Part I: Preparations of cyclopropane-1 1-dicarbonitrile and its reactions with amines. Part II: Preparation of 1 1-disubstituted 2-methyl 2-cyclopropyl ethenes and their reactions with nucleophiles

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PART I: PREPARATIONS OF CYCLOPROPANE-1,1-DICARBONITRILE AND ITS REACTIONS WITH AMINES.

PART II: PREPARATION OF 1,1-DISUBSTITUTED 2-METHYL 2-CYCLOPROPYL ETHENES AND THEIR REACTIONS WITH NUCLEOPHILES.

by

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B.A. University of Montana, 1964

Presented in partial fulfillment of the requirements for the degree of Master of Science

UNIVERSITY OF MONTANA

1966

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JUL 21, 1966
Date
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## PART I

PREPARATIONS OF CYCLOPROPANE-1,1-DICARBONITRILE
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INTRODUCTION

During the last several years a study has been in progress in this laboratory on ring-opening addition reactions of nucleophilic reagents with cyclopropane compounds having one or more electron-withdrawing substituents on the ring. It has been demonstrated\textsuperscript{1,2,3} that when two such groups are present on one carbon of the ring, the cyclopropane ring behaves in a manner analogous to that of an alkene linkage substituted on one carbon by one or more electron-withdrawing groups. Ring cleavage occurs adjacent to the substituted carbon, and addition of the nucleophile leads to 1,1,3-trisubstituted propanes:

\[
\begin{align*}
\triangle-A_B + ZH & \rightarrow ZCH_2CH_2CH_2-Z_B \\
& \text{Cyclopropane compounds used thus far in this investigation have been diethyl cyclopropane-1,1-dicarboxylate, ethyl 1-cyanocyclopropane-1-carboxylate, 1-cyanocyclopropane-1-carboxamide, cyclopropane-1,1-dicarboxamide and diethyl 2-vinylcyclopropane-1,1-dicarboxylate. Ring-opening additions have been successfully demonstrated with secondary amines, mercaptans, phenol and thiophenol.}
\end{align*}
\]

Cyclopropane-1,1-dicarbonitrile has recently been prepared in this laboratory, but because the initial methods of preparation involved several steps and overall yields were low, a more direct method of synthesis with improved yield is desirable.

A few preliminary experiments have shown that cyclopropane-1,1-dicarbonitrile will give the ring-opening addition type of reaction described above in ethanol at low temperatures.\textsuperscript{2} It appears that
under other conditions a different type of addition reaction involving one or both of the nitrile groups may occur. It is suggested that amidines may be formed by the following type of reaction:

\[ \text{C\equiv N} + R_2\text{NH} \rightarrow \text{C\equiv N} \]

This would be analogous to the reaction observed when cyanogen \((\text{CN})_2\) or trihaloacetonitriles \((X_3\text{CCN})\) are treated with secondary amines\(^4,5\):

\[
\text{NC\equiv CN} + R_2\text{NH} \rightarrow \text{NC\equiv CN} \]

\[
\text{Cl}_3\text{C\equiv CN} + R_2\text{NH} \rightarrow \text{Cl}_3\text{C\equiv CN} \]

The simple addition products \(\text{C\equiv N} \)

The simple addition products have not as yet been isolated—apparently because of further interaction, leading to more complex structures and probably polymers.

Since simple nitriles will not undergo such addition reactions with nucleophiles, these additions are explained\(^4,5\) as being due to the greater mobility of the electron pair of the nitrogen atom and also to the higher electron deficiency of the carbon atom due to an added inductive electron withdrawal by \(-\text{CN}\) or \(\text{Cl}_3\text{C}^-\). Acetonitrile does not react with amines because the inductive effect of the methyl group compensates the mesomeric effect of the nitrile group as follows:

\[
\text{CH}_3\text{C\equiv N}^+ \quad \text{whereas} \quad \text{Cl}_3\text{C\equiv N}^- \]

acetonitrile
trichloroacetonitrile
DISCUSSION

The first portion of this discussion contains a summary of the synthetic methods which have been investigated for preparation of cyclopropane-1,1-dicarbonitrile:

Cyclopropane-1,1-dicarbonitrile was initially prepared by Stewart and Westberg\(^1\) by two methods. The first of these involved the initial preparation of diethyl cyclopropane-1,1-dicarboxylate by a method originally described by Dox and Yoder\(^6\) and later modified by Stewart and Westberg.\(^1\) The diester was then converted to cyclopropane-1,1-dicarboxamide with concentrated aqueous ammonia and the diamide was dehydrated with phosphorus pentoxide to give cyclopropane-1,1-dicarbonitrile. The second synthesis involved the initial preparation of ethyl 1-cyanocyclopropane-1-carboxylate by a method originally described by Jones and Scott\(^7\) and later modified by Stewart and Westberg.\(^1\) The ethyl 1-cyanocyclopropane-1-carboxylate was then converted to 1-cyanocyclopropane-1-carboxamide by shaking with concentrated aqueous ammonia and the 1-cyanocyclopropane-1-carboxamide was dehydrated with phosphorus pentoxide to give the desired cyclopropane-1,1-dicarbonitrile.

Each of these methods required three steps and overall yields were poor, 7% and 21-28% respectively. Therefore, it was desirable to reduce the number of synthetic steps to two or, preferably, one. Efforts were made to develop Perkin type condensations of malononitrile or 2-cyanoacetamide with ethylene bromide in the presence of various basic catalysts and in various solvents for the preparation of both cyclopropane-1,1-dicarbonitrile and 1-cyanocyclopro-
pane-1-carboxamide:

\[
\begin{align*}
\text{CH}_2\text{CN} & + \text{NaNH}_2 \rightarrow \text{Na}^{+}\text{CH}_2\text{(-)}\text{CN} \\
\text{Na}^{+}\text{CH}_2\text{(-)}\text{CN} + RX & \rightarrow \text{RCH}_2\text{CN} + \text{NaX}
\end{align*}
\]

where R = phenyl

Previous dialkylation of this type leading to open-chain compounds have been reported using dimethylformamide (DMF)\(^8\) and dimethyl sulfoxide (DMSO)\(^9\) as solvents.

The direct condensation of 2-cyanoacetamide and ethylene bromide with sodium hydride as catalyst in DMF resulted in a yield of 44 percent 1-cyanocyclopropane-1-carboxamide. When DMSO was used in place of DMF, a side reaction occurred between the hydride and solvent which resulted in a reduced yield of 18%. The 1-cyanocyclopropane-1-carboxamide was dehydrated using both phosphorus pentoxide (38%) and phosphorus oxychloride (25%). The best overall yield by this route was 16.7% compared to 7% and 21% by the two original routes.

Bergström and Agostinho\(^10\) reported that they were successful in dialkylating acetonitrile using sodium amide in liquid ammonia as follows:

\[
\begin{align*}
\text{CH}_3\text{CN} + \text{NaNH}_2 \rightarrow \text{Na}^{+}\text{CH}_2\text{(-)}\text{CN} \\
\text{Na}^{+}\text{CH}_2\text{(-)}\text{CN} + RX \rightarrow \text{RCH}_2\text{CN} + \text{NaX}
\end{align*}
\]

where R = phenyl
\[
\text{RCH}_2\text{CN} + \text{Na}^{(+)} \text{CH}_2\text{CN} \xrightarrow{-5-} \text{RCHCN} + \text{CH}_3\text{CN}
\]

\[
\text{RCHCN} + \text{RX} \xrightarrow{(-)\text{Na}^{(+)}} \text{R}_2\text{CHCN} + \text{NaX}
\]

However an attempt to dialkylate malononitrile with ethylene bromide using a similar method described by Klundt\textsuperscript{11} resulted only in recovered starting materials.

