Bicyclo[1.1.0]butane Chemistry. II. Cycloaddition Reactions of 3-Methylbicyclo[1.1.0]butanecarbonitriles. The Formation of Bicyclo[2.1.1]hexanes

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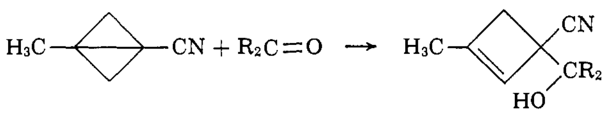
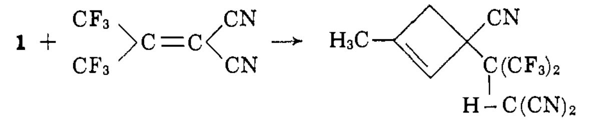
Abstract: 3-Methylbicyclo[1.1.0]butanecarbonitrile (**1**) reacts with butadiene, acrylonitrile, maleonitrile, fumaronitrile, ethylene, styrene, *p*-methoxystyrene, and 1-(N,N-dimethylamino)cyclopentene to form 1:1 adducts. In all cases, derivatives of 4-methylbicyclo[2.1.1]hexanecarbonitrile were formed along with other products. Evidence is presented which strongly suggests diradical intermediates in the cycloaddition reaction as well as in the formation of monocyclic products from ethylene. Thermolysis of **1** in the liquid phase at 150° produces several dimers, two of which have been partially identified as cycloadducts between **1** and its pyrolysis products. Brief attempts to observe thermally activated inversion of derivatives of bicyclo[1.1.0]butane failed because of competitive decomposition.

As part of a study[1] of the chemistry of 3-methylbicyclo[1.1.0]butanecarbonitrile (**1**), several cycloaddition reactions were attempted with unsaturated molecules. At first, compounds with highly electron-deficient multiple bonds were tried and found to react at room temperature or lower. In many cases (*i.e.*, with tetracyanoethylene), the products were dark, amorphous solids which resisted characterization. The reaction products of **1** with hexafluoroacetone, *sym*-dichlorotetrafluoroacetone, and 1,1-bis(trifluoromethyl)-2,2-dicyanoethylene were shown to be 1:1 adducts but not cycloadducts. Spectral evidence indicated that the adducts were the cyclobutenes **2a**, **2b**, and **3**.



1 **2a**, R = CF$_3$
b, R = CF$_2$Cl



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In contrast, ethylene and monosubstituted ethylenes failed to react with 3-methylbicyclo[1.1.0]butanecarbonitrile at room temperature. Under more vigorous conditions, namely heating to around 150°, many simple olefins reacted with **1**. Phenothiazine or hydroquinone was added to inhibit polymerization of the olefins. The products were quite different from those encountered with highly electron-deficient multiple bonds and several were shown to be cycloadducts having a bicyclo[2.1.1]hexane skeleton.

Butadiene. Butadiene was a particularly interesting reagent since it could undergo 1,4-cycloaddition with the internal (C$_1$–C$_3$) or external (C$_1$–C$_2$, C$_2$–C$_3$) bonds of 3-methylbicyclo[1.1.0]butanecarbonitrile to give bicyclooctenes or 1,2-cycloaddition to give vinyl bicyclohexanes. Monocyclic products were also possible.

Upon heating butadiene and **1** at 150° for 8 hr, a single, volatile 1:1 adduct was formed in 65% yield. The adduct readily took up hydrogen in the presence of platinum oxide to form a dihydro derivative (**4**) and could be hydrolyzed with hot 10% NaOH to a monocarboxylic acid **5**. The infrared spectrum of the adduct (neat) had strong absorption at 2240 cm^{-1} characteristic of nonconjugated nitriles and at 3100, 1640, 995, and 920 cm^{-1} suggestive of CH=CH$_2$. The latter assignment was confirmed by the nmr spectrum (CCl$_4$) of the adduct which displayed a complex multiplet at τ 3.7–4.9 (3.10 H, typical pattern of $>\mathrm{CH{-}C}H\mathrm{{=}C}H_2$), a multiplet at 7.0 (1.00 H, $>\mathrm{C}H\mathrm{{-}CH{=}CH_2}$), several multiplets from 7.5 to 8.6 (6.31 H), and a singlet at 8.75 (2.78 H, methyl group on quaternary carbon). The absence of nmr absorption above τ 8.75 probably excludes any structure with a methylene group in a cyclopropane ring, since cyanocyclopropane has greater than 90% of its absorption pattern between τ 8.75 and 9.15. Aside from the pendant vinyl group, the cycloadduct has no olefinic protons. The second double bond which would be required for a monocyclic adduct would have to be tetrasubstituted; however, as pointed out earlier, one CH$_3$, C≡N, and CH=CH$_2$ are not bound to a double bond.

Oxidation of the pure adduct with aqueous potassium permanganate gave two products, carboxylic acid **6** with one less carbon atom, C$_9$H$_{11}$NO$_2$ in 44% yield, and ketone **7** with two fewer carbon atoms, C$_8$H$_9$NO in 6% yield. The ketone absorbed in the infrared (KBr disk) at 2248 and 1772 cm^{-1} indicating a nonconjugated nitrile and a strained ketone. The latter may be compared with cyclobutanone which absorbs at 1775 cm^{-1} [2] and bicyclo[2.1.1]hexan-2-ones which absorb at 1764–1770 cm^{-1}.[3,4] The carbonyl group of **7** must be β to the nitrile since the adduct readily reacted with 10% sodium hydroxide at room temperature giving, after acidification, a new cyanocarboxylic acid **8** with infrared absorption at 2250 cm^{-1}.

Further hydrolysis of the cyanocarboxylic acid **8** with hot base gave a 67:33 mixture of *cis*- and *trans*-3-

