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NEW CHEMISTRY OF SMALL RING NITRILES.
THE UNIVERSITY OF ARIZONA, PH.D., 1978
NEW CHEMISTRY OF SMALL RING NITRILES

by

Scott Christian Snider

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

1978
THE UNIVERSITY OF ARIZONA

GRADUATE COLLEGE

I hereby recommend that this dissertation prepared under my
direction by Scott Christian Snider
entitled New Chemistry of Small Ring Nitriles
be accepted as fulfilling the dissertation requirement for the
degree of Doctor of Philosophy

H.K. Hall, Jr.                  Sept. 11, 1978
Dissertation Director          Date

As members of the Final Examination Committee, we certify
that we have read this dissertation and agree that it may be
presented for final defense.

[Signatures]

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Final approval and acceptance of this dissertation is contingent
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SIGNED: Scott C. Snider
DEDICATION

To my wife, Lynda
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ABSTRACT

The correct structure for the compound originally reported as 3-methylene[2.1.0]bicyclopentane-1-carbonitrile [H. K. Hall, Jr. and R. E. Yancy, J. Org. Chem., 39, 3862 (1974)] is 3-methylene-2-methylcyclobutene-1-carbonitrile 1, as shown by uv, nmr, cmr spectra and the structure of the homopolymer. Compound 1 was synthesized from 2-butyne-1,4-diol.

By treating 3-methylenecyclobutane-1-carbonitrile with phosphorus pentachloride, followed by 1,5-diazabicyclo[4.3.0]non-5-ene(DBN), the new compound 3-methylenecyclobutene-1-carbonitrile 2 was obtained. Monomers 1 and 2 were free radically homopolymerized by 1,5 addition to film forming polymers. Both 1 and 2 were free radically copolymerized with representative comonomers.

Dehydrohalogenation of 2-cyano-3,3-dimethyl-4-chlorooxetane with two equivalents of potassium t-butoxide in THF gave t-butyl 3,3-dimethylacrylate 3. Formation of 3 is consistent with an oxabicyclobutane intermediate. The treatment of bicyclobutane-1-carbonitrile with tungsten hexachloride/ethylaluminum sesquichloride and the attempted formation of an anion of 3-methylenecyclobutane-1-carbonitrile are described.
INTRODUCTION

The search for new monomers which polymerize to useful materials has always been a primary goal of the organic polymer chemist. The presence of nitrile groups in polymers often results in many desirable properties. The most common vinyl nitrile monomer is acrylonitrile which polymerizes free radically to a fiber-forming polymer.

\[
\text{R}^* + \text{H}_2\text{C} = \text{CHCN} \rightarrow \text{RCH}_2\text{CHC} = \text{N} \rightarrow \text{RCH}_2\text{CH} = \text{C} = \text{N} \rightarrow \text{CH}_2\text{CHCN} etc \rightarrow \left[ \begin{array}{c} \text{CN} \\ \text{CH} \\ \text{CH} \\ \text{CH} \end{array} \right]_n
\]

Although polyacrylonitrile is an important polymer (Idol 1974, Houtz 1950), it has several shortcomings: a tendency to yellow on exposure to base; blackening when heated; and being too hydrophilic as a fiber. One cause of the problems with polyacrylonitrile is that the nitrile groups are too close together. For example, when polyacrylonitrile is heated, "Black Orlon" results.

Considerable effort has been directed towards developing new nitrile monomers that do not have the shortcomings of polyacrylonitrile while having better mechanical properties.
One class of compounds, the dienenitriles, have been explored for applications in the production of rubbers with uses similar to neoprene (poly-2-chloro-1,3-butadiene). The dienenitriles, 2,4-pentadienenitrile (1-cyanoprene) and 2-methylene-3-butenenitrile (2-cyanoprene) have been extensively studied. The first synthesis of 1-cyanoprene was by the following route (Coffman 1935):

\[
\begin{align*}
\text{O} & \xrightarrow{\text{HCl}} \quad \text{OH} \quad \xrightarrow{\text{NaCN}} \quad \text{CN} \\
\text{CN} \quad \text{+} \quad \text{CN} & \xrightarrow{500 \degree C, \ 20 \ \text{mm Hg}} \quad \text{OOCCH}_3
\end{align*}
\]

2-Cyanoprene was prepared by similarly cracking 2-acetoxy-2-methyl-3-butenenitrile, which was made from methyl vinyl ketone (Carter and Johnson 1940). The free radical homopolymerization of 1-cyanoprene (Coffman 1935) and copolymerization of both cis and trans 1-cyanoprene (Wall et al. 1948, Snyder, Murdock and Marvel 1953) have been examined. Anionic polymerization of 1-cyanoprene has also been studied (Wei and Milliman 1969). Polymerization of 2-cyanoprene by several methods has been reported (Mueller 1973, Mueller, Mayer-Mader and Dinges 1972).

The incorporation of rings into polymers generally results in desirable properties, such as high glass temperature, high melting point, increased crystallinity and improved mechanical properties, which generally give more
useful polymers. Addition polymerization of cyclobutene and bicyclobutane monomers was recently reviewed (Hall and Ykman 1976). Cyclobutene-1-carbonitrile \( \text{2} \) is a reactive monomer comparable to acrylonitrile in free radical polymerization (Gale et al. 1974).

\[ R^\ast + \underbrace{\text{2}}_{\text{R-CN}} \rightarrow R^\ast \text{C=N} \leftrightarrow R \text{C=N} \text{etc} \rightarrow \underbrace{[\text{R-CN}]}_{n} \]

Synthesis of \( \text{2} \) involved dehydrocyanation of cyclobutane-1,2-dicarbonitrile (Gale and Cherkofsky 1973).

\[ \text{2} \underbrace{\text{CN}}_{\text{CN}} \rightarrow \underbrace{\text{CN}}_{\text{CN}} \rightarrow \underbrace{\text{CN}}_{\text{CN}} \]

Methylenecyclobutenes would be analogous to cyclobutenes as butadienes are to their corresponding ethylenes. As a class of potential monomers, methylenecyclobutenes have not been extensively studied. Nitrile-containing methylenecyclobutenes have not been examined as possible monomers, indeed the parent 3-methylenecyclobutene-1-carbonitrile is not reported in the literature. One of the goals of the present research was to synthesize and polymerize a 3-methylenecyclobutene-1-carbonitrile.

Methylenecyclobutene \( \text{3} \) was first made by the pyrolysis of 2-methylenecyclobutyl trimethyl ammonium hydroxide
(Howton and Buchman 1956) and from diethyl methylenemalonate through 3-methylenecyclobutane carboxylic acid and 3-methylenecyclobutyl amine (Applequist and Roberts 1956). The cycloaddition of allene and acrylonitrile is the starting step of a more recent synthesis (Kiefer and Roberts 1961, Wu and Lenz 1972a):

\[
\text{C} + \text{CN} \rightarrow \text{H} \rightarrow \text{COOH} \rightarrow \text{Br} \rightarrow \text{COOH}
\]

Methylenecyclobutene 3 polymerizes cationically by 1,5 addition, anionically by 1,2 addition (Wu and Lenz 1972a) and free radically by 1,2; 1,5; and 3,5 addition (Applequist and Roberts 1956). Doubt has been cast on the interpretation of data originally attributed to 3,5 free radical propagation (Wu and Lenz 1972b).
Methyl substituted methylenecyclobutenes that are known include 4,4-dimethyl-3-methylenecyclobutene (Applequist and Roberts 1956) and 1-methyl-3-methylenecyclobutene (Caserio et al. 1958). The polymerization of the latter was studied (Wu and Lenz 1972a,b). Cycloaddition of allene and phenylacetylene at 130°C gives 1-phenyl-3-methylenecyclobutene in 1% yield (Applequist and Roberts 1956). Also known are 3-methylene-2-methyl-1,4-diphenylcyclobutene and related compounds (Blomquist and Meinwald 1959).

Several fluorine substituted methylene cyclobutenes are reported in the literature. Cycloaddition of the appropriate allene and ethylene derivatives, followed by treatment with strong base gave the substituted methylenecyclobutenes (Taylor, Warburton and Wright 1972):

\[
\begin{align*}
\text{R} = \text{H, CH}_3 &;& \text{X} = \text{F, Cl}
\end{align*}
\]

The following have also been reported (Kirk and Taylor 1974, Banks et al. 1966):

\[
\begin{align*}
\text{R'} = \text{R} = \text{CH}_3 &;& \text{R' = CH}_3, \text{R} = \text{H} \\
\text{R'} = \text{H}, \text{R} = \text{CH}_3 &;& \text{R' = R = F}
\end{align*}
\]
Examples of other methylenecyclobutenes known can be found in the following references: (Beetz et al. 1975, Moss, Dolling and Whittle 1971, Coller, Hefferman and Jones 1968, Brandmuller and Ziegler 1964). No polymerization studies of these methylenecyclobutenes have been reported.

Only two methylenecyclobutenes systems containing a nitrile group have been reported. The first one is obtained in 61% yield by the scheme (Kristol 1973):

The second report used the pathway shown (Madsen and Lawesson 1974) to give 4.

