H, 3000, 2950, 2900 cm^{-1}, m,s,s; C=O, 1720, shoulder 1700 cm^{-1}, s,w; C=C, shoulder 1690 cm^{-1}, 1595 cm^{-1}, w,m

Mass spectra (70 eV) m/e: 182 (P, 91%); 183 (P+1, 9%); 151 (base); 123 (49%)

High resolution on 182: $C_9H_{10}O_4$:
Calc'd 182.0579 - found 182.0574

Anal. Calc'd for $C_9H_{10}O_4$: C, 59.34; H, 5.53
Found: C, 58.62; H, 5.61

Sample Polymerizations

Photolytic Free Radical Homopolymerization

A dry polymerization tube containing a small magnetic stir bar was degassed by alternately evacuating and filling with argon. Into this tube was introduced 0.182 ml of an 0.0758 mole solution of azobisisobutyronitrile (1.38×10^{-5}

mole AIBN) in anhydrous ethyl ether. The ether was then removed under vacuum. Into this vessel with argon flow was introduced 0.1714 g (1.38×10^{-3} mole) freshly distilled methyl 3-methylenecyclobutene-1-carboxylate and 1.7 ml dimethylsulfoxide. The contents were then freeze degassed and placed in a UV reactor containing a magnetic stirrer. The contents were stirred at 38°C and irradiated for 19.75 hours. At this time the contents were added dropwise to 35 ml AR methanol containing a small spatula of 3-t-butyl-4-hydroxy-5-methylphenyl sulfide. The precipitated polymer was stirred in the methanol for two hours and then filtered. The crude polymer was then dried under vacuum for two hours and dissolved in chloroform. The chloroform solution was then added dropwise to a 10-fold excess of methanol containing 3-t-butyl-4-hydroxy-5-methylphenyl sulfide to reprecipitate the polymer. The polymer was then filtered and dried under vacuum for 48 hours yielding 0.0645 g (37.6%) poly methyl 3-methylenecyclobutene-1-carboxylate $\eta_{inh} = 0.44$ dl/g at 30°C (0.0039 g/3.9 ml $DCCl_3$).

Anal. Calc'd for $C_7H_8O_2$: C, 67.73; H, 6.50

Found:

Photolytic Free Radical
Copolymerization

The procedure used in homopolymerization was duplicated with the modification that total concentration of

freshly distilled monomers was kept at approximately 10% and approximately a 1:1 molar ratio of comonomer was used in each case.

Thermal Homopolymerization

Polymerization mixtures were prepared in solution and bulk in the same manner as those used in photolytic polymerizations. Instead of placing in a UV reactor, these samples were then immersed in a 70°C oil bath for varying lengths of time. Bulk polymerization of methyl 3-methylene-cyclobutene-1-carboxylate produced insoluble crosslinked polymer in 0.50 hour. Solution polymerization of this monomer in toulene gave both soluble polymer (23%) and gel (7%) in 3.67 hours. Dimethyl 3-methylenecyclobutene-1,2-dicarboxylate gave crosslinked polymer in two minutes when heated at 70°C in bulk. Linear polymers were obtained from dimethylsulfoxide solution at 70°C with this monomer.

Model Compound for ^{13}C Nmr Structural Elucidation of Poly Bicyclobutane-1-carbonitrile

cis- and trans-3-(1'-Cyclobutyl-1'-carbonitrile)-cyclobutane-1-carbonitrile

A one liter three neck, roundbottom flask was equipped with a magnetic stir bar, an argon inlet and a coarse sintered-glass filter to which a second one liter, three neck, roundbottom flask was attached. All unused necks were securely sealed (all glassware and syringes had

been baked dry in a 120°C oven for 24 hours). This apparatus was then alternately evacuated and filled with argon six to eight times.