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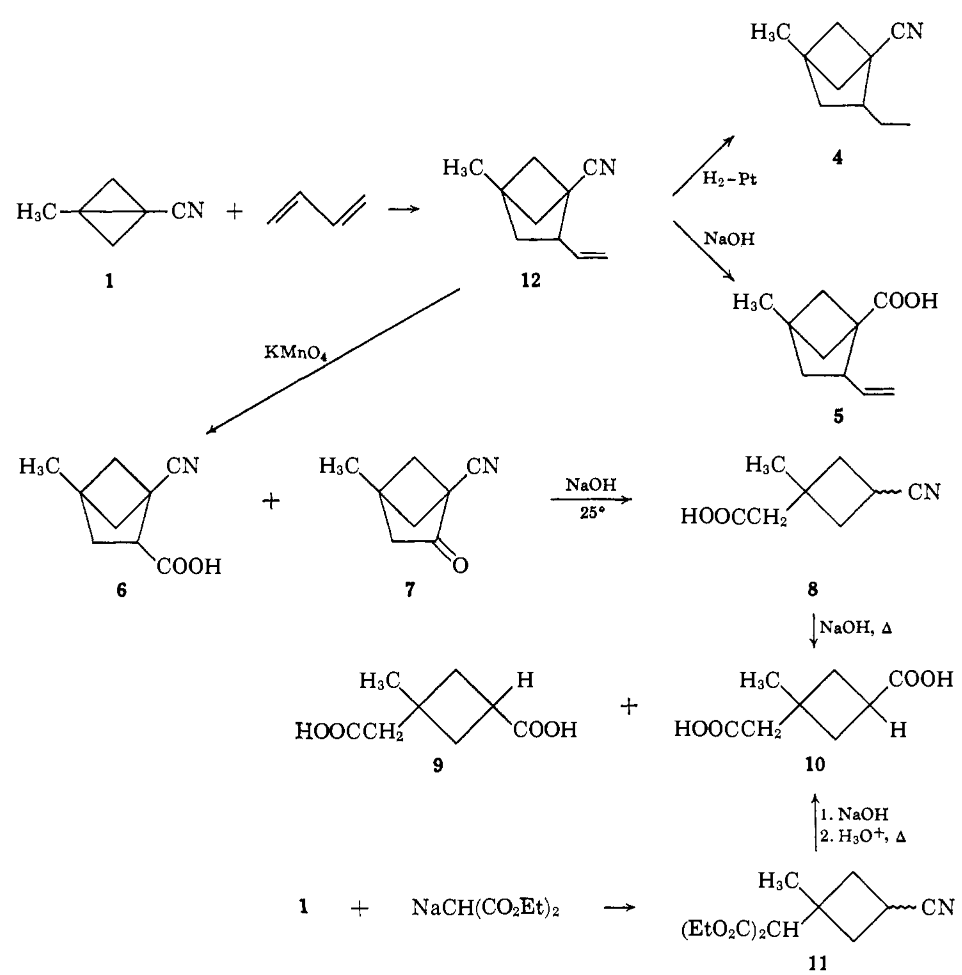
(1) E. P. Blanchard and A. Cairncross, *J. Am. Chem. Soc.*, **88**, 487 (1966).

(2) D. H. Whiffen and H. W. Thompson, *J. Chem. Soc.*, 1005 (1946).

(3) J. Meinwald and P. G. Gassman, *J. Am. Chem. Soc.*, **82**, 2857 (1960).

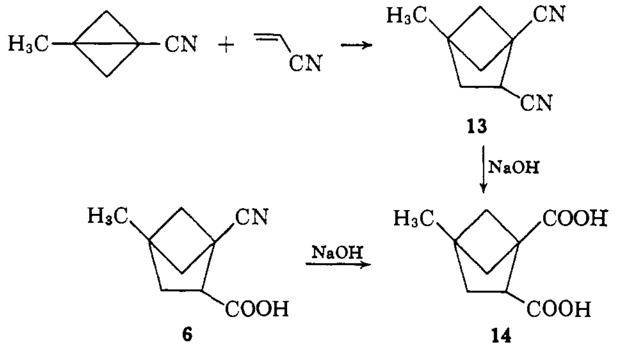
(4) G. Büchi and I. M. Goldman, *ibid.*, **79**, 4741 (1957).



methyl-3-(carboxymethyl)cyclobutanecarboxylic acids (**9** and **10**) in 67% yield. This mixture was identified by its nmr spectrum and established by independent synthesis. We previously reported that nucleophiles react with **1** to give 3-substituted 3-methylcyclobutanecarbonitriles.[1] The reaction of **1** with the sodium salt of diethyl malonate in ethanol gave the expected adduct **11** in 58% yield which was hydrolyzed with base, acidified, and decarboxylated in 80% yield to a 42:58 mixture of **9** and **10**. Thus, **7** is 1-cyano-4-methylbicyclo[2.1.1]hexan-2-one. The original cycloadduct must then be 2-vinyl-4-methylbicyclo[2.1.1]-hexanecarbonitrile **12**, the product expected from 1,2-cycloaddition of butadiene with the internal bond of **1**. The other oxidation product then is 1-cyano-4-methylbicyclo[2.1.1]hexane-2-carboxylic acid (**6**).

The acid **6** may be an intermediate in the permanganate oxidation of **12** to the ketone **7**. Support for this hypothesis is found in reports by Meinwald and Gassman[3] and Büchi and Goldman[4] who oxidized bicyclo[2.1.1]hexane-2-carboxylic acids with basic permanganate to bicyclo[2.1.1]hexan-2-ones perhaps *via* intermediate α-hydroxy acids.[5]

Acrylonitrile. After 8 hr at 160°, acrylonitrile and **1** likewise gave a 1:1 adduct in 46% yield. More than one isomeric adduct may have been produced since crude distillation led to crystalline material that melted over a *ca.* 20° range. Fractional distillation readily afforded pure material in 33% over-all yield. The product was hydrolyzed with hot NaOH to a dicarboxylic acid **14** which was identical with that from the basic hydrolysis of **6**. Thus, acrylonitrile and **1** give 4-methylbicyclo[2.1.1]hexane-1,2-dicarbonitrile (**13**) as the major volatile product.



Maleonitrile–Fumaronitrile. Maleonitrile and fumaronitrile reacted readily with 3-methylbicyclo[1.1.0]-butanecarbonitrile at 150° to give complex mixtures from which cycloadducts were recovered in 4% yield by chromatography over neutral alumina and oxidation of impurities by potassium permanganate. In both cases, the cycloadducts were shown to be mixtures of *cis*- and *trans*-4-methylbicyclo[2.1.1]hexane-1,2,3-tricarbonitriles by their infrared and nmr spectra which were very similar to those of **13**. The nmr of each isomer has a set of eight lines for the protons at C_2 and C_3 due to coupling between the two protons in a typical AB pattern plus long-range coupling to a single

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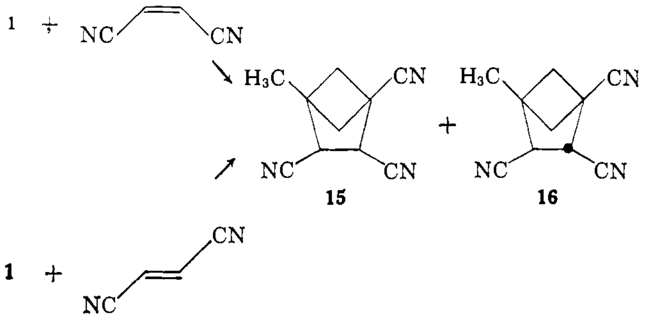
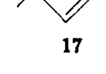
(5) For a more extensive discussion, see H. Kwart and G. D. Null, *J. Am. Chem. Soc.*, **82**, 2348 (1960).

proton.[6] The long-range coupling was determined by a decoupling experiment to be $J = 2.0$ cps for the *cis* isomer and $J = 2.1$ cps for the *trans*. The stereochemistry was assigned on the expectation that maleonitrile would give more of the *cis* isomer than fumaronitrile and that the *cis* product would have a larger $J_{2,3}$ than the *trans*.[7] The major cycloadduct (74%) from maleonitrile has $J_{2,3} = 8.9$ cps and must be the *cis* isomer **15** while the major cycloadduct (73%) from fumaronitrile has $J_{2,3} = 4.0$ cps and must be the *trans* isomer **16**. The stereochemical impurity of the products may be due to a reaction intermediate (see Discussion) or isomerization of the product during the reaction and subsequent work-up. Although the pure isomers were available in small quantities to test the latter alternative, it was not possible to devise satisfactory controls that would duplicate reaction conditions and work-up in the presence of a 96% yield of unknown tarry product. Small amounts of maleonitrile and fumaronitrile were recovered from the products in their original stereopurity. One and probably both of the product mixtures is the result of kinetic control. It may be significant that both reactions lead to 26–27% loss of stereopurity.