Compound 4 was noted to polymerize on heating to 100°C and on treatment with dilute hydrochloric acid, but the system was not studied.
Another group of ring-containing nitrile monomers are the bicyclo compounds that polymerize by C-C ring opening. Of the bicyclo nitriles made, the most studied are bicyclobutane-1-carbonitrile monomers, for example bicyclobutane-1-carbonitrile 5 was synthesized by the following method (Hall et al. 1971):

\[
\begin{align*}
    \text{H}_2\text{CCCH}_2 + \text{H}_2\text{CCCHCN} & \xrightarrow{\Delta} \text{Bicyclobutane} \\
    \text{Bicyclobutane} & \xrightarrow{\text{NaIO}_4/\text{OsO}_4} \text{OsO}_4 \xrightarrow{\text{NaBH}_4} \text{Bicyclobutane} \\
    \text{HO-Bicyclobutane} & \xrightarrow{\text{SOCl}_2} \text{Cl-Bicyclobutane} \\
    \text{Cl-Bicyclobutane} & \xrightarrow{\text{KOH/ether}} \text{Bicyclobutane}
\end{align*}
\]

Bicyclobutane 5 polymerizes in a 1,3 fashion and is reactive in both homo and copolymerization, giving polymers with good physical properties. Bicyclo[2.1.0]pentane-1-carbonitrile 6 and bicyclo[3.1.0]hexane-1-carbonitrile do not homo or copolymerize by free radical initiation, although 6 polymerizes anionically (Hall 1971):

\[
\begin{align*}
    \text{Cl-Bicyclopentane} & \xrightarrow{\text{KOH/ether}} \text{Bicyclopentane} \\
    \text{Bicyclopentane} & \xrightarrow{\text{n}} \text{Bicyclopentane}_n
\end{align*}
\]

Hall and Yancy (1974) claimed to have synthesized the closely related 4-methylene[2.1.0]bicyclopentane-1-carbonitrile 10 by the scheme:
In the first step monovinylacetylene is converted to 4-chloro-1,2-butadiene 7 (isochloroprene) with hydrochloric acid. Isochloroprene 7 was cycloadded to acrylonitrile to give two products, the desired cyclobutane 8 and the Diels-Alder adduct of 2-chloro-1,3-butadiene and acrylonitrile 9. The treatment of 8 with base was proposed to give 10. This potential monomer was not studied extensively, but had been observed to polymerize when left at room temperature. It was decided to study the polymerization of this new monomer in greater detail and to determine the structure of its polymer.

An 2-oxabicyclobutane has not been isolated. Of the several routes used in the attempted synthesis of a 2-oxabicyclobutane, the epoxidation of cyclopropene derivatives has been most often used (Ciabattoni and Kocienski 1969, 1971, Friedrich and Cormier 1971, Havel, Chamberlain
and Krautter 1974, Friedrich and Faito 1974). Although the products isolated and the kinetics of epoxidation agree with the intermediacy of oxabicyclobutane derivatives, these compounds have never been isolated. Irradiation of $\alpha,\beta$-unsaturated ketones have also failed (Friedrich and Schuster 1972). By analogy with the formation of bicyclobutane derivatives by photolysis of 2,3-diazabicyclo[3.1.0]hex-2-enes, a 2,3-diaza-6-oxabicyclo[3.1.0]hex-2-ene derivative was subjected to photolysis and thermolysis (Friedrich et al. 1974). Although on photolysis no nitrogen is lost, thermolysis gives mesityl oxide:

Recently in this laboratory, Ykman attempted to make a 2-oxabicyclobutane. Ykman prepared 2-oxa-4,4-dimethylcyclobutane-1-carbonitrile 11:

\[
\text{CH}_3\text{HOCH}_2\text{CCOOCH}_3\text{CH}_3 \xrightarrow{p-C_7H_7SO_2Cl/\text{pyr}} \text{p-C}_7\text{H}_7\text{SO}_2\text{OCH}_2\text{CCOOCH}_3\text{CH}_3 \xrightarrow{\text{KCN}} \text{H}_3\text{C}_\text{CN}\text{C}_\text{O}\text{H}_3\text{C}_\text{CH}_3
\]

Nitrile 11 was chlorinated in carbon disulfide with chlorine and light. The product mixture was separated to give the
α chloro 12, λ chloro 13 and a mixture of λ' chloro 14 and λ, λ' dichloro 15 compounds (Ykman 1975).

When 13 and 14 were treated with strong base, results were not conclusive. Sodium hydride in N-methylpyrrolidone with the λ' isomer 14 did give 1-cyanoisobutene 16.

The reactions of 13 and 14 with strong bases were reexamined in the present work.

The olefin disproportionation reaction commonly referred to as olefin metathesis has been an area of extensive research (Haines and Leigh 1975, Calderon 1972).

Two recent developments prompted the screening of the highly strained bicyclobutane-1-carbonitrile 5 for unusual chemistry under olefin metathesis conditions. One development was
that esters and nitriles do not interfere with olefin meta-
thesis when not conjugated with the reactive double bond
(Ast, Rheinwald and Keiber 1976a,b, Nakamura, Matsumoto and
Echigoya 1976, Matsumoto, Komatsu and Igarashi 1977):

The second development was the reactivity of the strained
cyclopropane ring system in olefin metathesis. Cyclopro-
panes can be converted into olefins. Alkenes conjugated
with electron withdrawing groups can also trap the inter-
mediate of olefin metathesis to give cyclopropanes (Gassman
and Johnson 1976a,b,c,d, Casey, Albin and Burkhardt 1977).

The central bond of 5 often reacts like a double bond; thus
several reactions were considered possible.
Bicyclobutane-1-carbonitrile polymers referred to on the previous page (Hall and Ykman 1976) have not been studied with regards to stereochemistry.

In connection with a cmr study of the polymers of 5, a 1,3-dialkylated cyclobutane-1-carbonitrile of known stereochemistry was needed:

Two routes to the cis compound were investigated, both starting with 3-methylenecyclobutene-1-carbonitrile 17. The first route involves addition to the double bond followed by cyclization and elimination of sulfur:
The second method started with the anion of 17, which would be reacted thus:

\[
\begin{align*}
\text{CN} & \quad + \quad \text{S} \\
\text{HC} & \quad \text{CN} \\
\text{CH}_3 & \quad \text{CH}_2\text{CH}_3 \\
\end{align*}
\]

Since the anion of 17 was not known, it would have to be synthesized.

To summarize, the goals of this research were:

1. the synthesis of a 3-methylenecyclobutene-1-carbonitrile;
2. the further study of 3-methylene[2.1.0]bicyclobutane-1-carbonitrile;
3. reexamination of the dehydrohalogenation of 2-cyano-3,3-dimethy-4-chlorooxetane;
4. the synthesis of an anion of 3-methylenecyclobutane-1-carbonitrile and of a stereo isomer of a 1,3-dialkyl cyclobutane-1-carbonitrile.
RESULTS

Synthesis of 3-Methylene-2-methylcyclobutene-1-carbonitrile

The literature method for the synthesis of 4-methylenebicyclo[2.1.0]pentane-1-carbonitrile (Hall and Yancy 1974) was reproduced, but the current unavailability of monovinylacetylene, a required intermediate, necessitated developing a new synthetic scheme. The method chosen started with 2-butyne-1,4-diol 18. The diol 18 was converted to 1,2-butadien-4-ol 19 in two steps:

\[
\text{HOCH}_2\text{C}≡\text{CCH}_2\text{OH} \xrightarrow{\text{SOCl}_2, \text{H}_2\text{CCl}_2, \text{pyr}} \text{ClCH}_2\text{C}≡\text{CCH}_2\text{OH} \xrightarrow{\text{LAI, ether}} \text{H}_2\text{C}≡\text{C}≡\text{CHCH}_2\text{OH}
\]

The 4-chloro-2-butyne-1-ol 20 was made by a minor modification of the literature method (Bailey and Fujiwara 1955). The modification involved using dichloromethane instead of benzene because more consistent results were obtainable in the new solvent. With benzene as the solvent, pyridine hydrochloride which forms in the reaction sometimes precipitated. The precipitate coincided with low yields. In dichloromethane, the pyridine hydrochloride did not form a precipitate, and consistently good yields were obtained. The conversion of 20 to allene 19 was done with lithium aluminum hydride in ether (Bailey and Pfeifer 1955). The
product was isolated from lithium-aluminum salts by basic workup instead of the usual acidic method used in the literature procedure. Basic workup permitted a shorter and cleaner isolation of 19 without the necessity of a several day continuous extraction from water that would otherwise be required. A lower ratio of LAH to chlorohydrin 20 than reported was found to give good results. Care was observed in the handling of 1,2-butadien-4-ol 19 because it is a strong vesicant. The allenic alcohol 19 was converted to the acetate 21 (Carothers and Berchet 1933) and to the silyl ether 22 with hexamethyldisilazane/chlorotrimethylsilane:

\[
\begin{align*}
\text{H}_2\text{C}=\text{C}=\text{CHCH}_2\text{O}\text{CH}_3^{\text{O}} & \xleftarrow{\text{Ac}_2\text{O}} \text{H}_2\text{C}=\text{C}=\text{CHCH}_2\text{OH} \\
\text{H}_2\text{C}=\text{C}=\text{CHCH}_2\text{OSi(CH}_3\text{)}_3 \xrightarrow{\text{HMDS/ClSiMe}_3} & \text{H}_2\text{C}=\text{C}=\text{CHCH}_2\text{OSi(CH}_3\text{)}_3
\end{align*}
\]

Silyl ether 22 was very sensitive to moisture and slowly decomposed even in a sealed vial.

The allenes 19, 21, 22 and 7 were cycloadded to acrylonitrile by one of two methods (Hall and Yancy 1974, Cripps, Williams and Sharkey 1959). The main difference in the two methods is whether the reaction vessel walls are made of Pyrex glass or of stainless steel. Table 1 presents the results of the cycloaddition of the substituted allenes to acrylonitrile at 200°C for 8 hr.
Table 1. Comparison of Cycloaddition of Substituted Allenes and Acrylonitrile in Pyrex and Stainless Steel Vessels

<table>
<thead>
<tr>
<th>H₂C=CHCH₂X, Cycloadducts in Stainless Steel Vessel</th>
<th>Yield of Cycloadducts in Pyrex Tube</th>
<th>Yield of Cycloadducts in Stainless Steel Vessel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl</td>
<td>20.6%</td>
<td>62.5%a</td>
</tr>
<tr>
<td>-OH</td>
<td>29.7%</td>
<td>&lt;5.0%</td>
</tr>
<tr>
<td>-OSi(CH₃)₃</td>
<td>51.6%</td>
<td>0.0%</td>
</tr>
<tr>
<td>-OOCCH₃</td>
<td>49.7%</td>
<td>52.0%</td>
</tr>
</tbody>
</table>

a: Diels-Alder adduct only

With isochloroprene 7, the cycloadducts previously described were obtained in 20.6% yield when a sealed Pyrex tube was used. With a stainless steel tube, only the cyclohexene 9 was obtained.