Into this dry argon-filled reaction vessel was transferred 250 ml (0.0625 mole) of a freshly prepared 0.25 M triphenylmethylsodium solution in ether via 50 ml hypodermic syringe (Hall et al., 1977). This was stirred in a 0°C ice bath for approximately ten minutes. To this chilled dark red solution was added a room temperature solution of 4.9 g (0.06 mole) dry cyanocyclobutane in 40 ml anhydrous ether dropwise via 50 ml hypodermic syringe. Time of addition was approximately ten minutes. The pinkish precipitate of sodiocyanocyclobutane was then filtered using positive argon pressure and dissolved in 150 ml freshly distilled tetrahydrofuran (from sodium/benzophenone). With a rapid flow of argon through the system, the apparatus was rearranged to accommodate a mechanical stirrer and a dropping funnel (50 ml) equipped with a side arm and a chilling bowl.

The reaction vessel was returned to the 0°C bath and a solution of 3.1 g (0.039 mole) bicyclobutane-1-carbonitrile (prepared by method of Hall et al., 1971a) in 300 ml of dry tetrahydrofuran (from sodium/benzophenone) was prepared in a 500 ml roundbottom flask. This solution and the dropping funnel were each chilled with a Dry Ice/acetone cold bath. With vigorous stirring, the bicyclobutane-1-carbonitrile solution was added as a steady stream by cannulation from

the 500 ml flask through the chilled dropping funnel into the reaction vessel. The time of addition was minimized (approximately five minutes), after which the reaction was quenched immediately with 8 ml propionic acid.

The reaction mixture was then transferred to a one liter roundbottom flask, concentrated on a rotary evaporator and redissolved in ether. The salts and polymeric products were then filtered out and the filtrate concentrated again on a rotary evaporator. Most of the excess propionic acid and cyclobutanecarbonitrile were removed by vacuum distillation (25°C/0.5 mm Hg). The remaining crude organic product was dissolved in a minimum volume of acetone and applied to a silica gel column (22 cm x 2.5 cm MCG Grade 12, 28-200 mesh) packed in hexane. This was eluted with hexane until all of the triphenylmethane remnants had been removed. The remainder of the organic product was eluted with acetone, reconcentrated and subjected to kugelrohr distillation. The volatiles were separated into four fractions. The distillate collected at a pressure of 0.3 mm Hg and an oven temperature range of 80-90°C was shown to be rich in the two dimers by gas chromatography. Based on peak areas the total yield of dimers in this distillate was 1.02 g (16% yield based on starting bicyclobutane-1-carbonitrile).

From the distillate 112 mg of one isomer and 165 mg of the other were isolated by preparative GC. The column used was 6' x 1/4" Carbowax 6000 on Chromasorb (80-100 mesh).

At a temperature of 200°C and a helium pressure of 20 psi one isomer had a retention time of 180 seconds and the other a retention time of 310 seconds.

The isomer with a retention time of 180 seconds showed the following spectral characteristics:

nmr ($DCCl_3$)δ: 2 complex multiplets, one centered at 3.18 and the other centered at 2.4 (ratio of 1:2.5 respectively)

ir (neat): C-H, 3000, 2960, 2875 cm^{-1}, s,s,s; C=N, 2250 with small shoulder 2210 cm^{-1}, m,w

Mass spectra (70 eV) m/e: 160 (P, 0.76%); 159 (P-H, 5.6%); 133 (P-HCN, 9.2%); 79 (base)

Anal. Calc'd for $C_{10}H_{12}N_2$: C, 74.97; H, 7.55; N, 17.48

Found: C, 69.49; H, 7.69; N, 15.53

The isomer corresponding to a 310 second retention time showed the following spectral characteristics:

nmr ($DCCl_3$)δ: 2 broad overlapping multiplets, one centered at 3.0 and the other at 2.5 in a ratio of 1:10 respectively

ir (neat): C-H, 3000, 2960, 2875 cm^{-1}, s,s,s; C≡N, 2250, 2200 cm^{-1}, m,w

Mass spectra (70 eV) m/e: 160 (P, 1.8%); 159 (P-H, 18.8%); 133 (P-HCN, 18.5%); 79 (base)

High resolution on 160 and 159:

$C_{10}H_{12}N_2$: Calculated 160.1000

Found 160.1059

$C_{10}H_{11}N_2$: Calculated 159.0922

Found 159.0946

Anal. Calc'd for $C_{10}H_{12}N_2$: C, 74.97; H, 7.55; N, 17.48

Found: C, 74.70; H, 7.70; N, 17.29

Chlorinations

All of the chlorination reactions were adapted from the literature procedure (Hall and Snider, 1979).