Ethylene. At 140–170° and 3000 atm, ethylene and 3-methylbicyclo[1.1.0]butanecarbonitrile reacted to give three products having the correct elemental analysis and mass spectra for 1:1 adducts, **17**, **18**, and **20**. These are the major products at lower temperatures and shorter reaction times. Under conditions at which **1** is 95% consumed, 170° for 16 hr, we were able to isolate 1% of **17**, 2% of **18**, and 11.5% of **20**. The structure of **17** follows tentatively from its infrared, nmr, and mass spectra with absorption characteristic of a methyl and an ethyl group on quaternary carbon and the grouping HC=CCN.



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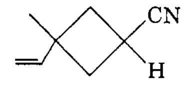
The structure of **18** rests on elemental analyses, infrared, nmr, and mass spectral data. Absorption characteristics of $CH=CH_2$, methyl on quaternary carbon, and >C(H)CN were found. The spectra are consistent with **18** and **19**. We prefer **18** on mechanistic grounds. A careful search of the reaction products by capillary gas chromatography and nmr spectroscopy did not reveal more than 0.1% (if any) of a stereoisomer of **18**, although an isomer with much lower thermal stability or volatility than **18** would have been missed.



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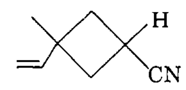

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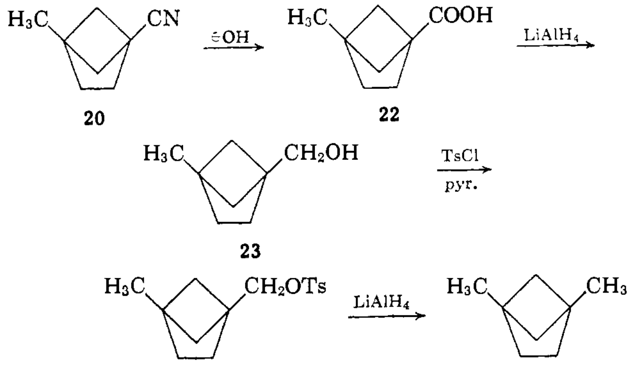
The third 1:1 adduct **20** resisted oxidation by aqueous permanganate, had no absorption in the infrared, ultraviolet, or nmr diagnostic for an olefin, and thus is a cycloadduct. The presence of a nonconjugated nitrile was revealed by infrared absorption at 2239 cm^{-1}. The nitrile was readily converted to an amide by basic hydrogen peroxide, to an aminomethyl group by lithium aluminum hydride, and to a carboxylic acid by hot aqueous sodium hydroxide. The nmr spectrum (CCl_4) of **20** showed complex multiplets at τ 7.8 to 8.6 (8 H, methylene groups) and a singlet at 8.73 (3 H, methyl on quaternary carbon). The spectra of **20** is inconsistent with a bicyclo[3.1.0]hexane structure since the methylene protons of **20** are at too low field for a cyclopropane ring and there is no absorption around 1.64 and 2.22 μ in the near-infrared.[8] Compound **20** was pyrolyzed cleanly at 400–600° over quartz chips in a flow system to 2-cyano-5-methyl-1,5-hexadiene (**21**). These data narrow the structure down to a bicyclo[2.1.1]- or bicyclo[2.2.0]hexane derivative. The bicyclo[2.2.0]hexane system seems unlikely since it should pyrolyze at a lower temperature. Bicyclo[2.2.0]hexane pyrolyzes around 200° while bicyclo[2.1.1]hexane is considerably more stable, pyrolyzing at a reasonable rate only above 300°.[9]

The structure of **20** was established as 4-methylbicyclo[2.1.1]hexanecarbonitrile by conversion of the nitrile to a methyl group by the standard procedure outlined below. The nmr spectrum (CCl_4) of **25** (see Figure 1) shows peaks at τ 8.51 (4.0 H, half-width 3.2 cps), 8.84 (6.0 H, half-width 1.2 cps, methyls on quaternary carbon), and 8.91 (4.2 H, half-width >4 cps). At 100 Mc, only the upfield peak appears to change. The change is more pronounced at 200 Mc. Clearly, **25** has at least four kinds of hydrogen, ruling



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(6) For leading references to observations of similar long-range couplings in rigid systems see: (a) A. Rassat, C. W. Jefford, J. M. Lehn, and B. Waegell, *Tetrahedron Letters*, No. 5, 233 (1964); (b) E. I. Snyder and B. Franzus, *J. Am. Chem. Soc.*, **86**, 1166 (1964); (c) P. Laszlo and P. R. Schleyer, *ibid.*, **86**, 1171 (1964); (d) A. D. Cross and P. W. Landis, *ibid.*, **86**, 4005 (1964); (e) A. D. Cross, *ibid.*, **86**, 4011 (1964); (f) J. Meinwald, Y. C. Meinwald, and T. N. Baker, *ibid.*, **86**, 4074 (1964).

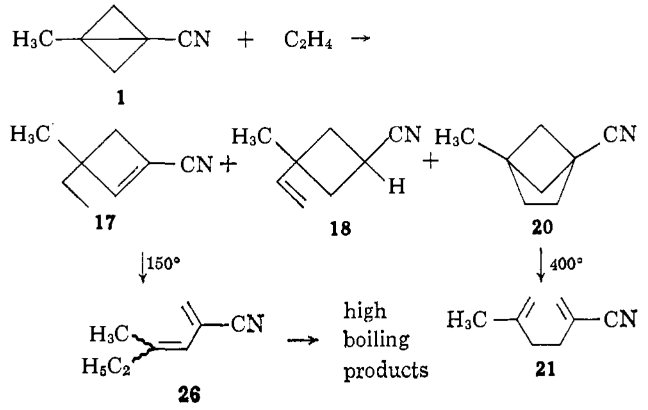
(7) (a) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959); (b) M. Karplus, *J. Am. Chem. Soc.*, **85**, 2870 (1963).

(8) Absorption at 1.64 and 2.22 μ is diagnostic of methylene in a cyclopropane ring: (a) W. H. Washburn and M. J. Mahoney, *ibid.*, **80**, 504 (1958); (b) P. G. Gassman, *Chem. Ind.* (London), 740 (1962).