The cycloaddition of the other substituted allenes 19, 21 and 22 gave the following products in approximately 1:1 ratio.
With alcohol 19 and silyl ether 22, the presence of stainless steel resulted in very poor yields. However, with allene acetate 21, the yield of cycloadducts improved slightly, presumably because temperature control was better then when the Pyrex tube was used. Cycloadducts 23 and 24 are best prepared from the acetate 21 because the yield of cycloadduct was good and a stainless steel tube allows the reaction to be more easily scaled up. With silyl ether 22, the reaction was sensitive to temperature conditions. In two of sixteen cycloadditions with 22, uncontrollable exothermic reactions occurred.

The easiest way to separate alcohols 23a, 24a and acetates 23b, 24b was to convert them to silyl ethers 23c, 24c and carefully distill on a spinning band column. Silyl ether 23c could be converted to chloride 8 by the following method:

\[
\begin{align*}
\text{OSiMe}_3^+ & \xrightarrow{\text{KOH}} \text{CN} \text{H}_2\text{O} \\
\text{23c} & \\sim \text{23a} \\sim \text{8}
\end{align*}
\]

The direct conversion of 23c to 8 can be carried out with phosphorus pentachloride, but the yield of 8 was much less than when 23c was hydrolyzed to 23a and treated with thionylchloride.
Chloride 8 was treated with base as described in the literature to obtain material identical to an authentic sample (Hall and Yancy 1974).

**Structure of 3-Methylene-2-methylcyclobutene-1-carbonitrile**

The product of the dehydrochlorination of 8 possessed nmr, ir and mass spectra identical to material reported as 4-methylenebicyclo[2.1.0]pentane-1-carbonitrile 10 (Hall and Yancy 1974), but the correct structure is 3-methylene-2-methylcyclobutene-1-carbonitrile 25.

![Structure 25]

The uv spectrum of 25 shows an absorption at 252 nm, $\epsilon = 19,600$ in hexane. This compares with uv data of model compounds found in the literature (Descotes and Robbe 1969).

![UV spectra of model compounds]

Structure 10 could show uv absorption, but $\epsilon$ would be expected to be much lower as conjugation through cyclopropyl bonds is less efficient than through a double bond.

The nmr spectrum was reexamined and the spectra is shown in Figure 1.
Figure 1. Nmr of 3-Methylene-2-methyl-cyclobutene-1-carbonitrile
The peak at 1.94 δ (triplet, 3H) had been attributed to the three cyclopropyl hydrogens in structure 10. The absorption was reassigned to the methyl group of structure 25 as a triplet coupled with the methylene hydrogens of the cyclobutene ring (J = 2.3 Hz). When the methylene protons at 3.1 δ were decoupled, the triplet collapsed to a singlet and the vinyl absorption at 5.1 δ also became a singlet. Decoupling the triplet at 1.94 δ results in the sharpening of the peak at 3.1 δ. From the nmr data the following assignments were made:

\[ \begin{align*}
&d \quad H_3C \quad C=\quad C \quad CN \\
&b \quad H-C \quad C=\quad H \\
&a \quad H \quad C \quad H \\
&c \quad H \quad C \quad H \\
\end{align*} \]

\[ a = 5.10 \text{ δ} \quad b = 4.80 \text{ δ} \quad c = 3.10 \text{ δ} \quad d = 1.94 \text{ δ} \]

The decoupling data make structure 10 extremely unlikely as the three cyclopropyl hydrogens would not be expected to have exactly the same chemical shift and not to couple with each other. In fact, the two methylene hydrogens would not be expected to have the same chemical shift because they are not magnetically equivalent with respect to the nitrile and cyclobutyl groups.
Broad band and gated decoupled cmr spectra were taken with the results reported in Table 2:

Table 2. CMR of 3-Methylene-2-methylcyclobutene-1-carbonitrile in DCCl₃

<table>
<thead>
<tr>
<th>Absorption</th>
<th>Shift (δ)</th>
<th>Number of Hydrogens</th>
<th>J₁₃ Hz</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>12.15</td>
<td>3</td>
<td>128</td>
<td>H₃C-C=</td>
</tr>
<tr>
<td>2</td>
<td>37.43</td>
<td>2</td>
<td>143</td>
<td>H₂C=C</td>
</tr>
<tr>
<td>3</td>
<td>105.02</td>
<td>2</td>
<td>160</td>
<td>H₂C=</td>
</tr>
<tr>
<td>4</td>
<td>145.25</td>
<td>-</td>
<td>-</td>
<td>C≡N</td>
</tr>
<tr>
<td>5</td>
<td>161.05</td>
<td>-</td>
<td>-</td>
<td>(\overline{C=O})</td>
</tr>
</tbody>
</table>

The cmr spectrum was done in deuterochloroform with a trace of 2,5-di-tert-butyl hydroquinone to prevent polymerization. The quaternary carbon absorptions were very weak. The presence of a methyl group at 12.15 δ precludes 1₀ as the compounds structure. The 3-methylene-2-methylcyclobutene-1-carbonitrile structure 2₅ is completely consistent with the cmr data. The C-H coupling constants are in the expected range for the given assignments, for example cyclobutene C-H coupling constant is 140 Hz (Hill and Roberts 1967).
Homopolymerization of 3-Methylene-2-methylcyclobutene-1-carbonitrile

Monomer 25 was polymerized with AIBN in sulfolane and in bulk at 70°C or by irradiating with uv light (i_{n,inh} = 0.95). Monomer 25 polymerized when left at room temperature in the presence of air. In all cases, the polymers were soluble in acetone, DMF and DMSO. Clear films could be cast from acetone.

The structure of the polymer 26 arises from 1,5 addition.

![Structure of polymer 26]

Broad band and gated decoupled cmr spectra were taken to confirm the assigned structure. The results are given in Table 3. The difference in the C-H coupling constants of absorptions 2 and 4 of Table 3 show clearly that one is in a cyclobutene ring and the other is external to the ring. No evidence of 1,2 addition was detected in the polymers. Polymer 26 autoxidized slowly at room temperature and yellowed rapidly when heated, with carbonyl absorptions appearing in the ir spectra. The autoxidation of cyclobutene-containing polymers has been shown to be very facile (Wu and Lenz 1972b).
Table 3. CMR of Poly-3-methylene-2-methylcyclobutene-1-carbonitrile in Acetone-d6

<table>
<thead>
<tr>
<th>Absorption</th>
<th>Shift (δ)</th>
<th>Number of Hydrogens</th>
<th>J_{13} C-H Hz</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10.7</td>
<td>3</td>
<td>127</td>
<td>H_3-C-C=C</td>
</tr>
<tr>
<td>2</td>
<td>34.3</td>
<td>2</td>
<td>129</td>
<td>-CH_2-</td>
</tr>
<tr>
<td>3</td>
<td>40.6</td>
<td>-</td>
<td>-</td>
<td>NC</td>
</tr>
<tr>
<td>4</td>
<td>41.9</td>
<td>2</td>
<td>142</td>
<td>H_2C</td>
</tr>
<tr>
<td>5</td>
<td>122.0</td>
<td>-</td>
<td>-</td>
<td>C=C</td>
</tr>
<tr>
<td>6</td>
<td>139.5</td>
<td>-</td>
<td>-</td>
<td>C=C</td>
</tr>
<tr>
<td>7</td>
<td>142.3</td>
<td>-</td>
<td>-</td>
<td>-C≡N</td>
</tr>
</tbody>
</table>
The attempted anionic polymerization with n-butyl lithium resulted in a yellow oil in very low yield. The nmr spectra of the yellow oil in acetone-d6 had absorptions which were consistent with both 1,5 and 1,2 addition.

**Copolymerization of 3-Methylene-2-methylcyclobutene-1-carbonitrile**

Methylene cyclobutene 25 formed copolymers with styrene, p-methoxystyrene, methyl methacrylate and acrylonitrile when heated to 70°C in sulfolane with AIBN. The results of the copolymerizations are given in Table 4.

The ratio of monomers in the copolymers was determined by nmr and/or elemental analysis. Unreacted 25 and comonomer were detected in each copolymerization. As can be seen from Table 4, all copolymers were rich in methylenecyclobutene 25. The mode of polymerization of 25 appeared the same as the homopolymer on the bases of ir, nmr and for the styrene-25 copolymer, cmr spectra. The copolymers were all soluble in acetone and clear films could be cast.

**Synthesis of 3-Methylene-cyclobutene-1-carbonitrile**

Synthesis of 3-methylenecyclobutene-1-carbonitrile 27 was achieved by the following scheme:

\[
\begin{align*}
\text{H} & \quad \text{PCl}_5 \quad \text{HCl}_3 \quad \text{pyr} \\
\text{CN} & \quad \text{Cl} \\
\text{L2} & \quad \text{Cl} \\
\text{CN} & \quad \text{DBN} \quad \text{ether}
\end{align*}
\]
Table 4. Copolymers of 3-Methylene-2-methylcyclobutene-1-carbonitrile

<table>
<thead>
<tr>
<th>Comonomer</th>
<th>Feed Ratio(^a)</th>
<th>Yield(^b)</th>
<th>Ninh(^c)</th>
<th>Ratio(^d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Styrene</td>
<td>0.9906/1</td>
<td>53.0%</td>
<td>0.34</td>
<td>2.2/1</td>
</tr>
<tr>
<td>p-Methoxystyrene</td>
<td>0.9819/1</td>
<td>82.6%</td>
<td>0.35</td>
<td>1.5/1</td>
</tr>
<tr>
<td>Methyl methacrylate</td>
<td>0.9687/1</td>
<td>65.6%</td>
<td>0.25</td>
<td>5.7/1</td>
</tr>
<tr>
<td>Acrylonitrile</td>
<td>0.8717/1</td>
<td>43.0%</td>
<td>0.84</td>
<td>17.0/1</td>
</tr>
</tbody>
</table>

\(^a\) Moles 25/moles comonomer

\(^b\) Based on consumption of 25

\(^c\) In acetone at 30°C, g/100 cc

\(^d\) Moles 25 in polymer/moles comonomer in polymer
Chlorination of 17 was done with phosphorus pentachloride in chloroform and pyridine. The role of pyridine is to take up hydrogen chloride formed and thus protect the double bond (Freeman, Balls and Brown 1968). Product 28 was easier to purify if the reaction was allowed to proceed until all the starting material had been consumed. Dehydrochlorination of 28 was best done in ether with DBN. Since chloronitrile 28 is symmetrical, the only dehydrochlorination product possible is methylenecyclobutene 27. Monomer 27 is easily isolated from the reaction by vacuum distillation at room temperature using a Dry Ice-acetone bath to cool the receiver flask. Diene 27 is unstable at room temperature in the presence of air and gives an insoluble clear solid. Monomer 27 can be stored at -50°C, at which temperature it is crystalline.