1-Chlorocyclobutane-1-carbonitrile

A dry 25 ml three neck, roundbottom flask was fitted with a reflux condenser, magnetic stir bar and a nitrogen inlet. The apparatus was degassed by alternately evacuating and filling with nitrogen. With nitrogen flow through the system, phosphorus pentachloride (7.72 g, 0.037 mole) was added and then the flask was sealed with rubber septums. To this was added via syringe with stirring, 3.70 ml dry chloroform, 3.90 g (0.0494 mole) dry pyridine (caution: exotherm) and freshly distilled cyclobutane-1-carbonitrile (2.00 g, 0.0247 mole). This heterogeneous mixture was then brought to reflux and stirred for 47 hours. At this time, the reaction mixture was cooled to room temperature and

poured over 50 g of ice. After melting, the phases were separated and the aqueous washed twice with ether. The combined organics were then washed twice with saturated potassium chloride solution followed by two 10% potassium carbonate washes. The organics were then dried over magnesium sulfate, filtered, and concentrated on a rotary evaporator. This was then bulb-to-bulb distilled at room temperature and 0.2 mm Hg to yiled 1.80 g (0.0156 mole, 63%) 1-chlorocyclobutane-1-carbonitrile.

nmr ($DCCl_3$) δ: Broad complex multiplet from 2.5 to 3.3 with max at 2.8. Broad complex multiplet from 1.9 to 2.5 with max at 2.3. These two envelopes overlap with that at lower field integrating for 60% of the total absorption.

ir (neat): C-H, 2995, 2955, 2880 cm^{-1}, s,s,m; C-N, 2245 cm^{-1}, m

Mass spectra (70 eV) m/e: 117 (P+2, 0.2%); 115 (P, 0.6%); 90 (17%); 88 (55%); 80 (base)

Anal. Calc'd for C_5H_6NCl: C, 51.97; H, 5.23; N, 12.12

Found: C, 52.18; H, 5.45; N, 12.02

1-Chloro-3-(1'-cyclobutyl-1'-carbonitrile)-cyclobutane-1-carbonitrile

The chlorination of cyclobutane-1-carbonitrile was performed again and monitored by nmr in order to estimate the time of reaction necessary for the chlorination of the dimers. By comparing the integration intensities of the two envelopes observed in the proton nmr spectrum it was judged the reaction was complete after nine hours. Each of the two dimers was then chlorinated using the same procedure described above with the exception that the reaction time was shortened to nine hours.

Chlorination product from 3-(1'-cyclobutyl-1'-carbonitrile)-cyclobutane-1-carbonitrile (310 sec retention time):

77 mg (0.48 m mole) starting material yielded 53 mg (0.27 m mole, 52%) chlorination product by kugelrohr distillation (40-50°C/0.1-0.05 mm Hg)

Chlorination product from trans-3-(1'-cyclobutyl-1'-carbonitrile)-cyclobutane-1-carbonitrile (180 sec retention time):

36 mg (0.225 m mole) yielded 69 mg (0.35 m mole, 42%) chlorination product by kugelrohr distillation (40-50°C/0.1-0.05 mm Hg).