The direct condensation of ethylene bromide and malononitrile was attempted using various catalysts, solvents, and modes of addition. The best yields (17%-19%) were obtained by adding sodium hydride to a DMF solution of malononitrile and ethylene bromide at 60°. The mole ratio 4:5:5 of malononitrile: ethylene bromide: sodium hydride was considered best, however higher mole ratios of sodium hydride did not effect the yield. Despite the poor yield, the yield of final product was as good as that obtained by other methods and eliminated one or two steps.

When the ethylene bromide was added dropwise under varying conditions to a mixture of malononitrile and sodium hydride in DMF no product was obtained. It was assumed that the sodium hydride was catalyzing a polymerization of the malononitrile.

Tetrahydrofuran (THF), when used in place of DMF and under the same conditions as those above, reduced the yield to 12%. Use of sodium amide in THF under the above conditions yielded 12% of the cyclopropane-1,1-dicarbonitrile.

Direct condensation of ethylene bromide and malononitrile using sodium methoxide or ethoxide in DMF under the same conditions as with sodium hydride in DMF failed.
Ethyl 1-cyanocyclopropane-1-imidocarboxylate was prepared as reported previously. All attempts to dealcoholate it using heat alone, phosphorus pentoxide, phosphorus trichloride and phosphorus oxychloride as reagents, failed.

\[ \text{OC}_2\text{H}_5 \quad \xrightarrow{\text{heat, or } P_2\text{O}_5, \text{ or } \text{PCl}_3, \text{ or } \text{POCl}_3} \quad \Delta \text{CN} \quad (\text{No desired product}) \]

Another route investigated was that described by Korte, Scharf, and Büchel for the condensation of malononitrile with 1,4 dibromo-isoprene in THF, using suspended silver oxide as catalyst:

\[ \text{NCCH}_2\text{CN} + \text{Ag}_2\text{O} \xrightarrow{\text{THF}} \text{NCCAg}_2\text{CN} + \text{H}_2\text{O} \]

All attempts to condense malononitrile with ethylene bromide using this method failed.

Although the best yields obtained through the direct condensation reaction of malononitrile and ethylene bromide were in the order of 17-19%, this may well be the best method of preparation from the standpoint of the overall yield and the time saved by using a single step procedure. Starting with the same amount of ethylene bromide in all the cases shown, the preparation via the ethyl 1-cyanocyclopropane-1-carboxylate gave an overall yield of 28% (21-28% depending on yields in individual steps.) The method of direct condensation of 2-cyanoacetamide and ethylene bromide gave
a maximum yield of 22% (16-22%). The method starting with diethyl cyclopropane-1,1-dicarboxylate afforded an overall yield of only 7% of cyclopropane-1,1-dicarbonitrile.

**THE VARIOUS PREPARATIONS OF CYCLOPROPAKE-1,1-DICARBONITRILE**

![Chemical diagram showing various preparations of cyclopropane-1,1-dicarbonitrile](image-url)
Reactions of Cyclopropane-1,1-dicarbonitrile.

Experimental work directed at determining the possibility of ring opening of cyclopropane-1,1-dicarbonitrile by nucleophilic addition has been studied thus far only by the reaction of the dinitrile with several secondary amines. An earlier study showed that cyclopropanecarbonitrile (\(\text{\text{CN}}\)) would not react with secondary amines. Apparently this is due to insufficient electron delocalization through one substituent nitrile group to cause the ring to act as an electrophilic center. Westberg found that secondary amines reacted easily with cyclopropane-1,1-dicarbonitrile (\(\text{\text{CN}}\)) in benzene, but he was unable to isolate any simple product.

When cyclopropane-1,1-dicarbonitrile was treated with piperidine in the presence of absolute ethanol for 18 hours at room temperature, a product was obtained which could be distilled. It formed a hydrochloride and on the basis of its infrared spectrum and elemental analysis was found to be 2-(piperidino)ethylmalononitrile, (I).

\[\text{\text{CN}} \quad \text{CN} + \text{NH} \text{ absolute ethanol} \rightarrow \text{N-CH}_2-\text{CH}_2-\text{CH}_2\text{CN} \]

(I)

When dimethyl amine was used as the nucleophile under the same conditions with the exception that the reaction was run in the refrigerator, the ring of cyclopropane-1,1-dicarbonitrile was cleaved in a manner identical to that shown with piperidine to yield 2-(dimethylamino)ethylmalononitrile, (II).

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The infrared spectrum and elemental analysis confirmed structure II. A much higher boiling material was also obtained but its structure was never established.

The infrared spectra of both I and II exhibited several absorption peaks between 3.5 and 3.6μ which are typical of all products of ring-opening reactions between substituted cyclopropanes and secondary amines. These are attributed to the \( \text{N} = \text{CH}_2 \) grouping.¹ There were no absorption peaks around 3.0μ or 6.1μ which are indicative of \(-\text{C}=\text{NH}\) and \(-\text{C}=\text{N}^-\), respectively, therefore there was no evidence of formation of an amidine (\( \text{RN}_2 \)).
EXPERIMENTAL

1-Cyanocyclopropane-1-carboxamide. By condensation of 2-cyanoacetamide and ethylene bromide.—A.—To a cooled slurry of 8.7 g. (0.36 mole) of sodium hydride in 150 ml. of dry DMF in a 1-liter three-necked flask equipped with stirrer, a condenser topped with a calcium chloride drying tube, and a dropping funnel was added at a fast dropwise rate with stirring a solution of 30.2 g. (0.36 mole) of 2-cyanoacetamide in 100 ml. of DMF. After the mixture had stirred at room temperature for one hour, it was again cooled and 66.5 g. (0.354 mole) of ethylene bromide was added rapidly through the dropping funnel. The addition required about 90 minutes. The mixture was then stirred at room temperature for two and a half hours and then at 50° for one hour. It was then cooled and filtered to remove precipitated sodium bromide. Most of the DMF was removed by distillation at reduced pressure (40 mm.) with stirring. The residue was dissolved in a minimum of boiling water and on chilling gave 17 g. (44%) of crude product. Recrystallization from water gave 15.5 g. (40%) of colorless crystals, m.p. 158-160° (lit.1,13 m.p. 160°).

B. A solution of 21.0 g. (0.25 mole) of 2-cyanoacetamide in 50 ml. DMSO was added dropwise to a slurry of 12.0 g. (0.5 mole) of sodium hydride in 75 ml. of DMSO as described in A. After the mixture had stirred for 45 minutes, 47.0 g. (0.25 mole) of ethylene bromide was added through the dropping funnel with cooling and

aElemental analyses were by Galbraith Laboratories, Inc., Knoxville, Tennessee. Infrared spectra were run on a Beckman IR-5 infrared spectrophotometer.
stirring. After about 70% of the ethylene bromide was added the mixture became solid. The solid was dissolved by adding 100 ml. of benzene and heating over a steam cone. After heating the mixture for one hour 15 ml. of glacial acetic acid in 50 ml. of benzene was added and heating was continued for an additional 30 minutes. The boiling solution was then filtered by suction to remove the sodium bromide. On cooling the filtrate, long crystals were formed. The mixture was again filtered. The crystals were highly soluble in water and absolute ethanol and gave a precipitate with alcoholic silver nitrate solution. They melted readily and when burned, left a white inorganic ash which was water soluble. The filtrate was distilled to remove most of the remaining DMSO. A dark crystalline solid remained which, after two recrystallizations from water with decolorizing charcoal, gave 5 g. (18%) of colorless crystals, m.p. 159-162°.