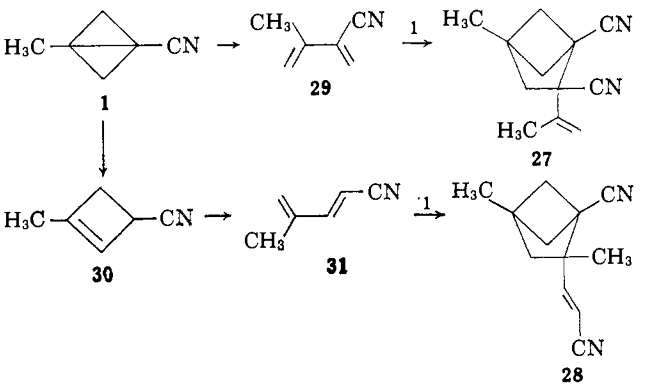
(9) S. Cremer and R. Srinivasan, *Tetrahedron Letters*, No. 21, 24 (1960); R. Srinivasan and A. A. Levi, *J. Am. Chem. Soc.*, **85**, 3363 (1963); R. Srinivasan and A. A. Levi, *ibid.*, **86**, 3756 (1964).

out 1,4-dimethylbicyclo[2.2.0]hexane but accommodating 1,4-dimethylbicyclo[2.1.1]hexane. The spectra appear to be poorly resolved because of the complicated spin–spin coupling of the protons in **25**.

At lower temperatures and short reaction times, the ethylene cycloaddition mainly gives **17** and **20**. Under more vigorous conditions, **17** nearly disappears from the product mixture, while the ratio of 18:20 remains nearly constant through the range of reaction conditions. Apparently the cyclobutene ring of **17** is opening, and the new butadiene **26** reacts with **1**, itself, or ethylene to give the high-boiling products. Compound **20** is stable under the reaction conditions.



Dimerization. The thermal decomposition of **1** competed with the cycloaddition reaction when less active olefins were used. When pure **1** was heated at 150° for 64 hr, only 25% was recovered unchanged. The remainder consisted of a dimeric fraction (38%) and a tarry residue. Two crystalline dimers, 63% and 29% of the mixture of **5**, were isolated in pure state and their structures were assigned tentatively from their spectra. The most abundant dimer was assigned structure **27** based on the identification of a $C(CH_3)=CH_2$ group, nonconjugated nitrile, and a methyl on quaternary carbon. The second most abundant dimer was tentatively assigned structure **28** based on identification of a nonconjugated nitrile, a conjugated nitrile, a *trans*-$HC=C(H)CN$ group, and two different methyl groups on quaternary carbon. Compound **27** probably arises from the pyrolysis of 3-methylbicyclo[1.1.0]butanecarbonitrile to 2-methyl-3-cyanobutadiene (**29**), a process shown to occur cleanly in the gas phase,[1] followed by cycloaddition of **29** with **1**. Compound **28** probably originates from isomerization of **1** to 1-methyl-3-cyanocyclobutene (**30**) pyrolysis of **30** to *trans*-1-cyano-3-methylbutadiene **31**, and cycloaddition of **31** with **1**. During slow distillations of **1** below 100° (reduced pressure) substantial quantities of **30** could be isolated.



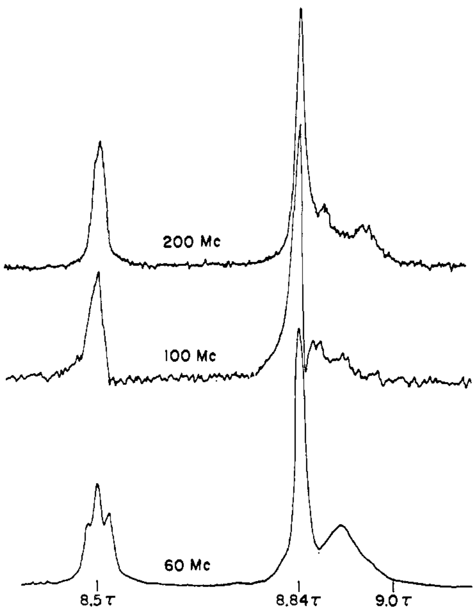
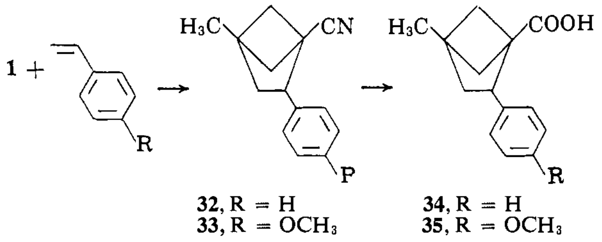
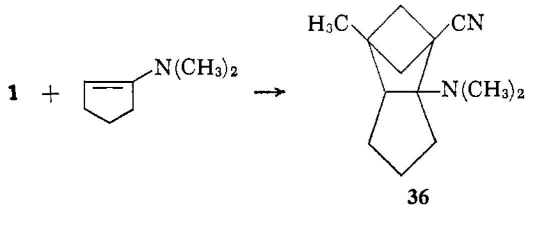


Figure 1. The nmr spectrum of 1,4-dimethylbicyclo[2.1.1]hexane in carbon tetrachloride.

Other Olefins. Good yields (48%) of the cycloadducts **32** and **33** were obtained when **1** was heated to 150° with styrene and *p*-methoxystyrene. In both cases, it was necessary to hydrolyze the cycloadducts to crystalline carboxylic acids **34** and **35** to obtain satisfactory analyses. Hydroquinone inhibitor and dimers of **1** apparently codistil with **32** and **33**. The infrared, ultraviolet, and nmr spectra of the cycloadducts are in accord with the structural assignments. The direction of addition was assumed to be analogous to that for **12**.



The most facile cycloaddition occurred between **1** and 1-(N,N-dimethylamino)cyclopentene. Reaction started at 110° and gave a 65% yield of product in 5 hr. Spectral data and elemental analyses suggest a saturated tricyclic product such as **36**.



In general, 3-methylbicyclo[1.1.0]butanecarbonitrile reacts best with simple olefins. This behavior is quite common to 1,2-cycloadditions.[10] In contrast to the

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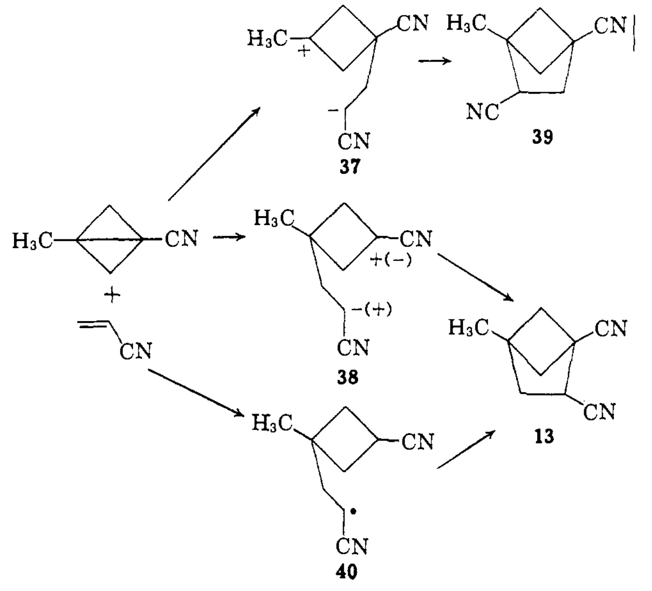
[10] J. D. Roberts and C. M. Sharts, *Org. Reactions*, **12**, 1 (1962).