Broad band and gated decoupled cmr spectra were taken with the results reported in Table 5. A trace of 2,5-tert-butyl hydroquinone was used to prevent the polymerization of 27 while the cmr spectra were being obtained. The absorption of the quaternary carbons were very weak, which is a generally found occurrence. The data are consistent with the structure 27 and the expected similarities in the cmr spectra 25 and 27 are present, such as in the cyclobutene methylene groups.
Table 5. CMR Spectra of 3-Methylenecyclobutene-1-carbonitrile in DCCl$_3$

<table>
<thead>
<tr>
<th>Absorption</th>
<th>Shift (δ)</th>
<th>Number of Hydrogens</th>
<th>$J_{13}$ C-H Hz</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>40.05</td>
<td>2</td>
<td>144</td>
<td>$\text{H}_2\text{C}$</td>
</tr>
<tr>
<td>2</td>
<td>108.19</td>
<td>2</td>
<td>160</td>
<td>$\text{H}_2\text{C}=\text{C}$</td>
</tr>
<tr>
<td>3</td>
<td>119.26</td>
<td>-</td>
<td>-</td>
<td>$\text{C}=\text{C}$</td>
</tr>
<tr>
<td>4</td>
<td>143.30</td>
<td>-</td>
<td>-</td>
<td>$-\text{C}=\text{N}$</td>
</tr>
<tr>
<td>5</td>
<td>149.35</td>
<td>1</td>
<td>179</td>
<td>$\text{H}-\text{C}$</td>
</tr>
</tbody>
</table>
Homopolymerization of 3-Methylenecyclobutene-1-carbonitrile

When monomer 27 was polymerized in sulfolane or in bulk with AIBN at 70°C, the polymers were always cross-linked and insoluble, but swelled in solvents like DMF. Non-cross-linked polymers ($\eta_{inh} = 1.15$) were obtainable in sulfolane solution by irradiating monomer 27 and a catalytic amount of AIBN with uv light at 40°C. The resulting polymers are insoluble in acetone, but soluble in DMF and DMSO. Clear films were cast from DMF. The structure of the polymer is considered to be 29, which comes from 1,5 addition. Other possible structures include 30 and 31.

The nmr spectrum of 27 has a peak at 6.10 $\delta$, assigned to the vinyl hydrogen. This compares with a peak at 6.0 $\delta$ in the spectra of cyclobutene (Silverstein, Bassler and Morrill 1974), 6.70 $\delta$ for cyclobutene-1-carbonitrile 2 (Gale and Cherkofsky 1973) and 4.82 $\delta$ for 17.
The vinyl absorption in the nmr spectra is most consistent with structure 29.

Data from the broad band and gated decoupled cmr are given in Table 6:

Table 6. CMR Spectra of Poly-3-methylenecyclobutene-1-carbonitrile in DMSO-d6

<table>
<thead>
<tr>
<th>Absorption</th>
<th>Shift (δ)</th>
<th>Number of Hydrogens</th>
<th>J_{13} C-H (Hz)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>41.96</td>
<td>2</td>
<td>(a)</td>
<td>-CH₂⁻</td>
</tr>
<tr>
<td>2</td>
<td>47.94</td>
<td>2</td>
<td>(a)</td>
<td>H₂C≡C</td>
</tr>
<tr>
<td>3</td>
<td>127.00</td>
<td>-</td>
<td>-</td>
<td>C≡C</td>
</tr>
<tr>
<td>4</td>
<td>136.50</td>
<td>1</td>
<td>183.8</td>
<td>HC≡C</td>
</tr>
<tr>
<td>5</td>
<td>153.40</td>
<td>-</td>
<td>-</td>
<td>C≡N</td>
</tr>
</tbody>
</table>

(a) Obscured by solvent absorptions

The cmr data is completely consistent with structure 29. No 3,5 addition was detected by cmr, nmr or ir spectroscopy.

Polymer 29 is more thermally stable than 26. No yellowing of 29 has been observed at room temperature,
although rapid yellowing does occur above 170°C. The DSC spectra shows an irreversible exotherm starting at 160°C.

Attempted anionic polymerization of 27 with n-butyl lithium in dry THF gave material insoluble DMF, DMSO and hexafluoroisopropanol. The ir spectra of the light brown material showed carbonyl absorptions.

Free Radical Copolymerization of 3-Methylenecyclobutene-1-carbonitrile

Methylenecyclobutene 27 formed copolymers with styrene, p-methoxystyrene, methyl methacrylate and acrylonitrile. The copolymerizations were carried out in sulfolane and initiated by irradiating AIBN with uv light at 40°C. Co-polymerization of isobutyl vinyl ether and 27 gave polymer that appeared from nmr data to be the homopolymer of 27 as no isobutyl groups were detectable. The physical properties of the polymer were also identical to 29. Copolymerization results are given in Table 7. The ratio of monomers in the copolymers were determined by nmr and/or elemental analysis. In all of the copolymerizations, unreacted comonomers were detected. Again, all the copolymers are rich in the methylenecyclobutene monomer. The copolymers are all film-forming and soluble in acetone except for the case of isobutyl vinyl ether, which was considered to be homopolymer 29.
<table>
<thead>
<tr>
<th>Comonomer</th>
<th>Feed Ratio&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Yield&lt;sup&gt;b&lt;/sup&gt;</th>
<th>η&lt;sub&gt;inh&lt;/sub&gt;&lt;sup&gt;c&lt;/sup&gt;</th>
<th>Ratio&lt;sup&gt;d&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Styrene</td>
<td>0.9753/1</td>
<td>65.0%</td>
<td>1.62</td>
<td>2.3/1</td>
</tr>
<tr>
<td>p-Methoxystyrene</td>
<td>1.0000/1</td>
<td>59.0%</td>
<td>0.83</td>
<td>1.2/1</td>
</tr>
<tr>
<td>Methyl methacrylate</td>
<td>0.9915/1</td>
<td>34.0%</td>
<td>1.11</td>
<td>5.1/1</td>
</tr>
<tr>
<td>Acrylonitrile</td>
<td>0.9367/1</td>
<td>68.4%</td>
<td>1.26</td>
<td>20.0/1</td>
</tr>
<tr>
<td>Isobutyl vinyl ether</td>
<td>0.9985/1</td>
<td>57.7%</td>
<td>1.48</td>
<td>∞</td>
</tr>
</tbody>
</table>

<sup>a</sup>Moles 27/moles comonomer
<sup>b</sup>Based on consumption of 27
<sup>c</sup>In DMF at 30°C, g/100 cc
<sup>d</sup>Moles 27 in polymer/moles comonomer in polymer
Dehydrohalogenation of 2-Cyano-3,3-dimethyl-4-chlorooxetane

Dehydrohalogenation of 13 and 14 was the final step in a proposed synthesis of 2-oxa-4,4-dimethylbicyclobutane-1-carbonitrile 32.

\[
\begin{align*}
\text{CN} & \\
H_3C & |
\end{align*}
\]

Treatment of 13 and 14 with base did not give 32 in this or a previous study (Ykman 1975). The reaction of 13 and 14, in most cases, gave an insoluble brown material in low yield. However, two equivalents of potassium tert-butoxide in THF at room temperature gave tert-butyl 3,3-dimethylacrylate 33 in poor yield.

\[
\begin{align*}
\text{CN} & \\
H_3C & |
\end{align*}
\]

Ester 33 was identified by nmr and G.C.-mass spectra.

"Metathesis" Polymerization of Bicyclobutane-1-carbonitrile

When bicyclobutane 5 was subjected to olefin metathesis conditions, insoluble cross-linked polymer was obtained. The metathesis catalyst used was the tungsten hexachloride/ethylaluminum sesquichloride system, which polymerized norbornene in good yield in the control
reactions. The ir spectrum of the polymer from 5 indicated both ring-opening polymerization in the usual way and polymerization through the nitrile group. Ethylaluminum ses­quichloride was found to cationically polymerize 5 through the nitrile group.

\[ \text{R}^\ominus + \text{R-C=N} \rightarrow \text{R}^\ominus \text{R-C=N} \text{etc} \]

Cationic polymerization of nitriles is known (Woehrle 1972).

**Attempted Synthesis of a Stereospecific 1,3-Dialkyl Cyclobutane-1-carbonitrile**

The synthesis of 3-methyl-1-ethylcyclobutane-1-carbonitrile of known stereochemistry was attempted by the following scheme:

The synthesis proceeded in good yield to the cyclization step. Instead of cyclization to 35, the treatment of 36 with base resulted in elimination to 37.
Several bases were used in the attempt to make the anion of 3-methylenecyclobutane 17 by hydrogen abstraction.

Although cyclobutanecarbonitrile anion can be prepared with trityl sodium in ether (Hall et al. 1977), methylenecyclobutane 17 fails to give the anion with this system. Cyclopropanecarbonitrile anion can be prepared with lithium diisopropyl amine in ether (Walborsky and Hornak 1955). This system also failed to give the anion of 17. Other bases tried include trityl potassium in hexane/THF, ether, THF, glyme and glyme/TMEDA; trityl lithium in glyme; n-butyl lithium in TMEDA.

In several cases, a tar was obtained, the ir spectrum of which contained a strong absorption at 1700 cm$^{-1}$. Dicyclobutyl ketone has an ir absorption at 1700 cm$^{-1}$ (Hall et al. 1977).