Preparations of Cyclopropane-1,1-dicarbonitrile. A. By dehydration of 1-cyanocyclopropane-1-carboxamide.—A mixture of 12.5 g. (0.13 mole) of 1-cyanocyclopropane-1-carboxamide, 10 g. of sodium chloride, 50 ml. of ethylene chloride, and 13.4 g. (0.09 mole) of phosphorus oxychloride was heated by a hot water bath with stirring for 5 hours and allowed to stand for 2 days at room temperature. The mixture was then filtered and the solvent was removed on a steam cone. The residue was distilled and 4 g. (33%) of a fraction, b.p. 85-110° (20 mm.), n^25D 1.4405 was taken. This fraction was dissolved in ether, washed twice with water and dried over anhydrous magnesium sulfate. A final distillation gave a middle fraction of
2.5 g. (25%) of cyclopropane-1,1-dicarbonitrile b.p. 102-105° (20 mm.), n^25D 1.4430 [lit.1 b.p. 103° (20 mm.), n^25D 1.4463].

B. By direct condensation of malononitrile and ethylene bromide.

(1) Use of sodium hydride in dimethylformamide (DMF).—The apparatus consisted of a 1-liter three necked flask equipped with solid dropping funnel, argon inlet, reflux condenser topped with a calcium chloride drying tube, and a magnetic stirrer. All equipment was flame-dried and provided with an argon atmosphere. Sodium hydride, 5.5 g. (0.23 mole) was added through a solid dropping funnel to a stirred solution of 12.6 g. (0.19 mole) of malononitrile and 43.2 g. (0.23 mole) of ethylene bromide in 75 ml. of dry DMF at 50-60°. The addition required about two hours and the reaction was exothermic. After an additional two hours, the mixture was cooled and filtered to remove the precipitated sodium bromide. Most of the DMF was removed by distillation under reduced pressure with stirring, the residue was cooled, 100 ml. of ether was added, and a further precipitate of sodium bromide was removed by filtration. Stripping of the ether under reduced pressure left a red liquid and distillation gave 3 g. (19%) of cyclopropane-1,1-dicarbonitrile, b.p. 103-106° (20 mm.), n^25D 1.4400.

(2) Use of sodium amide in tetrahydrofuran (THF).—Using the apparatus described in (1), a slurry of 11.7 g. (0.30 mole) of sodium amide in 50 ml. of THF was added through a solid dropping funnel over a 30 minute period to 10.0 g. (0.15 mole) of malononitrile in 50 ml. of THF with external cooling by an ice bath. After the addition of the sodium amide, 28.2 g. (0.15 mole) of...
Ethylene bromide were poured into the mixture and heating was initiated. At 60° an exothermic reaction began. The mixture was refluxed for 90 minutes, cooled and filtered to remove precipitated sodium bromide. Most of the THF was removed by distillation, the residue was cooled, 50 ml. of ether was added, and a further precipitate of sodium bromide was removed by filtration. Stripping of the ether under reduced pressure left a red liquid which distilled to give 1.6 g. (12%) of cyclopropane-1,1-dicarbonitrile, b.p. 115° (40 mm.), n25D 1.4438.

(3) Use of sodium hydride in tetrahydrofuran (THF) — The apparatus and method were generally the same as described in (1). A slurry of 20.7 g. (0.90 mole) of sodium hydride in 100 ml. of THF was added to a solution containing 39.6 g. (0.6 mole) of malononitrile and 124 g. (0.66 mole) of ethylene bromide in 250 ml. of THF. The purification was similar to that described in (2) with the following changes. The solution was made slightly acidic with dilute hydrochloric acid before the THF was removed, and the ether extracts were washed with water, and with saturated sodium chloride solution and were then dried over magnesium sulfate. Stripping of the ether under reduced pressure left 54 g. of red liquid which distilled to give 5.0 g. (12%) of cyclopropane-1,1-dicarbonitrile.

Preparation of ethyl 1-cyanocyclopropane-1-imidocarboxylate.
The preparation followed the method described by Stewart and Westberg, and distillation gave 35% of crude product.

Attempted removal of ethanol from ethyl 1-cyanocyclopropane-1-imidocarboxylate. — A mixture of 6 g. (0.043 mole) of ethyl 1-cyano-
cyclopropane-1-imidocarboxylate and 2.1 g. of phosphorus pentoxide was mixed thoroughly by shaking in a 125-ml. Claisen distilling flask at 20 mm. pressure. The flask was then submerged in an oil bath preheated to 175° and the bath temperature raised to 200°. No distillate was obtained and a nondistillable tar remained.

Other attempts using phosphorus trichloride and phosphorus oxychloride also gave none of the desired product.

Reaction of piperidine with cyclopropane-1,1-dicarbonitrile in absolute ethanol.—To a solution of 1.5 g. (0.019 mole) cyclopropane-1,1-dicarbonitrile in 18 ml. of absolute ethanol was added at a fast dropwise rate 1.9 g. (0.022 mole) of piperidine. The mixture was allowed to stand for eighteen hours and then was distilled to give 1.2 g. (36%) of colorless distillate, b.p. 104–108° (0.5 mm.). A final distillation gave three fractions, all having about the same boiling point and refractive index. The product proved to be 2-(piperidino)ethylmalononitrile, b.p. 102.5–103.5° (0.5 mm.), n25D 1.4687.

Anal. Calcd. for C10H15N3: C, 67.76; H, 8.48
Found: C, 67.62; H, 8.70

The infrared spectrum in carbon tetrachloride solution showed peaks at the following wave lengths in μ: 3.40 (s), 3.50 (m), 3.57 (m), 4.43 (vw), 6.80 (m, sh at 6.91), 7.25 (m), 7.39 (m), 7.67 (m), 7.95 (m), 8.25 (m), 8.63 (m), 8.87 (s), 9.60 (m), 9.9 (w), 10.36 (m). There were no -C=NH peaks at 3.00 μ or 6.1 μ to indicate amine addition across the nitrile group.

The hydrochloride was prepared and after one recrystallization from absolute ethanol melted at 191–192°.
Reaction of dimethylamine with cyclopropane-1,1-dicarbonitrile in absolute ethanol.—To a cool solution of 2.3 g. (0.025 mole) of cyclopropane-1,1-dicarbonitrile in 20 ml. of absolute ethanol in a pressure bottle was added rapidly 2.25 g. (0.050 mole) of dimethylamine. The mixture was allowed to stand for 48 hours in the refrigerator and distilled to give 2.1 g. (61%) of colorless distillate, b.p. 73-75° (0.5 mm.) and 1.0 g. (29%) of a viscous yellow liquid, b.p. 130° (0.5 mm.). The first fraction was redistilled yielding 1.05 g. (30%) of colorless liquid, b.p. 69-70° (0.5 mm.), \( \eta^D_{25} 1.4420 \), assumed to be 2-(dimethylamino)ethylmalononitrile.

**Anal.** Calcd. for C\( \text{H}_7 \text{N}_3 \): C, 61.28; H, 8.08

Found: C, 61.12; H, 8.14

The infrared spectrum in carbon tetrachloride solution showed peaks at the following wave lengths in \( \mu \): 3.4 (s), 3.5 (s), 3.55 (s), 3.6 (s), 4.44 (w), 6.1 (m), 6.84 (s), 7.25 (m) 7.44 (m), 7.9 (m-s), 8.3 (m-s), 8.65 (m-s), 9.1 (m), 9.4 (m-s), 9.62 (s), 10.2 (w-m). Again there were no -C=NH peaks at 3.9μ or 6.1μ indicative of amidines.