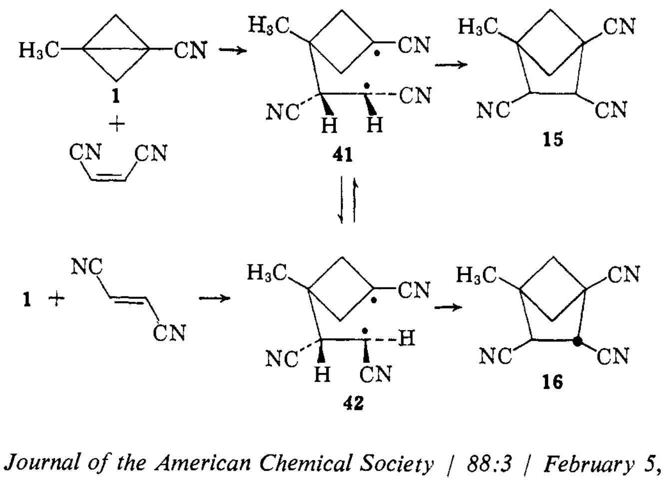
high reactivity of styrene and acrylonitrile, *trans*-stilbene and crotononitrile were much less reactive while maleonitrile and fumaronitrile primarily chose another reaction pathway. Success with an enamine prompted trial of dihydropyran, vinyl acetate, and isobutyl vinyl ether. Equimolar mixtures of these enol ethers and **1** at 150° for 8 hr gave starting materials and small amounts (*ca.* 5%) of high-boiling compounds.

Discussion

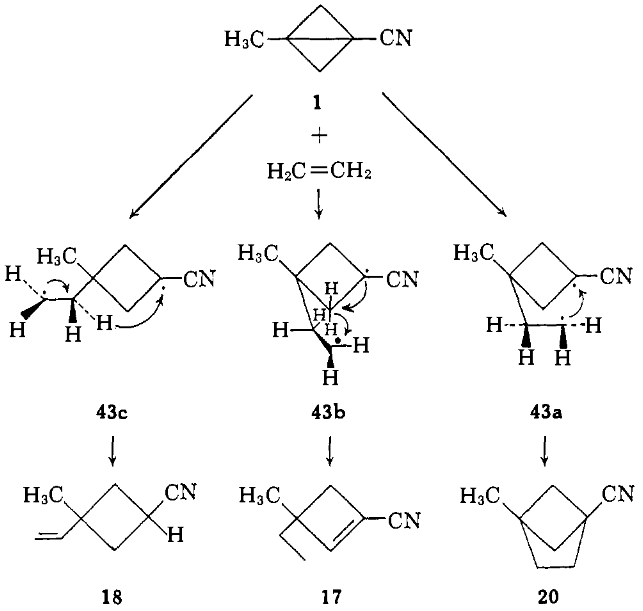
All cycloadditions of 3-methylbicyclo[1.1.0]butanecarbonitrile appear to have similar mechanisms. The existence of a dipolar ion intermediate can be eliminated on the basis of the structure of the main acrylonitrile cycloadduct **13**. Of the many dipolar structures, **37** and **38** are considered to be among the most reasonable, with **37** appearing to be as or more stable than **38**. To the extent that the transition state for formation of the intermediate resembles the intermediate, one would predict **37** and subsequently **39** to be major contributors to the product. This was not observed. The absence of head-to-tail product was proposed to rule out dipolar ion intermediates in the analogous dimerization of acrylonitrile[10] and speaks against them here. More reasonable mechanisms for the formation of **13** are either a concerted reaction or a reaction involving the delocalized biradical intermediate **40**.



The partial loss of stereochemistry during the cycloadditions of **1** with maleonitrile and fumaronitrile may well be the result of initial formation of biradical intermediates **41** and **42**. In both cases, the intermediates close to a cycloadduct faster than one undergoes a half-rotation to the other. Alternatively, the reactions may be stereospecific with simultaneous formation of both new bonds followed by partial epimerization of product during work-up.



Likewise, the products of **1** and ethylene may be formed from different rotomers of a common biradical intermediate **43**.



The adduct with butadiene likewise can be rationalized as the result of ring closure of the most stable biradical intermediate.

While all of the products may be rationalized on the basis of biradical intermediates, further experiments are necessary to establish this point. Precedent for this interpretation is found in the elegant work of Bartlett and co-workers[11] who studied the 1,2-cycloaddition of 1,1-dichloro-2,2-difluoroethylene with dienes. They clearly demonstrated for the first time biradical intermediates by observing the nonstereospecific reaction with the geometrical isomers of 2,4-hexadiene, confirming the earlier suggestions of Roberts and Sharts.[10]

The proposed 1,5-biradical in our cycloaddition reactions could arise in two ways, from either a rate-determining bimolecular reaction between **1** and olefin or an initial rate-determining activation of the bicyclobutane **1** to a 1,3-biradical or 1,3-dipolar ion **44** followed by addition to the olefin. There have been many observations of thermal activation of strained rings to biradical intermediates,[12] and in one case[13] the intermediate from tetracyanoethylene oxide underwent stereospecific cycloaddition with olefins. Dipolar ions, particularly 1,3-dipolar ions, are well known for their ability to undergo cycloaddition reactions.[14]

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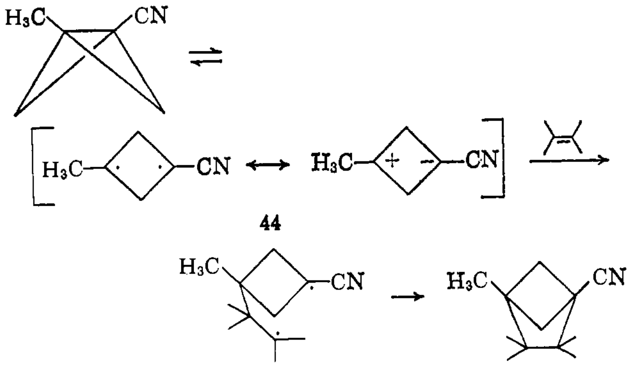
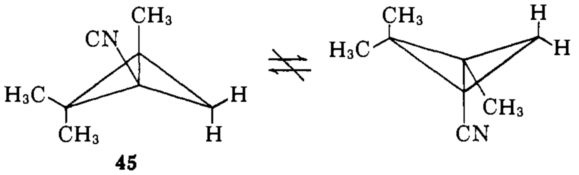
(11) (a) P. D. Bartlett, L. K. Montgomery, and B. Seidel, *J. Am. Chem. Soc.*, **86**, 616 (1964); (b) L. K. Montgomery, K. Schueller, and P. D. Bartlett, *ibid.*, **86**, 622 (1964); (c) P. D. Bartlett and L. K. Montgomery, *ibid.*, **86**, 628 (1964).

(12) (a) D. W. Setser and B. S. Rabinovitch, *ibid.*, **86**, 564 (1964); (b) C. Steel, R. Zand, P. Harwitz, and S. C. Cohen, *ibid.*, **86**, 679 (1964); (c) M. L. Halberstadt and J. P. Chesick, *ibid.*, **84**, 2688 (1962); (d) J. P. Chesick, *ibid.*, **84**, 3250 (1962); (e) J. P. Chesick, *ibid.*, **85**, 2720 (1963); (f) G. S. Hammond and C. D. DeBoer, *ibid.*, **86**, 899 (1964).