Chloro-nitrile 28 was treated with magnesium in ether and in THF in an attempt to make the Grignard. In ether, no
reaction took place, while in refluxing THF, a tar was obtained. This tar also had a strong absorption at 1700 cm\(^{-1}\) in the ir spectrum. An attempt at trapping the postulated Grignard with acetaldehyde failed, as no reaction would take place. Attempts to replace the chloride of 28 with bromide and iodide by displacement failed, presumably due to presence of the cyclobutyl ring.
DISCUSSION

Synthesis of 3-Methylene-2-methylcyclobutene-1-carbonitrile

The new route to 25 is straightforward to the point of the thermal 2+2 cycloaddition. In forming the substituted allene, chlorohydrin 20 is converted to 2,3-butadiene-1-ol with LAH. The first step of this conversion is the reaction of the alcohol group. An inter- or intramolecular 1,3 displacement of chlorine then occurs to give the allene.

\[
\text{Cl-CH}_2-\text{C}=\text{C-CH}_2\text{OH} + \text{LiAlH}_4 \rightarrow \text{Cl-CH}_2-\text{C}^\text{=\text{C-CH}_2\text{OL}} \rightarrow \text{H}_2\text{C}=\text{C-CH}_2\text{O-Al} \rightarrow \text{H}_2\text{C}=\text{C-CH}_2\text{O-Al}
\]

The thermal 2+2 cycloaddition giving 23 and 24 is not concerted, but is presumed to proceed by the diradical mechanism:

\[
\begin{align*}
\text{X} = \text{OH, OOCCH}_3, \text{OSi(CH}_3)_3 & \quad \rightarrow \quad \text{H}_2\text{C}=\text{CH-CH}_2\text{X} \\
\text{H}_2\text{C-CHCN} & \quad \rightarrow \quad \text{23} \quad \text{and} \quad \text{24}
\end{align*}
\]

The diradical can collapse to either of the two cyclobutanes, and assuming that rotation of the C-C bonds is much faster than collapse of the diradical, the ratio of 23 to 24 should be determined by steric factors. With the substituted alkenes of this study, steric factors were found to be
relatively unimportant in the cycloaddition reaction with acrylonitrile.

The cycloaddition of isochloroprene 7 to acrylonitrile gives only one cyclobutane product. The other cycloadduct is a cyclohexene 9, which is presumably formed by isomerization of 7 to chloroprene, followed by the known Diels-Alder reaction (Doucet and Rumpf 1954). The dramatic increase in the yield of 9 when a steel surface is present in the reaction supports the isomerization viewpoint, as steel is known to isomerize isochloroprene to chloroprene (Carothers, Berchet and Collins 1933). A reason suggested that cyclobutane of the type 24 was not found in the cycloaddition with 7 was because of a great degree of regioselectivity in the reaction (Yancy 1973). An alternate view, is that the allylic chloride cannot survive the reaction conditions.

With the formation of chloride 8 from 23, the synthesis has converged with a known procedure (Hall and Yancy 1974).

Structure of 3-Methylene-2-methylcyclobutene-1-carbonitrile

The data unequivocally shows that bicyclopentane structure 10 (Hall and Yancy 1974) is wrong. The correct structure is methylenecyclobutene 25. The mechanism for
the formation of 25 from 8 was not determined. Two possible mechanisms are:

In the first mechanism, HCl is eliminated to give the diene 38, which isomerizes either in a concerted or a base catalyzed manner to the completely conjugated 25. The second method postulates that 10 was formed and then ring-opened in either a concerted or a stepwise fashion to 25. Since no intermediates were found in the reaction, the correct mechanism must involve a very facile rearrangement. A concerted ring-opening is not favored at present because it would be a thermal analog of the generalized photochemical di-methane reaction.

**Synthesis of 3-Methylene-cyclobutene-1-carbonitrile**

The synthesis of 27 proceeded without any problems. The method chosen should be of general utility, although
with unsymmetrically substituted methylenecyclobutenes, the possibility of more than one product must be considered:

\[
\begin{align*}
R & \quad CN \\
\text{Cl} & \quad \text{base} \\
\rightarrow & \\
R & \quad CN \\
\end{align*}
\]

Another possible route to substituted methylenecyclobutenes could be 1,2 addition of an anion to diene 27, followed by treatment with bromine to give the necessary substituted 1-bromo-3-methylenecyclobutane-1-carbonitrile. This bromide could be dehydrohalogenated to the diene.

**Homopolymerization of 3-Methylene-2-Methylcyclobutene-1-carbonitrile and 3-Methylene-cyclobutene-1-carbonitrile**

Compounds 25 and 27 polymerize free radically in a 1,5 fashion to 26 and 29. The 1,5 polymerization is the expected reaction of 25 and 27, which proceeds by the following mechanism:

\[
\begin{align*}
R' & \quad CN \\
R' & \quad \text{CH}_2 \\
\text{etc} & \\
R' & \quad \text{H}, \text{CH}_3
\end{align*}
\]

No 1,2 or 3,5 polymerization were detected in either case. Appreciable 1,2 addition did not occur because of relatively high steric hindrance compared to the methylene position. Trisubstituted (27) and tetrasubstituted (25) systems generally do not polymerize. The unhindered methylene group would
be the expected point of attack by a growing radical, as it offers a lower energy pathway than attack at the 2 position. The lack of appreciable 3,5 addition in the soluble polymers can also be attributed to steric hindrance of the free radical from the polymer. Another reason is the contribution of the resonance structure that would give 3,5 addition is less than the resonance structure giving 1,5 addition.

If 3,5 addition did occur, then crosslinking could happen by the following mechanism:

This could account for cross-linked polymer obtained in the thermally initiated free radical polymerization of 27. Only a trace of 3,5 addition is needed to leave enough reactive cyclobutene-carbonitrile 39 that eventual incorporation into growing polymers would occur, thus forming cross-links. The cyclobutenecarbonitrile group is known to be reactive in free radical polymerization (Gale et al. 1974).

The autoxidation of cyclobutene containing polymers is facile (Wu and Lenz 1972b). Polymer 29 is much more stable than 26 to autoxidation. The presence of the methyl group on the double bond in 26 must enhance autoxidation.
Anionic polymerization of 25 and 27 with n-butyl lithium is not a suitable system for study and other methods need to be examined. The polymers from methylmethylenecyclobutene 27 may autoxidize too readily to be useful. Diene 25, however, is a promising new monomer, which may find applications as a replacement for acrylonitrile and in thermosetting polymers.

Copolymerization of 3-Methylene-2-methylcyclobutene-1-carbonitrile and 3-Methylene-cyclobutene-1-carbonitrile

The copolymerizations of 25 and 27 show that they are very reactive monomers. This is shown by all the copolymers being rich in the diene 25 and 27. If the Alfrey-Price Q-e scheme is considered and given the following Q-e values (Table 8) (Young 1975), then qualitative information can be obtained.

Isobutyl vinyl ether was not reactive enough to give copolymer with 27 even though the large negative e value would be expected to be favorable, as 27 should have a positive e value. The low incorporation of acrylonitrile in the copolymers can be attributed to acrylonitrile having similar e values as 25 and 27, but a much lower Q value. Acrylonitrile must be much less reactive than 25 and 27 while little resonance stabilization in cross-propagation. Methyl methacrylate, styrene and p-methoxystyrene show a monotonic progression in tendency to copolymerize with 25 and 27 that
Table 8. Selected Q-e Values

<table>
<thead>
<tr>
<th>Monomer</th>
<th>e</th>
<th>Q</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isobutyl vinyl ether</td>
<td>-1.77</td>
<td>0.023</td>
</tr>
<tr>
<td>P-Methoxystyrene</td>
<td>-1.11</td>
<td>1.36</td>
</tr>
<tr>
<td>Styrene</td>
<td>-0.80</td>
<td>1.00</td>
</tr>
<tr>
<td>2,4-Pentadieninitrile</td>
<td>0.28</td>
<td>5.98</td>
</tr>
<tr>
<td>Methyl methacrylate</td>
<td>0.40</td>
<td>0.74</td>
</tr>
<tr>
<td>Acrylonitrile</td>
<td>1.20</td>
<td>0.60</td>
</tr>
</tbody>
</table>

corresponds to the change in Q-e values. p-Methoxystyrene thus has good reactivity and resonance stabilization in the cross-propagation.
The Q-e values for 2,4-pentadienenitrile were included in Table 8 because they should be similar to the values for dienes 25 and 27. Quantitative Q-e data should be obtained in future studies.

**Dehydrohalogenation of 2-Cyano-3,3-dimethyl-4-chlorooxetane**

Formation of t-butyl 3,3-dimethylacrylate 33 by the treatment of 13 and 14 with two equivalents of potassium t-butoxide can be explained thus:

The 1-cyanoisobutene 16 resulting when 14 is treated with sodium hydride was explained by the following scheme:
If pathway 1 of the scheme is correct, then the direction of ring-opening for 16 and 33 are the opposite. Pathway 2 avoids this problem, which could also be attributed to the difference in solvents.

The reason one equivalent of potassium t-butoxide did not give good results is that there was an insufficient amount of base present to trap the intermediate.

"Metathesis" Polymerization of Bicyclobutane-1-carbonitrile

Polymerization of 5 by the tungsten hexachloride/ethylaluminum sesquichloride gives crosslinked polymer that contains both 1,3 linkages and linkages through the nitrile. Since ethylaluminum sesquichloride can cationically polymerize 5, it is not clear whether the cross-linking is the result of one polymerization mechanism or of two independent mechanisms. For this reason, bicyclobutanenitrile 5 was deemed not to be suitable for detailed studies. Using methyl bicyclobutane-1-carboxylate should avoid the problem of cationic polymerization through the nitrile group, while still showing any unusual chemistry of the bicyclobutane group with an electron withdrawing group attached.

Attempted Formation of the Anion of 3-Methylenecyclobutane-1-carbonitrile

Conditions that give anions of other small ring nitriles, failed to give the anion of 17. The tars obtained
in several of the reactions contained ketone groups as
determined from ir spectra. The ketones can be explained
if the anion of 5 had been formed. The anion of cyclo-
butanecarbonitrile reacts with cyclobutanecarbonitrile to
form dicyclobutyl ketone by an intermolecular Thorpe-Ziegler
reaction (Hall et al. 1977).

\[
\begin{align*}
\text{CN}^- & + \text{CN}^- \\
\text{H}^+ & \text{Na}^+ \\
\text{C}=\text{N}^- & \text{H}_2\text{O} \\
\text{C}=\text{O}^- & \text{Na}^+ \\
\end{align*}
\]

The anion of \(17\) could be expected to react similarly with \(17\).
A clean method of making the anion has not yet been found.