The hydrochloride was prepared and, after two recrystallizations from absolute ethanol, melted at 160-162°. The infrared spectrum in DMF solution showed peaks at the following wave lengths in \( \mu \): 2.81 (s), 3.54 (m), 5.9-6.1 (s, broad), 6.7-7.3 (s, broad), 8.1 (m), 9.2-9.4 (s, broad), 11.57 (w), 15.3 (m, broad).

An attempted distillation of the second fraction [b.p. 130° (1 mm.)] resulted in decomposition. A small amount did distill at 125° (1 mm.) after a forerun of 70-115°. No elemental analysis was obtained, but its infrared spectrum was quite different from that of the lower boiling fraction. It was not identified.
SUMMARY

a. Attempts were made to improve the established methods of preparing cyclopropane-1,1-dicarbonitrile from the standpoints of yield and time requirement. A method was found to directly condense malononitrile and ethylene bromide in the presence of bases, such as sodium hydride and sodium amide, in several solvents.

b. The ring-opening additions of cyclopropane-1,1-dicarbonitrile with piperidine and dimethylamine were studied, and structures were established for the products.
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## PART II

**PREPARATION OF 1,1-DISUBSTITUTED 2-METHYL 2-CYCLOPROPYL ETHENES**

AND THEIR REACTIONS WITH NUCLEOPHILES

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INTRODUCTION

The physical and chemical properties of cyclopropane are quite different from saturated hydrocarbons and it exhibits some olefinic character. There are, however, many conflicting reports regarding the ability of a cyclopropane ring to enter into conjugation with unsaturated groups. The ability of the cyclopropane ring to transmit or extend conjugation has been under study in the chemistry laboratory at the University of Montana as well as several other laboratories.

In order for cyclopropane to exhibit double bond character its electrons must be delocalized. This delocalization was predicted theoretically by Coulson and Moffitt. They suggested that each carbon atom is at the corner of an equilateral triangle and the hybridization is such that the two orbitals from any one carbon, in the plane of the ring, make an angle between each other of 106°. This implies that the external valence angle should be near 113°. The C-C bond lengths in the ring are therefore shorter than those of saturated hydrocarbons.

![Diagram of hybrid orbitals of cyclopropyl carbons](image)

Rogers reported that the ultraviolet absorption band of cyclopropyl methyl ketones lies between those of isopropyl methyl ketone and vinyl methyl ketone, indicating some olefinic character of the ring.
Smith and Rogier\(^3\) studied 2-phenylbicyclopropane (\(\text{\includegraphics[width=1em]{cyclopropane}}\)) using molecular refraction, ultraviolet and infrared spectra, and its reactions and found that it did not exhibit any conjugative effects beyond those shown by phenylcyclopropane (\(\text{\includegraphics[width=1em]{cyclopropane}}\)).

A study of the ultraviolet absorption of umbellulone\(^4\) (\(\text{\includegraphics[width=1em]{umbellulone}}\)) showed that the unsaturation of the cyclopropane system is much different from that of an olefin, in that it appears capable of extending conjugation but incapable of transmitting conjugation. The cyclopropane ring of umbellulone exerts a pronounced effect upon the ultraviolet absorption of this compound not observed in the ultraviolet spectra of the tricyclic ketone (\(\text{\includegraphics[width=1em]{tricyclic_ketone}}\)) or \(\text{\includegraphics[width=1em]{dihydrourmbellulone}}\). These observations can be explained theoretically by the non-classical cyclopropylmethyl carbonium ion: \(\text{\includegraphics[width=1em]{carbonium}}\). The bathochromic effect of the cyclopropane ring in umbellulone is believed due to this carbonium ion, wherein the unsaturation of the cyclopropane apparently enters into conjugation with the alpha, beta unsaturated carbonyl system.

Fuson and Baumgartner report\(^6\) that mesityl propenyl ketone (\(\text{\includegraphics[width=1em]{mesityl_propenyl_ketone}}\)) adds Grignard reagents and active methylene compounds in a 1,4 manner, whereas the same is not true for mesityl cyclopropyl ketone (\(\text{\includegraphics[width=1em]{mesityl_cyclopropyl_ketone}}\)).

Trachenberg and Odian\(^7\) studied the relative conjugative effects in trans-cinnamic acid, trans-2-phenylcyclopropane carboxylic acid, and \(\beta\)-phenyl propionic acid by comparing the relative abilities of various m- and p-substituents to affect the acidity of the carboxyl group in the above acids. They concluded that the cyclopropane
ring behaves like the saturated analog and differs markedly in its behavior from an olefinic group, showing no tendency to transmit conjugation.

R. W. Kierstead, R. P. Linstead and B. C. L. Weeden\(^8\) studied the addition of ethyl sodiomalonate to diethyl 2-vinylcyclopropane-1,1-dicarboxylate.

\[
\text{CH}_2=\text{CH-CH-CH}_2\text{CO}_2\text{C}_2\text{H}_5 + \text{Na}^+\left[\text{CH}_2\text{CO}_2\text{C}_2\text{H}_5\right]^- \rightarrow \text{CH}_2=\text{CHCHCH}_2\text{CO}_2\text{C}_2\text{H}_5
\]

The isolation of C as well as A and B demonstrated that in this reaction the cyclopropane ring is apparently capable of transmitting conjugation between the vinyl group and the carboxylate groups.

Mohrbacher and Cromwell\(^9\) studied the ultraviolet and infrared spectra of some trans-2-phenylcyclopropyl aryl ketones and reported that the cyclopropane ring was capable of transmitting conjugative effects from the 2-phenyl group to the ketone group.

E. P. Carr and C. P. Burt\(^10\) studied the ultraviolet spectra of the three compounds IV, V, VI and found that the saturated compounds showed the least general absorption, the cyclopropyl

\[
\begin{align*}
\text{C}_6\text{H}_5\text{CH-CH-CH}_2\text{COC}_6\text{H}_5 & \quad \text{IV} \\
\text{C}_6\text{H}_5\text{CH-CH-COC}_6\text{H}_5 & \quad \text{V} \\
\text{C}_6\text{H}_5\text{CH}=\text{C-COC}_6\text{H}_5 & \quad \text{VI}
\end{align*}
\]
derivatives slightly more, and the ethylenic compound the greatest absorption. Their conclusion was that the cyclopropane ring could transmit conjugation to a limited extent.