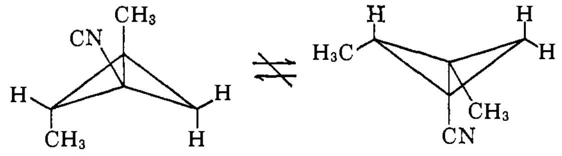
(13) W. J. Linn, O. W. Webster, and R. E. Benson, *ibid.*, **85**, 2032 (1963).



If the cycloaddition of **1** with olefins required prior activation of **1** to **44**, then it should be possible to observe the inversion of the bicyclobutane ring at 150°. The hypothetical intermediate **44** should either have a coplanar four-membered ring or be a rapidly interconverting pair of intermediates with puckered four-membered rings. In either case, formation of the intermediate would make the *exo* and *endo* substituents equivalent. The nmr spectrum of 2,2,3-trimethylbicyclo[1.1.0]butanecarbonitrile (**45**) which has three well-resolved singlets for the three methyl groups, did not change with heating to 175°. At 175–185°, extensive ring opening occurred. To detect a slower inversion, the thermal behavior of *exo*- and *endo*-2,3-dimethylbicyclo[1.1.0]butanecarbonitrile (**46**) was examined. Unfortunately, the *exo* and *endo* isomers could not be separated by gas chromatography. However, when prepared from *cis*-2-methyl-3-methylenecyclobutanecarbonitrile, the *exo*/*endo* ratio of **46** is 56:44 and from the *trans* isomer it is 19:81. The two different *exo–endo* mixtures were dissolved in nitrobenzene, sealed in nmr tubes, and heated at 160 ± 1°. The reaction was followed by nmr and is summarized in Table I. At no point did the absolute amount of either isomer increase. There was no evidence for *exo–endo* interconversion. Therefore, the cycloaddition reactions of **1** do not require prior activation of the bicyclobutane to **44**.



45



endo **46** *exo* **46**

Table I. Isomerization of *exo*- and *endo*-2,3-Dimethylbicyclo[1.1.0]butanecarbonitrile at 160 ± 1° in Nitrobenzene

Time, min	% *endo*	% *exo*	*endo*/*exo*	% decomp
		Run 1		
0	44	56	0.77	0
63	38	37	1.04	25
186	33	25	1.35	42
		Run 2		
0	81	19	4.32	0
30	77	15	5.00	8
127	71	12	5.93	17

Experimental Section[15]

Cycloaddition of 3-Methylbicyclo[1.1.0]butanecarbonitrile (1) and Butadiene. In a 500-ml, stainless steel shaker tube, **1** (46.5 g, 0.50 mole) and butadiene (135 g, 2.50 moles) were heated for 8 hr at 145–148°. The reaction mixture was fractionally distilled to give a forerun of 4-vinylcyclohexene and **1**, 48 g (65%) of 2-vinyl-4-methylbicyclo[2.1.1]hexanecarbonitrile (**12**), bp 83–90° (8 mm), and a polymeric pot residue. A heart cut had bp 83–85° (8 mm), $n^{25}\text{D}$ 1.4695. Gas chromatographic analysis using capillary columns revealed only one component. The adduct showed infrared absorption (neat) at 3100, 2240, 1640, 995, and 920 cm^{-1}, and nmr absorption (CCl_4) at τ 3.7–4.9 (3.10 H, typical vinyl pattern), 7.0 (1.00 H, multiplet), 7.5–8.6 (6.31 H, multiplets), and 8.75 (2.78 H, singlet). *Anal.* Calcd for $C_{10}H_{13}N$: C, 81.58; H, 8.90; N, 9.52. Found: C, 81.65, 81.84; H, 8.77, 8.86; N, 9.41, 9.23.

2-Vinyl-4-methylbicyclo[2.1.1]hexanecarboxylic Acid (5). A mixture of 2-vinyl-4-methylbicyclo[2.1.1]hexanecarbonitrile (**12**) (2.93 g, 20 mmoles), NaOH (4 g, 0.1 mole), and 20 ml of water was heated at reflux for 16 hr, then chilled in ice–water, acidified with 50% H_2SO_4, and extracted with ether. The ether extract was dried over $MgSO_4$, filtered, and concentrated to leave 3.0 g (91%) of **5**, mp 43–44°. The acid had infrared absorption ($CHCl_3$) at 1630, 990, and 920 cm^{-1}, and nmr absorption (CCl_4) at τ −2.34 (1.0 H, singlet), 3.8–5.2 (3.1 H, typical vinyl pattern), 7.00 (1.1 H, multiplet), 7.9–8.6 (6.0 H, multiplets), and 8.82 (2.8 H, singlet). An analytical sample was prepared by recrystallization from petroleum ether at −78° followed by sublimation. *Anal.* Calcd for $C_{10}H_{14}O_2$: C, 72.25; H, 8.49. Found: C, 72.45, 72.65; H, 8.61, 8.66.

2-Ethyl-4-methylbicyclo[2.1.1]hexanecarbonitrile (4). In a Parr apparatus, a solution of 2-vinyl-4-methylbicyclo[2.1.1]hexanecarbonitrile (**12**) (14.7 g, 0.100 mole) in 100 ml of ethyl acetate was reduced in the presence of platinum oxide (*ca.* 0.3 g) and 40 psi hydrogen. The solution was filtered and distilled to give 14.4 g (97%) of **4**, bp 82–84° (8 mm), $n^{25}\text{D}$ 1.4532. The product displayed infrared absorption (neat) at 2240 and 1380 cm^{-1}, and complex nmr absorption (CCl_4) at τ 7.5–9.2. *Anal.* Calcd for $C_{10}H_{15}N$: C, 80.48; H, 10.13; N, 9.39. Found: C, 80.50, 80.40; H, 9.92, 9.89; N, 9.03. The product was further characterized by converting the C≡N to $CONH_2$, mp 152–153°.

Oxidation of 2-Vinyl-4-methylbicyclo[2.1.1]hexanecarbonitrile (12) with Potassium Permanganate. To a mixture of **12** (5.9 g, 40 mmoles) and potassium permanganate (25.3 g, 160 mmoles) was added cold water (200 ml).[16] The mixture quickly heated to *ca.* 100°. By the time the mixture could be cooled to 0° with an ice bath, the purple color of MnO_4 had disappeared. The mixture was extracted with ethyl acetate. The ethyl acetate solution was dried over $MgSO_4$, filtered, and concentrated. The colorless, crystalline residue was recrystallized as long needles from *n*-hexane and sublimed at 100° (10 mm) to give 0.30 g (6%) of 1-cyano-4-methylbicyclo[2.1.1]hexan-2-one (**7**), mp 66.5–69.0°, which was characterized by infrared absorption (KBr) at 2248 and 1772 cm^{-1}, and nmr absorption (CCl_4) at τ 7.5–8.0 (5.81 H, multiplets) and 8.65 (3.00 H, singlet). *Anal.* Calcd. for C_8H_9NO: C, 71.09; H, 6.71; N, 10.36; mol wt, 135. Found: C, 70.90, 70.89; H, 6.51, 6.49; N, 10.45; parent ion in mass spectrum at 135.