The spectral characteristics of these two chlorinated products were identical:

nmr ($DCCl_3$) δ: broad complex multiplet 1.9-2.4 with max at 2.1 overlapping broad complex multiplet from 2.4 to 3.5 with max at 2.85. Integration of the envelope at lower field corresponds to 54% of the entire absorption.

ir (neat): C-H, 2990, 2945, 2860 cm^{-1}, s,s,m; C≡N, 2240 cm^{-1}, s

Mass spectra (70 eV) m/e: 196 (P + 2, 0.27%); 194 (P, 0.56%); 169 (7.35%); 167 (23.43%) 159 (82.27%); 79 (base)

Anal. Calc'd for $C_{10}H_{11}N_2Cl$: C, 61.70; H, 5.70; N, 14.39

Found (from cis): C, 62.39; H, 5.85; N, 14.43

Found (from trans): C, 62.14; H, 5.77; N, 14.45

REFERENCES

Ahn, K. D. and H. K. Hall, Jr., J. Polym. Sci.; Polym. Chem. Ed., 19, 629 (1981).

Applequist, D. E. and J. D. Roberts, J. Am. Chem. Soc., 78, 4012 (1956).

Bando, Y. and Y. Minoura, J. Polym. Sci; Polym. Chem. Ed., 14, 1183 (1976).

Bando, Y., T. Dodow, and Y. Minoura, J. Polym. Sci.; Polym. Chem. Ed., 15, 1917 (1977).

Barfield, M., J. Kao, H. K. Hall, and L. G. Snow, to be published (1982).

Conant, J. B. and G. B. Kistiakowsky, Chem. Rev., 20, 181 (1937).

Cripps, H. N., J. K. Williams, and W. H. Sharkey, J. Am. Chem. Soc., 81, 2723 (1959).

Gale, D. M., S. C. Cherkofsky, T. D. Swartz, M. I. Kohan, and J. W. Callette, Appl. Polym. Symp., 25, 113 (1974).

Hall, H. K., Jr., E. P. Blanchard, Jr., S. C. Cherkofsky, J. B. Siega, and W. A. Sheppard, J. Am. Chem. Soc., 93, 110 (1971a).

Hall, H. K., Jr., C. D. Smith, E. P. Blanchard, Jr., S. C. Cherkofsky, and J. B. Siega, J. Am. Chem. Soc., 93, 121 (1971b).

Hall, H. K., Jr. and P. Ykman, J. Polym. Sci.; Macro. Rev., 11, 1 (1976).

Hall, H. K., Jr., H. Tsuchiya, P. Ykman, J. Otton, S. C. Snider, and A. Deutschman, Jr., "Ring-opening Polymerization," T. Saegusa and E. Goethals, eds., American Chemical Society, Washington, D.C., 1977, p. 285.

Hall, H. K., Jr. and S. C. Snider, Polym. Bull. 1, 625 (1979).

Hall, H. K., Jr. and L. G. Snow, to be published in "Ring-opening Polymerization," K. J. Ivin and T. Saegusa, eds., Elservier's Applied Science Publishers, Ltd., 1982.

Howton, D. R. and E. R. Buchman, J. Am. Chem. Soc., 78, 4011 (1956).

Joh, Y., T. Yoshihara, Y. Kotake, Y. Imai, and S. Kurihara, J. Polym. Sci.; A-1, 5, 2503 (1967).

Joh, Y., S. Kurihara, T. Sakurai, Y. Imai, and T. Yoshihara, J. Polym. Sci., A-1, 8, 377 (1970).

Kiefer, E. F. and J. D. Roberts, J. Am. Chem. Soc., 84, 784 (1961).

Radin, N. S., A. K. Hajra, and Y. Akahari, J. Lipid Res., 1, 250 (1960).

Stanley, Charles W., J. Agr. Food Chem., 14, 321 (1966).

Turner, R. B., Theoretical Organic Chemistry, Butterworths, London (1959).

Worley, R. and R. N. Young, Eur. Polym. J., 8, 1355 (1972).

Wu, C. C. and R. W. Lenz, J. Polym. Sci.; Polym. Chem. Ed., 10, 3529 (1972a).

Wu, C. C. and R. W. Lenz, J. Polym. Sci.; Polym. Chem. Ed., 10, 3555 (1972b).