Pagenkopf studied the product mixtures from reactions of typical nucleophiles with diethyl 2-vinylcyclopropane-1,1-dicarboxylate, and found that mainly a simple ring-opening reaction (1,4-addition) had occurred. In most cases, however, some of the 1,6-addition product was also isolated.

\[
\begin{align*}
\text{H}_2\text{C}=\text{CH} & \quad \text{CO}_2\text{C}_2\text{H}_5 & \quad \text{H}_2\text{C}=\text{CH} & \quad \text{CO}_2\text{C}_2\text{H}_5 \\
\text{H}_2\text{C}=\text{CH} & \quad \text{CH}_2\text{C}-\text{OC}_2\text{H}_5 & \quad \text{H}_2\text{C}=\text{CH} & \quad \text{CH}_2\text{C}-\text{OC}_2\text{H}_5 \\
\end{align*}
\]

\[
\begin{align*}
\overset{1,4 \text{addition}}{\text{1,4 addition}} & \\
\overset{1,6 \text{addition}}{\text{1,6 addition}} & \\
\end{align*}
\]

This indicated that there is some tendency for transmission of conjugation through the cyclopropane ring in this compound.
DISCUSSION

The purpose of this study was to further elucidate the question of whether or not a cyclopropane ring can extend a chain of conjugation. This was to be determined by the analysis of the reaction products of amines and other nucleophiles with $\text{1,1-disubstituted 2-cyclopropylethenes}$, $\bigtriangleup \text{CH} = \text{C}^X_{\ Y}$ (where $X$ and $Y$ represent electron-withdrawing groups).

\[ \text{1,4 addition} \]

\[ \text{1,6 addition} \]

Products of 1,6-addition would indicate that the cyclopropane ring had extended the chain of conjugation.

Syntheses of the desired compounds of the type $\bigtriangleup \text{CH} = \text{C}^X_{\ Y}$, followed the method described by A. C. Cope.\textsuperscript{12,13} He condensed ketones with cyanoacetic acid esters in the presence of various catalysts in a modification of the Knoevenagel reaction. The mechanism of the Knoevenagel reaction involves the following steps:

\[ \begin{align*}
\text{CN} & \quad \text{CN} \\
\text{CH}_2CO_2\text{CH}_3 & \quad (-)\text{CH}CO_2\text{CH}_3 + H^+ \quad \text{or} \quad \text{CN} \quad \text{C}=\text{NH} \\
\end{align*} \]
Either cyclopropane carboxaldehyde or a cyclopropyl ketone was required as initial starting material. Our first attempt was to prepare the aldehyde. The first preparation of cyclopropane carboxaldehyde was that described by Smith and Rogier\(^\text{14}\) who reported a 48\% yield. Our yields using this method were only 15-20\% of impure material. Modifications of this method failed to increase the yield.

H. C. Brown, et al.\(^\text{15}\) reported that cyclopropanecarbonitrile could be partially reduced to the aldehyde using lithium triethoxyaluminohydride \([\text{LiAl(O\text{Et})\text{H}}]_3\) with a yield of 69\%. Numerous attempts to repeat this work failed.

The method reported by Brown and McFarlin\(^\text{16}\) and by Brown and Rao\(^\text{17}\) for partial reduction of cyclopropane carboxyl chloride with lithium tri-\(t\)-butoxyaluminohydride \([\text{LiAl(O-t-Bu)}\text{H}]_3\) resulted in little product.

Attempts were made to reduce \(N,N\)-dimethyl cyclopropane carboxamide to the aldehyde using two methods. The first utilized lithium diethoxyaluminohydride\(^\text{18}\) \([\text{LiAl(OEt)}\text{_2H}_2]\) as a reducing agent and the second lithium aluminum hydride.\(^\text{19}\)

\[
\[
R_2\text{C}=\text{O} + (-)\text{CH} \quad \text{CN} \quad \text{HO}_2\text{CH}_3 \\
\text{CN} \quad \text{HO}_2\text{CH}_3 \\
R_2\text{C}=\text{C} \quad \text{CN} \\
\text{HO}_2\text{CH}_3 \\
\text{CN} \\
\text{HO}_2\text{CH}_3
\]

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\[
\[
\triangle_{\text{C}_2\text{O} \quad \text{N(CH}_3\text{)}_2 \quad \text{LiAl(OEt)}\text{_2H}_2 \quad \text{(or LiAlH}_4\text{)}} \quad \triangle_{\text{C}_2\text{O} \quad \text{(reported yield 78\%)}\text{18}}
\]
Both of these reactions failed to yield the desired aldehyde.

The only explanation for the failure of all of these reductions is that the lithium aluminum hydride may not have been of good grade.

Efforts were shifted to the use of cyclopropyl methyl ketone, which was prepared in good yields as described in Organic Synthesis. The ketone was readily condensed with ethyl cyanoacetate using ammonium acetate as catalyst. The product, 1-cyano 1-carboethoxy 2-methyl 2-cyclopropyl ethene (I), \( \text{CH}_3\text{C}=\text{C}(-\text{CO}_2\text{C}_2\text{H}_5) \) was found to be present as a mixture of geometrical isomers, a solid trans-isomer* (48%) and a liquid cis-isomer (35%). Both had the same infrared and near infrared spectra and elemental analysis. The liquid cis-isomer could be partially converted to the solid trans-isomer by heating at 140\(^\circ\). This was believed to be an equilibrium process since, if some of the solid trans-isomer was removed by some means, more would form on continued heating.

The condensation of methyl cyclopropyl ketone with malononitrile under the same conditions as described for the ethyl cyanoacetate reaction gave an 88% yield of 1,1-dicyano 2-methyl 2-cyclopropyl ethene (II), \( \text{CH}_3\text{C}=\text{C}(-\text{CN}) \). Proof of structure was based on its infrared and near infrared spectra and its elemental analysis.

The condensation of methyl cyclopropyl ketone with 2-cyanoacetamide resulted in a 31% yield of 1-cyano 1-carboxamido 2-methyl 2-cyclopropyl ethene (III), \( \text{CH}_3\text{C}=\text{C}(-\text{O-NH}_2) \). Elemental analysis and the infrared spectrum verified this structure.

*Assignment of cis, trans terms were arbitrary.
Attempts to prepare 1,1-dicarboethoxy 2-methyl 2-cyclopropyl ethene (IV), using the above method failed. Acetamide, diethylamine, piperidine, triethylamine and pyridine were also used as catalysts in this attempted reaction with no success. The direct conversion of I to IV was also tried according to the equations below, but only starting material was recovered.

\[
\begin{align*}
\text{CH}_3\text{CN} + \text{C}_2\text{H}_5\text{OH} & \xrightarrow{\text{H}_2\text{SO}_4} \text{CH}_3\text{CO}_2\text{C}_2\text{H}_5 \\
\text{CH}_3\text{CN} + \text{dry HCl} + \text{C}_2\text{H}_5\text{OH} & \rightarrow \text{CH}_3\text{CO}_2\text{C}_2\text{H}_5
\end{align*}
\]

The reaction of secondary amines with 1-cyano 1-carboethoxy 2-methyl 2-cyclopropyl ethene (I) was first investigated. The amine and I were dissolved in absolute ethanol, sealed in a test tube, and heated from 3-24 hour periods at 100-120°. The reactions that were run for shorter periods of time resulted in some recovered starting material and tars, while the reactions over longer periods of time formed five or six products as was shown by thin-layer and gas chromatography. None of these products appeared to have the expected properties of the desired product.

When I was dissolved in hot n-butanol and a solution of piperidine in n-butanol was added slowly at reflux temperature, a reaction occurred and a new liquid compound was isolated. When
morpholine, diethylamine, and Triton B (benzyltrimethyl ammonium hydroxide) were used in place of piperidine, a similar reaction occurred in each case and the same liquid product was obtained. This product was found to be the result of transesterification of the ethyl ester.

\[
\begin{align*}
\text{CH}_3\text{C} = \text{C}_\text{CO}_2\text{C}_2\text{H}_5 + \text{n-C}_4\text{H}_9\text{OH} & \xrightarrow{\text{secondary amine or Triton B}} \text{CH}_3\text{C} = \text{C}_\text{CO}_2\text{n-C}_4\text{H}_9 \\
\text{I} & \quad \text{V}
\end{align*}
\]

The product was shown to be 1-cyano 1-carbobutoxy 2-methyl 2-cyclopropyl ethene (V) by elemental analysis and by its near-infrared and infrared spectra. In the presence of the stronger base Triton B, more decomposition was observed than when a secondary amine was used. The use of triethylamine under the same conditions resulted in no transesterification.