The aqueous layer was filtered to remove the MnO_2. The filtrate was acidified with 2 *N* HCl and extracted with ethyl acetate. The ethyl acetate was dried over $MgSO_4$, filtered, and concentrated. The colorless, solid residue was recrystallized from water to give 2.9 g (44%) of 2-carboxy-4-methylbicyclo[2.1.1]hexanecarbonitrile (**6**), which after sublimation at 100° (0.1 mm) had mp 130–133.5° and infrared absorption (KBr) at 3650–2300 (broad),

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(14) R. Huisgen, *Angew. Chem. Intern. Ed. Engl.*, **2**, 565 (1963).

(15) Melting and boiling points are uncorrected.

(16) This mode of addition was not deliberate. It is potentially dangerous and probably should be avoided. Either the permanganate should have been added slowly to the aqueous mixture of **12** or *vice versa*.

2241, and 1702 cm^{-1}. *Anal.* Calcd for $C_9H_{11}NO_2$: C, 65.44; H, 6.71; N, 8.48; neut equiv, 165. Found: C, 65.48, 65.65; H, 6.76, 6.61; N, 8.26; neut equiv, 159.

Addition of Diethyl Malonate to 3-Methylbicyclo[1.1.0]butanecarbonitrile (1). Diethyl malonate (16.0 g, 0.10 mole) was converted to its sodium salt by reaction with sodium hydride, 53.4% dispersion in mineral oil (5.0 g, 0.11 mole of NaH) in ether (100 ml). To the sodium salt were added **1** (9.3 g, 0.10 mole) and absolute ethanol (50 ml), bringing the salt into solution. After refluxing overnight, the mixture was distilled to a boiling point of 75°, diluted with more ethanol (25 ml), refluxed for 1 hr, cooled, quenched in 200 ml of saturated aqueous $NaHCO_3$, and extracted with ether. The ether extract was dried over $MgSO_4$, filtered, and concentrated, and the residue was distilled to afford 14.6 g (58%) of 3-methyl-3-[bis(ethoxycarbonyl)methyl]cyclobutanecarbonitrile (**11**), bp 112–113° (0.1 mm), n^{26}D 1.4522. The product had infrared absorption (neat) at 2240 cm^{-1}. *Anal.* Calcd for $C_{13}H_{19}NO_4$: C, 61.64; H, 7.56; N, 5.53. Found: C, 61.17, 61.08; H, 7.70, 7.75; N, 6.53, 6.88.

cis **(9)- and** *trans***-3-Methyl-3-(carboxymethyl)cyclobutanecarboxylic Acid (10). Method A. From 1-Cyano-4-methylbicyclo-[2.1.1]hexan-2-one (7).** In a preliminary experiment, **7** was found to be insoluble in water but readily soluble in cool 10% NaOH. Acidification of the NaOH solution afforded a colorless solid with infrared absorption at 3500–2500, 2250, and 1715 cm^{-1}, probably 3-methyl-3-(carboxymethyl)cyclobutanecarbonitrile (**8**).

A mixture of **7** (0.100 g, 0.74 mmole) and 5 ml of 20% NaOH was heated at reflux for 4 hr, cooled, acidified with 2 *N* NaOH, and extracted with ethyl acetate. The ethyl acetate solution was dried over $MgSO_4$, filtered, and concentrated, and the residue was sublimed at 120–150° (0.1 mm) to give 0.085 g (67%) of a mixture of **9** and **10**, mp 76–86°. The product had nmr absorption (acetone-d_6) at τ −0.10 (2 H, singlet), 6.88 (1 H, multiplet), 7.53 (2 H, two peaks), 7.60–8.20 (4 H, multiplets), and 8.75 (3 H, two peaks). The two peaks at τ 7.49 and 8.79 probably belong to **10** (26%) and those at τ 7.57 and 8.71 to **9** (74%). *Anal.* Calcd for $C_8H_{12}O_4$: C, 55.80; H, 7.03. Found: C, 55.37; H, 6.86.

Method B. From 3-Methyl-3-[bis(ethoxycarbonyl)methyl]cyclobutanecarbonitrile (11). A mixture of **11** (2.0 g, 7.6 mmoles) and NaOH (4.0 g) in water (20 ml) was heated at reflux for 4 hr, treated with 20 ml of ethanol, refluxed for 1 hr, cooled, extracted with ether, acidified with 75 ml of 2 *N* HCl, and extracted with ethyl acetate. The ethyl acetate extract was dried over $MgSO_4$, filtered, and concentrated. The residue was heated for 3 hr at 150° (12 mm) and sublimed at 80–160° (0.05 mm) to give 1.08 g (80%) of a mixture of **9** and **10**, mp 87–96°.

The infrared and nmr spectra of this product had the same peaks as that from method A, and the nmr spectrum showed 55% **10** and 45% **9**. *Anal.* Calcd for $C_8H_{12}O_4$: C, 55.80; H, 7.03. Found: C, 55.87, 55.70; H, 7.01, 7.09.

Cycloaddition of 3-Methylbicyclo[1.1.0]butanecarbonitrile (1) and Acrylonitrile. In a 1-l., stainless steel, shaker tube, **1** (139.5 g, 1.50 moles), acrylonitrile (159.2 g, 3.00 moles), anhydrous reagent grade benzene (150 ml), and phenothiazine inhibitor (3.0 g) were heated at 160° for 8 hr. The product was distilled through a semimicro, spinning-band column to give 101.7 g (46%) partly crystalline product, bp 100° (0.20 mm) to 126° (0.55 mm) with superheating. The ultraviolet spectrum of the product showed weak absorption with λ_{max} 253 mμ (log ϵ 3.05) due to *ca.* 3% impurity of phenothiazine. Redistillation of the product afforded a center cut, bp 82.7° (0.09 mm) to 78.0° (0.08 mm) with superheating, mp 40°, 66.8 g (31%) of colorless 4-methylbicyclo[2.1.1]hexane-1,2-dicarbonitrile (**13**). The mass spectrum of the product displayed a parent ion at mass 146. Compound **13** showed nmr absorption (CCl_4) at τ 6.63–6.90 (1.00 H, multiplet), 7.2–8.7 (6.36 H, multiplets), and 8.74 (2.98 H, singlet), and infrared absorption at 2240 and 1380 cm^{-1}. *Anal.* Calcd for $C_9H_{10}N_2$: C, 73.94; H, 6.90; N, 19.17. Found: C, 74.04, 73.64, 74.27, 73.33, 73.88; H, 6.98, 7.00, 6.71; N, 19.07, 19.28, 19.24, 19.25.