The synthesis of a stereo specific 1,3 disubstituted
cyclobutane-1-carbonitrile could be done in several ways.
One way would be to add formaldehyde to the thiol instead of
2-chloroethanol. The thioacetal could be converted to the
chloride, which could not give elimination products in the
cyclization step.

The routes that begin with the anion of \(17\) would be
useful if the anion could be cleanly formed. If a solvent/
base system could be found in which the anion of \(17\) is in-
soluble, and yet the chosen base can quickly abstract the
\(\alpha\) hydrogen, then the Thorpe-Ziegler reaction would not occur.
The anion could then be isolated and dissolved in a different
solvent for the next step.
The Grignard may be obtainable from 1-bromo-3-methylenecyclobutane-1-carbonitrile, which might be obtainable by the thermal 2+2 cycloaddition of α-bromoacrylonitrile and allene.
SUMMARY

An easy two-step synthesis of 3-methylenecyclobutene-1-carbonitrile $\mathbf{27}$ from 3-methylenecyclobutane-1-carbonitrile $\mathbf{17}$ was developed. Compound $\mathbf{27}$ represents a new class of nitrile containing monomers. Ironically, a second member of this class was found to be already on hand, but had originally been assigned the wrong structure. The incorrect bicyclopentane $\mathbf{10}$ was shown to be the diene $\mathbf{25}$. A new synthesis of $\mathbf{25}$ starting with 2-butyne-1,4-diol was designed. New monomers $\mathbf{25}$ and $\mathbf{27}$ polymerize free radically to high molecular weight material. With nitrile $\mathbf{27}$, the free radical polymerization had to be done in solution using AIBN/uv initiation in order to prevent cross-linking. The homopolymers could be cast in films.

Monomers $\mathbf{25}, \mathbf{27}$ were copolymerized with styrene, p-methoxystyrene, methyl methacrylate and acrylonitrile. The copolymerizations show the new monomers to be very reactive. All the copolymers were film forming.

The polymers from methylmethylenecyclobutene $\mathbf{27}$ may autoxidize too readily to be useful. Diene $\mathbf{25}$, however, is a promising new monomer, which may find applications as a replacement for acrylonitrile and in thermosetting polymers.
Treatment of 2-cyano-3,3-dimethyl-4-chlorooxetane with two equivalents of potassium t-butoxide in THF gives t-butyl 3,3-dimethylacrylate 33 in low yield. The formation of 33 is consistent with the formation of an oxabicyclobutane intermediate.

Bicyclobutane-1-carbonitrile, when subjected to olefin metathesis conditions, gave crosslinked polymer caused by polymerization through both the bicyclobutane ring and the nitrile group.

An attempt to synthesize a stereospecific 1,3-dialkylcyclobutane-1-carbonitrile failed because of elimination occurring instead of cyclization in the key step.

Conditions known to give the anion of cyclobutane-carbonitrile and cyclopropanecarbonitrile did not give the anion of 3-methylenecyclobutane-1-carbonitrile cleanly.
EXPERIMENTAL

Instrumentation

All boiling 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 KBr, between NaCl 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 FT spectrometer. Mass spectra data were collected on a Hewlett-Packard 5930A quadrapole mass spectrometer. Preparative and analytical gas-liquid chromatography was done on a Varian Aerograph 1700 instrument. Elemental analyses were performed by Chemalytics, Inc., Tempe, Az. Ultra Violet spectra were obtained on a Cary 14 spectrophotometer.

Monomer Synthesis

3-Methylene-2-methylcyclobutene-1-carbonitrile (25)

4-Chloro-2-butyne-1-ol (20). The literature procedure (Bailey and Fujiwara 1955) was used with minor modifications. While the flask was cooled in an ice bath, purified thionyl chloride (1302.5g, 10.9 moles) was added over a period of 75 hours to a solution of 2-butyne-1,4-diol (18) (860g,
10 moles) and dry pyridine (925 g, 11.7 moles) in 1.5 liters of dichloromethane. The reaction mixture was stirred at room temperature for 18 hours and then poured into 2 liters of ice. After separating the organic layer, the aqueous layer was extracted with four 1-liter portions of ether, and the ether extracts were combined with the original dichloromethane layer. The organic layer was washed with a saturated sodium bicarbonate solution, followed by cold water. After drying over molecular sieves, the solvents were removed on a rotary evaporator. The residue was distilled to give 66 g (5.3%) of 1,4-dichloro-2-butyne, b.p. 70°C (20 mm Hg); and 530 g (50%) of 4-chloro-2-butyne-1-ol, b.p. 50°C (0.5 mm Hg).

1,2-Butadien-4-ol (19). The literature procedure (Bailey and Pfeifer 1955) was modified as follows: to 1.8 liters of anhydrous ethyl ether under a positive nitrogen atmosphere, was added 42 g (1.1 mole) of lithium aluminum hydride. The reaction was cooled in an ice bath and 155.24 g (1.48 moles) of 4-chloro-2-butyne-1-ol (20) in 300 ml of anhydrous ethyl ether was added, dropwise, over a period of 3 hours. The reaction was then allowed to warm to room temperature and stirred for 18 hours. The excess lithium aluminum hydride was destroyed by carefully adding, dropwise, a saturated solution of sodium sulfate in water until the lithium-aluminum salts formed hard white pellets. The reaction was filtered, and the pellets were washed twice
with ether. The ether was removed on a rotary evaporator and the residue distilled to give 79.8 g (68%) of 1,2-butadien-4-ol, b.p. 69°C (45 mm Hg).

\[\text{nmr (CCl}_4\text{)} \delta: 5.25(p, 1H); 4.80(m, 2H); 4.70(s, 1H); 4.06(d of t, 2H).\]

\[\text{ir (neat): } \text{O-H}, 3350 \text{ cm}^{-1}, \text{b, s}; \text{C-H}, 2940 \text{ and } 2885 \text{ cm}^{-1}, \text{m and m}; \text{C=C}, 1955 \text{ cm}^{-1}, \text{s}.\]

Mass spectra (70 Ev) m/e: 70 (17%), 69 (56%), 55 (100%), 42 (58%), 39 (98%).

(2,3-Butadienyloxy) trimethylsilane (22). Hexa-methylidisilazane, 25 g (0.15 mole), and 21 g (0.30 mole) of 1,2-butadiene-4-ol were mixed with stirring for 1 hour, during which time the temperature rose to 60°C. Chlorotrimethylsilane (0.5 ml) was added dropwise and the solution stirred for an additional 30 minutes. The mixture was briefly heated to 125°C. The reaction was filtered and distilled at 60°C (60 mm Hg) to obtain 31.96 g (96%) of the silylated product.

\[\text{nmr (CCl}_4\text{)} \delta: 5.10(p, 1H), 4.66(m, 2H); 4.03(d of t, 2H); 0.03(s, 9H).\]

\[\text{ir (neat): } \text{C-H}, 2960, 2900 \text{ and } 2870 \text{ cm}^{-1}, \text{s, m and m}; \text{C=C}, 1960 \text{ cm}^{-1}, \text{s}.\]

Mass spectra (70 Ev) m/e: 141 (3%, P-1), 127 (100%), 103 (71%), 75 (54%), 73 (86%).
1-Acetoxy-2,3-butadiene (21). The literature procedure (Carothers and Berchet 1933) gave the best results in converting the alcohol to the acetate.

\[ \text{nmr(CCl}_4\text{)} \delta: 5.13(p, 1H); 4.66(m, 2H); 4.46(d of t, 2H); 2.00(s, 3H). \]

4-Chloro-1,2-butadiene (7). The literature procedure (Carothers 1929) was used. The desired allene was separated from the 2-chloro-1,3-butadiene by-product on a 3-foot glass helix-filled column. Diene 7, b.p. 88°C (700 mm Hg), was stored in a refrigerator to prevent isomerization.

Cycloadditions of Substituted Allenes with Acrylonitrile. Two different procedures, both done at the University High Pressure Laboratory, were used. In the first method (Hall and Yancy 1974), a heavy-walled glass tube with a volume of about 3 times the volume of the reaction mixture was used. The glass tube had a constricted neck below the top. In a typical experiment, an acid-washed and dried tube was charged with 12.34 g (0.23 moles) of acrylonitrile, 6.50 g (0.058 moles) of 1-acetoxy-2,3-butadiene (21), 8.40 g of benzene, and 0.50 g of 2,5-di-tert-butylhydroquinone. The tube was degassed by freezing the mixture in liquid nitrogen and applying full pump vacuum, followed by alternately thawing and refreezing the contents until no gas bubbles were observed escaping from the liquid state. While the mixture was frozen and under reduced pressure, the tube was sealed
by heating at the constriction. After heating to 200°C for 8 hours in an autoclave which contained benzene to equalize the pressure on the glass tube, the reaction was allowed to cool, poured into 100 ml of ethyl ether and filtered. The ether was removed on a rotary evaporator and the residue distilled to give 4.76 g (0.029 moles) of reported cycloadducts (Cripps et al. 1959). The 49.7% yield is less than that reported by Cripps, probably because of the greater difficulty in maintaining a uniform temperature which was found to be critical. Another reason for the lower yield was the use of benzene as a diluent, which was necessary for safety reasons, as the acrylonitrile has explosively polymerized when no diluent was used (Kauer 1977).

With 4-chloro-1,2-butadiene (7) in the cycloaddition reaction, the 3-methylene-2-chloromethylcyclobutanecarbonitrile (8) and 1-chloro-1-cyclohexene-4-carbonitrile (9) mixture was obtained in 21% yield, and 3-chloropropionitrile in 15% yield. The three compounds showed physical properties identical to reported values (Hall and Yancy 1974).