Transesterifications using amines as catalysts have been reported a few times previously. For example, Woodward\textsuperscript{21} reported an ester interchange between glycols and dimethyl terephthalate in the presence of tertiary and secondary amines.

Other attempts to react piperidine with I using dimethylformamide or toluene in place of \text{n}-butanol failed. Attempts to force the addition reaction by use of a stronger basic catalyst, using V, morpholine and \text{n}-butanol as above, with three drops of Triton B, for example, resulted only in recovered starting material V.

When a solution of thiophenol and I were refluxed for 7 hours in absolute ethanol under argon in the presence of sodium ethoxide,
a ring-opening addition (1,6 addition) occurred. The liquid product showed strong absorption peaks at 14.5 \( \mu \) (indicative of -C-S-C-)\(^{22}\) and 6.21 \( \mu \) (indicative of -C=C-)\(^{22}\) and lacked an absorption peak in the near-infrared at 1.67 \( \mu \) (indicative of a cyclopropane ring). The ester peak of the product appeared at 1735 cm\(^{-1}\), compared to 1725 cm\(^{-1}\) in I, indicating that the double bond was no longer conjugated with the electron-withdrawing groups. Elemental analysis proved the product to be 1-cyano 1-carboethoxy 2-methyl 5-(phenylthio)pentene-2, \( \text{[ethyl 2-cyano 3-methyl 6-(phenylthio) 3-hexenoate]} \).

When a solution of 1-butanethiol and I was refluxed for 7 hours in absolute ethanol under argon in the presence of sodium ethoxide, a ring-opening addition occurred. The yellow liquid showed infrared absorption peaks at 6.21 \( \mu \) (indicative of -C=C-), 4.50 \( \mu \) (indicative of -C=N), a very weak peak at 1.67 \( \mu \) (indicative of the cyclopropane ring) and lacked a band at about 3.0 \( \mu \) (indicative of =NH). The product was assumed to be 1-cyano 1-carboethoxy 2-methyl 5-(butylthio)pentene-2, \( \text{[ethyl 2-cyano 3-methyl 6-(butylthio) 3-hexenoate]} \), \( \text{n-C}_4\text{H}_9\text{-S-CH}_2\text{CH=CH-CN CO}_2\text{C}_5\text{H}_5 \).

Elemental analysis gave an acceptable result for hydrogen but not for carbon. It would appear on the basis of the near-infrared and infrared spectra that the structure indicated is correct but that something is wrong with the analysis for carbon. An analysis for nitrogen will be obtained.

Reason for successful reaction here is undoubtedly the greater
nucleophilic strength of the thiophenoate and 1-butanethiolate anions as compared to amines.

An attempt to react phenol with I in the presence of sodium ethoxide in a sealed tube at 105° for 24 hours gave only starting material and a little nondistillable tar.

The reactions of 1,1-dicyano 2-methyl 2-cyclopropyl ethene with dimethylamine, diethylamine or piperidine resulted in isolation of new solid products. The infrared spectrum in chloroform solution of each showed peaks at 2.96μ and at 6.08 and 6.13μ. It has been reported\textsuperscript{22,23} that absorption peaks around 3.0μ are indicative of -C=NH group, and those around 6.1μ are indicative of -C=N-. It appeared likely that the reactions were taking the following course:

\[ \text{CH}_3\text{C} = \text{C}_\text{CN} + \text{R}_2\text{NH} \xrightarrow{\text{absolute ethanol}} \text{CH}_3\text{C} = \text{C}_\text{N} = \text{NH} \]

However, elemental analysis results for the products were not within acceptable limits and it was apparent that some impurity was present which had very similar properties.
EXPERIMENTAL

Cyclopropane carboxaldehyde A. Reduction of cyclopropane carbonitrile with lithium aluminum hydride.—The partial reduction of cyclopropane carbonitrile by lithium aluminum hydride as described by Smith and Rogier resulted in yields of only 15-20% of impure material, compared to a reported yield of 48%. Modifications of this method did not increase the yield.

B. Reduction of cyclopropane carboxyl chloride with lithium tri-t-butoxyaluminohydride.—Attempts to prepare cyclopropane carboxaldehyde by the partial reduction of cyclopropane carboxyl chloride with lithium tri-t-butoxyaluminohydride using the method of Brown gave only a 20% yield of impure material.

C. Reduction of cyclopropane carbonitrile with lithium triethoxyaluminohydride.—Attempts to prepare cyclopropane carboxaldehyde by the partial reduction of cyclopropanecarbonitrile with lithium triethoxyaluminohydride, reported by Brown Shoaf and Garg to give a yield of 69%, all failed.

D. Reduction of N,N-dimethyl cyclopropane carboxamide with lithium diethoxyaluminohydride.—Attempts to partially reduce N,N-dimethyl cyclopropane carboxamide with lithium diethoxyaluminohydride by the method of Brown and Tsukamoto failed.

Methyl cyclopropyl ketone.—The preparation procedure followed that described in Organic Syntheses.

Elemental analyses were by Galbraith Laboratories, Inc., Knoxville, Tennessee. Infrared spectra were run on a Beckman IR-5 infrared spectrophotometer. Near-infrared spectra were run on a Coleman Hitachi EPS-3T spectrophotometer.
Preparation of 1-cyano 1-carboethoxy 2-methyl 2-cyclopropyl ethene (I).—A. Using ammonium acetate, glacial acetic acid, and benzene.—In a 125 ml. extraction flask equipped with a water separator and condenser were mixed 20 g. (0.24 mole) of methyl cyclopropyl ketone, 25 g. (0.22 mole) of ethyl cyanoacetate, 1.9 g. (0.025 mole) of ammonium acetate, 5.7 ml. of glacial acetic acid and 50 ml. of benzene. The solution was heated at reflux (~100°) for 24 hours with stirring and the water formed during the reaction was removed in the water separator. The solution was cooled, 75 ml. of ether was added, and the whole solution was washed twice with water. The ether solution was then dried over calcium chloride and the ether and benzene were removed by evaporation on a steam cone. The residue was recrystallized from 70% ethanol, giving 19.0 g. (48%) of the trans-isomer of 1-cyano 1-carboethoxy 2-methyl 2-cyclopropyl ethene (I). After six recrystallizations, the solid isomer melted at 81.0-82.0°.

**Anal.** Calcd. for C_{10}H_{13}NO_2: C, 67.01; H, 7.33

**Found:** C, 66.68; H, 7.21

The mother liquor was diluted with water, the solution was saturated with sodium chloride and then extracted with ether. The ether extracts were dried over magnesium sulfate and the solvents were stripped under reduced pressure. Distillation of the residue gave 13.6 g. (35%) of the liquid cis-isomer of I, b.p. 98-99° (0.05 mm.), n^25D 1.5117.

**Anal.** Calcd. for C_{10}H_{13}NO_2: C, 67.01; H, 7.33; N, 7.81

**Found:** C, 66.84; H, 7.37; N, 7.91
The infrared spectra of both isomers of 1-cyano 1-carboethoxy 2-methyl 2-cyclopropyl ethene in carbon tetrachloride solution showed peaks at the following wave lengths in $\mu$: 3.45 (w), 4.50 (w), 5.80 (vs), 6.32 (s), 6.84 (vw), 6.92 (vw), 7.22 (vw), 7.31 (w), 7.67 (s), 8.02 (vs), 8.39 (s), 8.78 (w), 9.11 (w), 9.36 (s), 9.66 (vw), 10.7 (m), 11.35 (vw), 11.72 (w).

A similar reaction using acetamide in place of ammonium acetate resulted a yield of only 5% of the trans-isomer. No cis-isomer was isolated.

The cis-isomer was partially converted to the trans-isomer by heating at 140° for several hours.

B. Using piperidine in the presence of magnesium sulfate.—In a 50-ml. flask equipped with a reflux condenser were placed 8.4 g. (0.10 mole) of methyl cyclopropyl ketone, 11.3 g. (0.10 mole) of ethyl cyanoacetate, 1.7 g. (0.02 mole) of piperidine, and 2.0 g. of anhydrous magnesium sulfate. The mixture was refluxed for five hours, cooled, and enough water was added to dissolve the magnesium sulfate. The mixture was then extracted three times with ether and the ether extracts were dried over calcium chloride. Removal of the ether gave only 1.8 g. (10%) of the trans-isomer of I. No cis-isomer was isolated.

Preparation of 1,1-dicyano 2-methyl 2-cyclopropyl ethene (II).—Using ammonium acetate, glacial acetic acid, and benzene.—The reaction was run exactly as described for I above, using 22.3 g. (0.266 mole) of methyl cyclopropyl ketone, 21.0 g. (0.32 mole) of malononitrile, 2.0 g. (0.026 mole) of ammonium acetate, 6.4 ml.
of glacial acetic acid, and 60 ml. of benzene. Recrystallization of the crude product from 70% ethanol gave 31.9 g. (88%) of the solid, 1,1-dicyano 2-methyl 2-cyclopropyl ethene (II). After three recrystallizations from 70% ethanol, it melted at 64.0–64.5°.

Anal.  Calcd. for C₈H₈N₂:  C, 72.69; H, 6.11
       Found:  C, 72.76; H, 6.36

The infrared spectrum of II in carbon tetrachloride solution showed peaks at the following wave lengths in µ: 3.31 (m), 4.49 (s), 6.36 (vs), 6.98 (m), 7.26 (m), 7.62 (m-s), 8.22 (vs), 9.19 (m), 9.46 (m), 9.84 (w-m), 10.71 (vs), 11.23 (w), 11.97 (w-m), 15.0 (m).

Preparation of 1-cyano 1-carboxamido 2-methyl 2-cyclopropyl ethene (III). Using ammonium acetate, glacial acetic acid, and benzene (or toluene).—The reaction was run as described for the condensations in the preceding sections, using 4.2 g. (0.05 mole) of methyl cyclopropyl ketone, 4.2 g. (0.05 mole) of 2-cyanoacetamide, 0.4 g. (0.026 mole) of ammonium acetate, 1.2 ml. of glacial acetic acid, and 10 ml. of benzene (or toluene). Recrystallization from 95% ethanol gave 2.3 g. (31%) of white crystals, 1-cyano 1-carboxamido 2-methyl 2-cyclopropyl ethene (III) melting at 167–168.5°.

Anal.  Calcd. for C₈H₁₀N₂O:  C, 63.97; H, 6.72; N, 18.66
       Found:  C, 64.12; H, 6.71; N, 18.80

The infrared spectrum of III in a potassium bromide pellet showed peaks at the following wave lengths in µ: 2.97 (s), 3.15 (s), 3.6 (vw), 4.52 (m), 6.08 (s, sh at 6.16), 6.34 (s),
7.02 (vw), 7.20 (m), 7.34 (m), 7.75 (w), 8.35 (w), 8.47 (w),
8.72 (w-m), 8.8 (vw), 9.36 (w), 9.48 (m), 9.82 (w), 10.76 (m),
11.4 (vw), 12.4-12.7 (m, broad), 13.4 (w-m, broad), 14.45 (m).

**Attempted reactions of 1-cyano 1-carboethoxy 2-methyl 2-cyclopropyl ethene with secondary amines.**—The reactants were
dissolved in absolute ethanol and placed in a 200 mm. x 25 mm.
tube which was sealed with an argon atmosphere and heated in a
pressure-type bomb for periods of 3-20 hours at 100-120°. The
ethanol was removed and the residue distilled to give a mixture
of products which were not identified.

**Transesterification of 1-cyano 1-carboethoxy 2-methyl 2-cyclo-
propyl ethene (I) to 1-cyano 1-carbobutoxy 2-methyl 2-cyclo-
propyl ethene (V). A. Using diethylamine as catalyst.**—To a
refluxing solution of 7.1 g. (0.040 mole) of I and 30 ml. of n-butanol
in a 300 ml. three-necked flask equipped with a condenser, dropping
funnel and magnetic stirring bar, a solution of 3.47 g. (0.048 mole)
of diethylamine in 20 ml. of n-butanol was added slowly through a dropping funnel. The addition required two hours.
The mixture was then heated at reflux for an additional two
hours, cooled, and the diethylamine and excess n-butanol were
distilled under reduced pressure. The remaining liquid was
then distilled twice yielding a 4.9 g. (59%) of colorless distillate,
1-cyano 1-carbobutoxy 2-methyl 2-cyclopropyl ethene (V), b.p.
95-96° (0.05 mm.), n25D 1.5026.

**Anal.** Calcd. for C12H17NO2: C, 69.52; H, 8.28; N, 6.76

Found: C, 69.79; H, 8.55; N, 6.94
B. Using morpholine as catalyst.—The reaction was run exactly as described in A above, except that 4.28 g. (0.048 mole) of morpholine was used in place of the diethylamine. Final distillation gave 2.5 g. (32%) of pure liquid distillate V, b.p. 109° (0.1 mm.), $n^D_{25} 1.5029$.

**Anal.** Calcd. for $C_{12}H_{17}NO_2$: C, 69.52; H, 8.28; N, 6.76

Found: C, 69.86; H, 8.59; N, 7.08

C. Using piperidine as catalyst.—The reaction was run as described in A, using 11.0 g. (0.061 mole) of I, 4.75 g. (0.055 mole) of piperidine and 70 ml. of $n$-butanol. Distillation gave a crude yield of 7.3 g. (58%) of V. A second distillation gave a colorless distillate (V), b.p. 110° (0.1 mm.), $n^D_{25} 1.5022$.

**Anal.** Calcd. for $C_{12}H_{17}NO_2$: C, 69.52; H, 8.28; N, 6.76

Found: C, 69.34; H, 8.41; N, 6.90

D. Using Triton B. (benzyltrimethyl ammonium hydroxide) as catalyst.—The reaction was run as described in A, using 4.5 g. (0.025 mole) of I, 2.8 g. (0.0015 mole) of Triton B and 28 ml. of $n$-butanol. After the $n$-butanol was distilled, the residue was cooled, 25 ml. of benzene was added, and the benzene layer was washed twice with 3 N hydrochloric acid, twice with water, and then dried over anhydrous magnesium sulfate. Removal of the benzene left 3 g. of reddish liquid which distilled to give 1 g. (22%) of a colorless liquid V, b.p. 110-111° (0.1 mm.), $n^D_{25} 1.5010$.

No elemental analysis was obtained but this product was identical with that obtained in procedures A, B and C above.

The infrared and near-infrared spectra in carbon tetrachlor-
ide solution of the above products were identical and very similar to those of the starting material, 1-cyano 1-carboxyethyl 2-methyl 2-cyclopropyl ethene.