With 1,2-butadiene-4-ol (19), 3-(β-hydroxyethylidene)-1-cyclobutanecarbonitrile (24a), and cis and trans 3-methylene-2-hydroxymethyl-cyclobutanecarbonitrile (23a) were obtained in 29.7% yield after distillation on a spinning band column at 60-70°C (0.01 mm Hg). The two compounds were separated by preparative gc or by silylation, followed by careful distillation.
3-(β-Hydroxyethylidene)-1-cyclobutanecarbonitrile (24a):
nmr (acetone d-6) δ:  5.40(m,1H); 4.00(m,3H); 3.28
(m,5H); 3.66(s,1H).
ir (neat):  O-H, 3400 cm⁻¹, s; C-H, 2975, 2940, and
2880 cm⁻¹, s; C≡N, 2250 cm⁻¹, s; C=C, 1710 cm⁻¹, m.
Mass spectra (70 Ev) m/e:  123 (w,P), 104 (24%), 94
(76%), 80 (51%), 70 (100%).
Anal. Calc'd for C₇H₉ON:  C, 68.27; H, 7.37; N, 11.37.
Found: C, 68.35 H, 7.47 N, 11.28

3-Methylene-2-hydroxymethyl-cyclobutanecarbonitrile (23a):
nmr (acetone d-6) δ:  4.90(m,2H); 4.25(s,b,1H); 3.54
(m,2H); 3.5 to 3.1(m,b,2H); 3.00(m,2H).
ir (neat):  O-H, 3400 cm⁻¹, s,b; C-H, 2945, and 2880
cm⁻¹, s; C≡N, 2250 cm⁻¹, s; C=C, 1690 cm⁻¹, s.
Mass spectra (70 Ev) m/e:  123 (vw,p), 93 (52%), 66
(100%).
Anal. Calc'd for C₇H₉ON:  C, 68.27; H, 7.37; N, 11.37.
Found:  C, 67.97; H, 7.80; N, 11.58.

In the case of (2,3-butadienyloxy)trimethylsilane
(22), the cycloadducts were distilled on a spinning band
column twice to yield two main fractions in an overall yield
of 47%. The first fraction (43°C at 0.01 mm Hg) was found
to be 3-methylene-2-(trimethylsiloxy)methyl-cyclobutane-
carbonitrile (23c).
nmr (CCl\textsubscript{4}) \( \delta \): 4.80 (m, 2H); 3.64 (m, b, 2H); 3.4 to 3.0 (m, b, 2H); 2.80 (b, 2H); 0.04 (d, 9H).

ir (neat): C-H, 2950, 2900, and 2855 cm\(^{-1}\), s, m, and m; C≡N, 2240 cm\(^{-1}\), s, C=C, 1690 cm\(^{-1}\), m.

Mass spectra (70 Ev) m/e: 180 (100\%, p-15), 165 (64\%), 150 (87\%), 103 (64\%), 73 (92%).

Anal. Calc'd for C\textsubscript{10}H\textsubscript{17}ONSi: C, 61.49; H, 8.77; N, 7.17.

Found: C, 61.28; H, 8.81; N, 7.36.

The second fraction (60°C at 0.01 mm Hg) was the silyl ether of 3-(B-Hydroxyethylidene)-1-cyclobutanecarbonitrile (24c).

nmr (CCl\textsubscript{4}) \( \delta \): 5.22 (m, 1H); 3.90 (b, d, 2H); 3.03 (b, s, 5H); 0.02 (s, 9H).

ir (neat): C-H, 2955, 2900, and 2860 cm\(^{-1}\), s, m, and m; C≡N, 2250 cm\(^{-1}\), s, C=C, 1720 cm\(^{-1}\), w.

Mass spectra (70 Ev) m/e: 195 (w, p) w; 180 (22\%), 127 (23\%), 75 (91\%), 73 (100%).

Anal. Calc'd for C\textsubscript{10}H\textsubscript{17}ONSi: C, 61.49; H, 8.77.

Found: C, 61.48; H, 8.75.

In two of sixteen cycloaddition reactions using the silylated allene, uncontrollable exothermic reactions occurred.

The method of Cripps in which a steel tube is used, is not usable with isochloroprene due to the known metal-catalyzed rearrangement of the compound (Carothers and Berchet 1933). The presence of a stainless steel surface
also resulted in the formation of no cycloadduct when (2,3-butadienyloxy)trimethylsilane (22) was used. Lower yields of cycloadduct were obtained with 2,3-butadien-1-ol (19), but the yield with 1-acetoxy-2,3-butadiene (21) was found to be slightly higher using the Cripps method. The probable reason is that temperature control and homogeneity can be better controlled without the glass tube in the reaction. The Cripps reaction is also easier to scale up.

3-Methylene-2-chloromethyl-1-cyclobutanecarbonitrile (8). The 1-acetoxy-2,3-butadiene/acrylonitrile cycloadducts were hydrolyzed to the alcohols in 9:1 ethanol/water with excess potassium carbonate. The ethanol/water was removed by distillation. The residue was made slightly acidic in ethyl ether. The reaction was filtered, dried, and the ether was removed on a rotary evaporator. The alcohols were reacted with hexamethyldisilazane and distilled on a spinning band column to separate the cycloadducts. The silyl compound was hydrolyzed in 95% ethanol by the addition of a trace of base. The resulting alcohol was isolated and dried over MgSO₄ in ether. The conversion to the chloride was done by the dropwise addition of purified thionyl chloride to the alcohol in ether, with a yield of 80% from the acetate.

The conversion of the 3-methylene-2-(trimethylsiloxy)-methylcyclobutane (23c) directly to chloride 8 was carried
out by the following procedure: to a three neck flask fitted with a mechanical stirrer, a condenser and positive nitrogen pressure, was added 2.3 g (0.012 moles) of the silyl ether, 35 ml of dry CCl₄, and 3 g (0.014 moles) of PCl₅. The reaction was heated to 50°C until all of the PCl₅ had dissolved. After stirring for an additional hour, 1 g of K₂CO₃ was added and the reaction was filtered. The solvent was removed by rotary evaporation and the residue distilled to give 0.42 g (0.003 moles) of the chloro compound.

3-Methylene-2-methylcyclobutene-1-carbonitrile (25).

The literature procedure (Hall and Yancy 1974) was used, using freshly made potassium t-butoxide (see text).

3-Methylenecyclobutene-1-carbonitrile (27)

l-Chloro-3-methylenecyclobutane-1-carbonitrile (29).

Into a three neck flask, fitted with a mechanical stirrer, a condenser and a dropping funnel, were added 1200 ml of dry chloroform, 165 g (2.06 moles) of dry pyridine, and 313.1 g (1.5 moles) of phosphorus pentachloride. While under positive nitrogen pressure, 93.13 g (1.00 mole) of 3-methylenecyclobutane-1-carbonitrile (27) was added dropwise over 2 hours to the phosphorus pentachloride solution. The reaction was refluxed with stirring for 96 hours, by which time the solution was black. After cooling, the mixture was poured onto 2 kg of ice. The resulting layers were
separated and the aqueous phase was washed twice with ether. The organic layers were washed with a saturated solution of potassium chloride, followed by a 10% solution of sodium carbonate. The organic layer was dried over molecular sieves and the solvents removed on a rotary evaporator. The residue was distilled to give 92.3 g (0.72 moles) of chloride 28, b.p. 40°C (1.8 mm Hg).

\[ \text{nmr (CCl}_4 \text{)} \delta: \ 5.06 (m, 2H); \ 3.55 \text{ and } 3.42 (m, 4H). \]

ir (neat): C-H, 3080, 2990 and 2930 cm\(^{-1}\), m,s,m; C=N, 2340 cm\(^{-1}\), s; C=C, 1690 cm\(^{-1}\), s.

Mass spectra (70 Ev) m/e: 129 (20%, P37-C1), 127 (59%, P35-C1), 92 (100%), 91 (31%), 90 (35%), 88 (85%), 87 (37%), 65 (94%), 40 (90%).

3-Methylenecyclobutene-1-carbonitrile (27). A solution containing 150 ml of anhydrous ethyl ether, 13 g (0.10 moles) of 1-chloro-3-methylenecyclobutane-1-carbonitrile (28) and 0.05 g of 2,5-di-t-butylquinone was placed in a dried flask, along with a magnetic stirring bar. The flask was cooled to 5°C and 14.0 g (0.11 moles) of 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) was added dropwise with stirring over 10 minutes, while under positive nitrogen pressure. After stirring in an ice bath for 1½ hours, the reaction was filtered, returned to a flask, and kept at 5°C for 24 hours, during which more DBN-HCl had precipitated. The reaction was again filtered, followed by removing the ether on a
rotary evaporator at room temperature. The residue was distilled at room temperature using Dry Ice-acetone bath to cool the receiver flask. The fraction collected between 8 and 4 mm Hg gave 6.24 g (0.069 moles) of 3-methylenecyclobutene-1-carbonitrile (27) pure by nmr spectra (69% yield).

**nmr** (DCCl$_3$) $\delta$: 6.83(s,1H); 5.14(m,1H); 4.90(m,1H);
3.27(s,2H).

**ir** (neat): C-H, 3080, 2960, and 2925 cm$^{-1}$, m,m, and s;
C≡N, 2205 cm$^{-1}$, s; C=C, 1660 cm$^{-1}$, s.

**uv** (hexane): $\lambda_{max} = 253$ nm, $\epsilon = 18,600$

Mass spectra (70 Ev) m/e: 91 (15%), 64 (15%), 39 (100%);
(10 Ev) m/e: 91 (100%, P).

Anal. calc'd for C$_6$H$_5$N: C, 79.10; H, 5.53; N, 15.37
Found: C, 79.29; H, 5.54; N, 15.16.

Sample Polymerizations

3-Methylene-2-methylcyclobutene-1-carbonitrile Polymers

**Free Radical Homopolymerization.** A crystal of AIBN and 0.5 ml of sulfolane were placed in a dry flask. Freshly distilled diene 25 (0.1483 g) was added to the sulfolane. The flask was fitted with a rubber septum, flushed with argon, and heated at 70°C for 15 hours. The solution was
then poured into methanol, containing a trace of 2,5-di-
tert-butylhydroquinone, filtered, dissolved in acetone,
reprecipitated in ethyl ether and again filtered. The poly-
mer was dried over P$_2$O$_5$ under full vacuum at room temperature,
after flushing the vessel with nitrogen. The polymer was
obtained in 59% yield, $\eta_{inh}=0.95$ at 30°C (0.396 g/100 cc in
acetone). Polymerizations were done in bulk and with AIBN/
UV initiation with similar results.

Found: C, 80.04; H, 6.79; N, 13.25.