Thin layer chromatography showed only one product in each case.

E. Using triethylamine as catalyst.—When triethylamine was used in place of the secondary amines under the same conditions, no reaction occurred.

Reaction of 1-cyano 1-carboethoxy 2-methyl 2-cyclopropyl ethene with thiophenol.—A solution of sodium ethoxide was prepared under argon using 0.05 g. (0.0022 mole) of sodium in 20 ml. of absolute ethanol. To this solution was added 3.3 g. (0.030 mole) of thiophenol, and then 4.5 g. (0.025 mole) of I. The mixture was then heated at reflux for 7 hours. The ethanol was distilled under reduced pressure. The residue was cooled, dissolved in ether, washed three times with water and once with a saturated sodium chloride solution. The ether extracts were dried over calcium chloride. The ether was removed under reduced pressure, leaving 4.5 g. of yellow residue. Distillation gave 3.5 g. (48% based on an addition product) of colorless liquid assumed to be 1-cyano 1-carboethoxy 2-methyl 5-(phenylthio)pentene-2, b.p. 167-168° (0.10 mm.), n^25D 1.5558.

**Anal.** Calcd. for C_{16}H_{19}NSO_{2}: C, 66.39; H, 6.63; N, 4.84

**Found:** C, 66.28; H, 6.71; N, 4.88

The near infrared spectrum in carbon tetrachloride solution showed peaks at the following wave lengths in μ: 1.19 (w),
1.22 (w), 1.43 (w), 1.72 (s), 1.79 (m), 1.93 (w), 2.07 (w, broad),
2.18 (s), 2.21 (w), 2.23 (w), 2.29 (s), 2.33 (s), 2.38 (m), 2.44
(m), 2.50 (s).

The infrared spectrum in carbon tetrachloride solution
showed peaks at the following wave lengths in μ: 3.25 (w), 3.40
(s, sh at 3.48), 4.50 (m), 5.76 (s), 6.21 (s, sh 6.29), 6.75 (s),
6.93 (s), 7.29 (m), 7.75 (w, broad), 7.87 (w, broad), 8.15 (w,
broad), 8.65 (w-m), 9.10 (m), 9.30 (m), 9.72 (s), 10.68 (w),
11.6 (m), 13.6 (m), 14.5 (s).

Reaction of 1-cyano 1-carboethoxy 2-methyl 2-cyclopropyl
ethene (I) with 1-butanethiol.—The reaction was run exactly
as described for thiophenol, using 2.75 g. (0.03 mole) of
1-butanethiol in place of thiophenol. Final distillation gave
2.2 g. (32%) of light yellow distillate, 1-cyano 1-carboethoxy
2-methyl 5-(butythio)pentene-2, b.p. 142-143° (0.1 mm.), n^2^D
1.4995.

Anal. Calcd. for C_{12}H_{17}NO_{2}: C, 62.40; H, 8.62
Found: C, 63.19; H, 8.50

Attempted reaction of 1-cyano 1-carboethoxy 2-methyl
2-cyclopropyl ethene (I) with phenol.—To a solution of 0.05 g.
of sodium in 20 ml. of absolute ethanol in a pressure bottle was
added 2.8 g. (0.03 mole) of phenol and 4.5 g. (0.025 mole) of I.
The bottle was then flushed with argon, sealed, and heated at 105°
for 24 hours. The alcohol was stripped. The residue was dissolved
in ether and the solution was washed successively with water,
5% sodium hydroxide solution, and a saturated solution of sodium
chloride, and was dried over calcium chloride. The ether was stripped and the residue was distilled, yielding only recovered I.

A. Reaction of dimethylamine with 1,1-dicyano 2-methyl 2-cyclopropyl ethene (II).—Dimethylamine, 1.0 g. (0.022 mole), was added directly to 2.0 g. (0.015 mole) of II with external cooling by an ice bath. After a period of 20 minutes the excess dimethylamine was removed under reduced pressure, and the residue was allowed to stand for 2 days in the refrigerator. Recrystallization from 50% ethanol gave 0.7 g. (26% based on an addition compound) of light yellow crystals which melted at 111.5-113°. No elemental analysis was obtained.

The infrared spectra in chloroform solution showed peaks at the following wave lengths in μ: 2.36 (w), 2.88 (w), 2.95 (m) 3.3 (s), 4.18 (m), 4.52 (m), 6.08 (s), 6.13 (s), 6.32 (m), 6.54 (m), 7.0 (w), 7.4 (w), 8.17 (s), 8.30 (s), 9.72 (m), 10.78 (m), 14.9 (m), 15.1 (m).

B. Reaction of diethylamine with 1,1-dicyano 2-methyl 2-cyclopropyl ethene (II).—To a solution 2.0 g. (0.015 mole) of II in 14 ml. of absolute ethanol was added at a fast dropwise pace 1.6 g. (0.022 mole) of diethylamine. A reaction occurred immediately. The reaction mixture was allowed to stand for one hour at room temperature. Distillation of the solvent under reduced pressure left a thick red liquid which crystallized after standing in the refrigerator several days. Recrystallization from 50% ethanol gave .5 g. (16% based on an addition compound) of light yellow crystals which melted at 115.0-115.5°.
Anal. Calcd. for $\text{C}_12\text{H}_{19}\text{N}_3$: C, 70.19; H, 9.35; N, 20.47

Found: C, 71.97; H, 6.06; N, 19.53

The infrared spectrum in chloroform solution showed peaks at the following wave lengths in $\mu$: 2.36 (w), 2.88 (w), 2.96 (m), 3.3 (s), 4.53 (m), 6.08 (s), 6.13 (s), 6.33 (m), 6.88 (vw), 7.01 (vw), 7.3 (w), 8.3 (m-s, broad), 8.88 (vw), (9.46 (w), 9.72 (m), 10.0 (vw), 10.8 (w), 11.54 (w), 12.0 (w), 15.08 (m).

C. Reaction of piperidine with 1,1-dicyano 2-methyl 2-cyclopropyl ethene (II).—The reaction was run exactly as described in B above, except that 1.9 g. (0.022 mole) of piperidine was used in place of the diethylamine. Recrystallization from 50% ethanol gave 1.3 g. (39% based on addition compound) of light yellow crystals which melted at 115-116°.
(a) The preparation of cyclopropane carboxyaldehyde using reported methods failed to give even fair yields.

(b) Knoevenagel condensations of methyl cyclopropyl ketone with active methylene compounds gave three 1,1-disubstituted 2-methyl 2-cyclopropyl ethenes. Diethyl malonate could not be condensed under the conditions used.

(c) Transesterification occurred when 1-cyano 1-carboethoxy 2-methyl 2-cyclopropyl ethene was refluxed with excess n-butanol in the presence of various secondary amines.

(d) Thiophenol and 1-butanethiol reacted in the presence of sodium ethoxide with 1-cyano 1-carboethoxy 2-methyl 2-cyclopropyl ethene (I) forming ring-opening addition (1,6-addition) products, 1-cyano 1-carboethoxy 2-methyl 5-(phenylthio)pentene-2 and 1-cyano 1-carboethoxy 2-methyl 5-(butylthio)pentene-2. This suggests that the cyclopropane ring can extend conjugation in some cases.

(e) The reaction of 1,1-dicyano 2-methyl 2-cyclopropyl ethene with secondary amines resulted in the apparent formation of amidines by addition of the amines to one of the nitrile groups.
BIBLIOGRAPHY


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