**Free Radical Copolymerization.** A dry flask was
charged with 0.7121 g of sulfolane, 0.2003 g (1.493x10$^{-3}$
moles) of p-methoxystyrene, 0.1541 g (1.466x10$^{-3}$ moles) of
3-methylene-2-methylcyclobutene-1-carbonitrile (25), and a
crystal of AIBN. The flask was fitted with a rubber septum,
flushed with argon, and heated at 70°C for 21 hours. The
solution was poured into methanol and filtered. The result-
ing polymer was dried over P$_2$O$_5$ under full vacuum at room
temperature to give the product in 82.6% yield, $\eta_{inh}=0.35$
at 30°C (0.292 g/100 cc in acetone). The other copolymeri-
zation were done by the same general method.

3-Methylenecyclobutene-1-
carbonitrile Polymers

**Free Radical Homopolymerization.** A dry flask was
charged with 4.3378 g of sulfolane, 0.2902 g of
3-methylenecyclobutene-1-carbonitrile (27) and a crystal of AIBN. The flask was fitted with a rubber septum, flushed with argon, and placed under UV light for 21.5 hours at 40°C. The very viscous solution was poured dropwise into methanol, filtered and soaked in fresh methanol for 72 hours. The polymer was refiltered and dried under full vacuum to give 0.1166 g (40%) of product, \( \eta_{inh} = 1.15 \) at 30°C (0.343 g/100 cc in DMF).

 Anal. Calc'd for C H N: C, 79.10; H, 5.53; N, 15.37
Found: C, 79.45; H, 5.36; N, 15.19

Heating the monomer to 70°C in bulk or in sulfolane with AIBN resulted in cross-linked polymer that was insoluble, but swellable in DMF.

Free Radical Copolymerization. A dry flask was charged with 2.2294 g of sulfolane, 0.4036 g (3.01x10^{-3}) of para-methoxystyrene, 0.2742 g of 3-methylenecyclobutene-1-carbonitrile (27) and a crystal of AIBN. The flask was fitted with a rubber septum, flushed with argon, and placed under UV light for 41 hours at 40°C. The extremely viscous solution was diluted with twice the volume of acetone and slowly poured into ethyl ether. The polymer was filtered, soaked in methanol for 72 hours, refiltered, and dried under full vacuum. The resulting polymer was obtained in 59% yield, \( \eta_{inh} = 0.83 \) at 30°C (0.222 g/100 cc).
Attempted Anionic Polymerization

3-Methylene-2-methylcyclobutene-1-carbonitrile (25).

The general procedure described in the anionic polymerization of [2.1.0] bicyclopentanecarbonitrile (Hall 1971) was used. A solution containing 0.15 g (0.0014 moles) of 3-methylene-2-cyclobutene-1-carbonitrile in 2 ml of dry tetrahydrofuran was placed in a dry tube which had been capped with a rubber septum and flushed with argon. The tube was cooled to -78°C in a Dry Ice-acetone bath and 0.05 ml of 2.4 M n-butyl lithium in hexane was added. The tube was slowly warmed to 0°C, at which temperature the reaction was kept for 3 hours. The reaction was poured into 100 ml of ether containing a trace of HCl. After filtering, the solvent was removed on a rotary evaporator to give 0.030 g (0.28 moles, 20% yield) of yellow oil.

nmr (acetone d-6) δ: 5.1(b,m,1.6H); 3.16(m,1.6H);
2.8-2.2(m,0.7H); 1.73(s,0.57H); 1.6-1.3(m,2.4H);
[the H numbers correspond to a ratio of 4.25/1 for 3,4/1,4 addition]

Both [2.1.0] bicyclopentanecarbonitrile and acrylonitrile were polymerized successfully in control experiments by the above method.
Dehydrohalogenation of 2-Cyano-3,3-Dimethyl-4-Chlorooxetane

Potassium tert-butoxide, made from 0.51 g (1.30 x 10^{-2} M) of potassium metal, and 30 ml of dry tetrahydrofuran were placed in a two neck flask with a magnetic stirrer while under positive nitrogen pressure. To this, 1.004 g of γ 4-chloro-3,3-dimethyl-2-cyanooxetane (14) was added at 25°C. The temperature rose to 40°C and the solution turned brown. After 21 hours, 7 ml of chlorotrimethyl silane was added. The reaction was carefully distilled at room temperature into a dry ice-acetone bath to give a residue of 1.108 gm, which was extracted with pentane. The pentane-soluble fraction was distilled in a Kugelrohr apparatus to give 0.049 gm of material which by nmr contained γ and γ' 4-chloro-3,3-dimethyl-2-cyanooxetane and t-butyl-3,3-dimethyl acrylate (33) in 7:4:16 ratio. The structure of 33 was confirmed by G.C.-mass spectra.

nr (CDCl₃) 4.57 (m due to allylic coupling, 1, =CH), 7.93 (d, J=0.7 Hz, 3, Me), 8.20 (d, J=0.9 Hz, 3, Me), 8.60 (5, 9, Me).

Mass spectra (70 Ev) m/e: 101 (40%,P), 100 (63.6%), 83 (96%), 57. (72%), 55 (52%), 91 (100%).
"Metathesis" Polymerization of Bicyclobutane-1-carbonitrile

A flask which has a stopcork fitting was dried under nitrogen and flushed with argon. While in a glove bag, 0.7494 g (1.890 x 10^{-3} moles) of tungsten hexachloride was added to the flask. The tungsten hexachloride was heated under vacuum until sublimation began. The flask was then flushed with argon and fitted with a rubber septum so that the stopcork was between the reaction and the septum. Added by syringe was 10 ml of chlorobenzene which had been distilled from P_2O_5, degassed, and stored under argon. A test tube was dried, fitted with a rubber septum, and flushed with argon. After cooling the tube to -78^\circ C in a dry ice-acetone bath, 0.8 ml of 25% (by weight) ethylaluminum sesquichloride in heptane, 2 ml of the tungsten hexachloride chlorobenzene solution and 0.79 g (0.01 moles) of bicyclobutane-1-carbonitrile was injected into the test tube. The reaction was allowed to slowly warm to room temperature. After 18 hours, the reaction was poured into ether, filtered, washed with acetone, filtered, washed with water, filtered, washed with acetone and dried over P_2O_5 under full vacuum. The insoluble cross-linked polymer was obtained in 24% yield (0.190 g) and 0.40 g of bicyclobutane 5 was recovered from the ether fraction.
Attempted Synthesis of a Stereospecific 1,3-dimethylcyclobutane-carbonitrile

Synthesis of 3[S-(3-hydroxyethyl)-thiomethyl]cyclobutane-1-carbonitrile

3-(Acetyltthiomethyl)cyclobutane-1-carbonitrile. To 14.25 g (0.153 moles) of 3-methylenecyclobutane-1-carbonitrile was added with stirring at 5°C, 10 ml (0.14 moles) of thiol-acetic acid and a trace of benzoyl peroxide. After warming to room temperature, the reaction was fitted with a reflux condenser and carefully heated to 65°C (beware of a sudden exotherm). The reaction was short path distilled, with the residue after heating to 110°C at 0.2 mm. Hg being the desired fraction (22.3 g, 0.132 moles, 86%).

\[
\text{nmr (CCl}_4\text{) } \delta: \text{ 2.90(m,2H); 2.70 to 1.83(b,m) and 2.30(s), 9H.}
\]

\[
\text{ir (neat): C-H, 2990, 2950, and 2870 cm}^{-1}, s,s, \text{ and m; C=\text{N}, 2250 cm}^{-1}, s; C=O, 1680 cm}^{-1}, b,s.
\]

3-(Thiolmethyl)cyclobutane-1-carbonitrile. The thioacetate was placed in methanol which had been made basic by the addition of sodium hydroxide. The reaction was refluxed for 24 hours, at which time hydrogen chloride was added until a pH of 4 was obtained. After drying over molecular sieves, the methanol was removed by distillation. The residue was taken up in ether, filtered and distilled until 50°C and 0.4 mm Hg was obtained. The residue is the desired product in almost quantitative yield.
nmr (DCCl$_3$) $\delta$: 3.20 to 1.80, (b,m).

ir (neat): C-H, 2975, 2960, and 2850 cm$^{-1}$, s,s,m; w; C=N, 2230,s.

3[S-(B-hydroxyethyl)-thiomethyl]cyclobutane-1-carbonitrile. A dry three-neck flask fitted with a stirring bar and dropping funnel was charged with 100 ml of t-butanol. After placing under positive nitrogen pressure, 3.1 g (0.079 moles) of potassium metal was added to the t-butanol. Once the potassium metal had been consumed, 10.0 g (0.074 moles) of 3-(thiomethyl)cyclobutane-1-carbonitrile was added. After stirring for 20 minutes, 6.4 g (0.079 moles) of 2-chloro-ethanol was added. The resulting slurry was stirred for 3 hours, followed by heating to 60°C for 1 hour. Water (0.5 ml) was added and most of the t-butanol removed by distillation under vacuum. The reaction was taken up in ether, filtered, dried over molecular sieves. The ether was removed on a rotary evaporator and the resulting yellow oil was placed under a vacuum of 0.1 mm Hg at 70°C until no further distillation occurred, leaving 9.7 g (72%) of material.

nmr (DCCl$_4$) $\delta$: 3.70(t,2H); 3.2 to 1.8 (b,m,11H).

Example of Attempted Cyclization to 4-thiobicyclo-[4.1.1]octane-1-carbonitrile (35). Purified thionyl chloride (10 ml) was added dropwise to 10 g (0.07 moles) of 3[S-(B-hydroxyethyl)-thiomethyl]cyclobutane-1-carbonitrile in
50 ml of dry ether. The reaction was distilled under full vacuum at room temperature to give a light yellow oil residue (extreme vesicant). The oil 36 was placed in 25 ml of anhydrous ether and added to freshly prepared potassium t-butoxide in 50 ml of anhydrous ether dropwise with stirring and under nitrogen atmosphere. After 3 hours, the ether and t-butanol were flash distilled from the reaction. The residue was taken up in ether, filtered, washed with water, dried over molecular sieves and rotary evaporated. The product was distilled in a Kugelrohr apparatus.

\[
\text{nmr (CCl}_4\text{)} \delta: \ 6.25(q,1H); \ 5.06(dd,2H); \ 3.20 \text{ to } 1.80 (b,m,8H).
\]
REFERENCES


Hall, H. K., Jr., Macromolecules, 4, 139 (1971).