4-Methylbicyclo[2.1.1]hexane-1,2-dicarboxylic Acid (14). Method A. From 2-Carboxy-4-methylbicyclo[2.1.1]hexanecarbonitrile (6). A solution of **6** (1.00 g, 6.1 mmoles) and NaOH (2.0 g) in water (10 ml) was heated at reflux for 5 hr, cooled, acidified with 2 *N* HCl, and extracted with ethyl acetate. The extract was dried with $MgSO_4$, filtered, and concentrated to give 0.91 g. (81%) of **14**. A sample was purified for analysis by recrystallization from ethyl acetate and sublimation at 150° (0.05 mm) as colorless crystals, mp 172.2–172.8°, and identified by infrared absorption (Nujol) 3400–2000 and 1708 cm^{-1}, and nmr absorption (acetone-d_6) at τ −0.58 (2.0 H, singlet), 6.79 (1.00 H, four peak "X" multiplet of ABX system), 7.75–8.50 (6.06 H, multiplets), and 8.80 (2.84 H, singlet). *Anal.* Calcd for $C_9H_{12}O_4$: C, 58.69; H, 6.57. Found: C, 58.58, 59.03; H, 6.75, 6.93.

Method B. From 4-Methylbicyclo[2.1.1]hexane-1,2-dicarbonitrile (13). A mixture of **13** (2.00 g, 13.7 mmoles) and NaOH (4.0 g) in water (20 ml) was heated at reflux overnight, cooled, extracted with ether, filtered, acidified with 2 *N* HCl, and extracted with ethyl acetate. The extract was dried over $MgSO_4$, filtered, and concentrated to give 2.06 g (82%) of **14**. An analytical sample, mp 170.5–171.0°, was prepared by recrystallization from tetrahydrofuran–methylcyclohexane and sublimation at 155° (0.05 mm) and found to be identical with that from method A by comparison of infrared and nmr spectra and by an undepressed mixture melting point. *Anal.* Calcd for $C_9H_{12}O_4$: C, 58.69; H, 6.57; mol wt, 184. Found: C, 58.79, 59.07; H, 6.62, 6.42; mol wt, 166; neut equiv, first 95, second 191.

Cycloaddition of 3-Methylbicyclo[1.1.0]butanecarbonitrile (1) and Maleonitrile. Maleonitrile[17] (7.8 g, 0.100 mole) and **1** (9.3 g, 0.100 mole) under nitrogen were heated at 150 ± 5° for 7 hr. From the crude tarry product, a small amount of distillate was recovered at 90° (0.3 mm) which was shown to be 99% maleonitrile by gas chromatography. Chromatography of the residue on moist Woelm alumina (activity grade 2-2/3) with CH_2Cl_2 as the eluent afforded 6.3 g of crude product. This was oxidized with potassium permanganate (19.2 g, slight excess) in 200 ml of water and extracted twice with 150 ml of methylene chloride. The CH_2Cl_2 solution was dried over $MgSO_4$, filtered, and concentrated to give 4-methylbicyclo[2.1.1]hexane-1,2,3-tricarbonitrile (**15**, **16**) (0.71 g, 4.2%) as a pale brown solid with infrared absorption (KBr disk) at 2245 and 1389 cm^{-1}, and nmr absorption (CD_3CN) at τ 6.00 to 6.75 (1.92 H, multiplets), 7.6–8.5 (4.28 H, multiplets), and 8.64 (3.00 H, singlet). Nmr showed the product to be 74% **15** and 26% **16**. Recrystallization from hot chloroform gave colorless crystals of the *cis* isomer (**15**), mp 141–142°, with nmr absorption (CD_3CN) at τ 6.03, 6.18, 6.52, and 6.67 (2.00 H doublets with J = 2.0 cps, over-all AB pattern with J = 8.9 cps), 7.6–8.5 (4.12 H, complex multiplets), and 8.65 (3.06 H, singlet). *Anal.* Calcd for $C_{10}H_9N_3$: C, 70.16; H, 5.30; N, 24.55. Found: C, 70.59, 69.34, 69.24; H, 5.22, 4.90, 6.33; N, 24.72.

Cycloaddition of 3-Methylbicyclo[1.1.0]butanecarbonitrile (1) and Fumaronitrile. Fumaronitrile (7.8 g, 0.100 mole) and **1** (9.3 g, 0.100 mole) under nitrogen were heated at 150 ± 5° for 7 hr. From the crude, tarry product was recovered by sublimation at 90° (0.3 mm) a colorless solid (0.7 g, 9%) shown to be 99% fumaronitrile by gas chromatography. Chromatography of the residue on moist Woelm neutral alumina (activity grade 2-2/3) with CH_2Cl_2 as the eluent afforded 5.7 g of viscous oil with an nmr spectrum typical of a complex mixture. This mixture was oxidized with potassium permanganate (22.3 g, slight excess) in 200 ml of water and extracted twice with 125 ml of methylene chloride. The methylene chloride solution was dried with $MgSO_4$, filtered, and concentrated to give 4-methylbicyclo[2.1.1]hexane-1,2,3-tricarbonitrile (**15**, **16**) (0.6 g, 4%) as a pale brown solid. The product had nmr absorption (CD_3CN) at τ 6.00–6.75 (2.00 H, multiplets), 7.60–8.35 (4.0 H, multiplets), and 8.65 (3.38 H, singlet). Nmr indicated the product to be 27% **15** and 73% **16**. Slow evaporation of a chloroform solution allowed the isolation of large, colorless plates of the *trans* isomer (**16**), mp 104–111°, with nmr absorption (CD_3CN) at τ 6.18, 6.25, 6.65, and 6.71 (doublets with J = 2.1 cps, over-all AB pattern with J = 4.0 cps), 7.6–8.2 (multiplets), and 8.65 (singlet). *Anal.* Calcd for $C_{10}H_9N_3$: C, 70.16; H, 5.30. Found: C, 70.09; H, 5.65.

Cycloaddition of 3-Methylbicyclo[1.1.0]butanecarbonitrile (1) and Ethylene. In a 200-ml, stainless steel, shaker tube, **1** (50.0 g, 0.537 mole) and phenothiazine inhibitor (0.5 g) were heated for 16 hr at 170° at 3000 atm of ethylene. The products from four such runs were combined and distilled through a column packed with Podbielniak wire helices for the more volatile products and with a wire spiral column for the more viscous final cut.

A. 3-Methyl-3-ethylcyclobutenecarbonitrile (17). Fractions of bp 53° (19 mm) to 70° (17 mm), 14.4 g, were analyzed by capillary gas chromatography and shown to contain 9 g (4.5%) of unreacted **1**, 3-methylenecyclobutanecarbonitrile (a small impurity in **1** that is not found in the product when pure **1** is used), and a product, bp ~65° (10 mm), in about 1% yield which was best isolated by preparative gas chromatography (1,2,3-tris(cyanoethoxy)propane

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[17] G. E. Ficken, R. P. Linstead, E. Stephen, and M. Whalley, *J. Chem. Soc.*, 3879 (1958).

column). This product was found in much higher yields in runs at lower temperatures (140–150°) and lower conversions suggesting that it reacts further at elevated temperatures. Its identification as **17** follows from its mass spectrum with a parent mass at 121; its infrared spectrum featuring absorption at 3090, 2225, 1380, and 1370 cm^{-1}, and its nmr spectrum (CCl_4) with absorption at τ 3.03 (1 H, singlet), 7.43 (2 H, AB pattern), 8.37 (2 H, quartet), 8.72 (3 H, singlet), and 8.99 (3 H, triplet).

B. **3-Vinyl-3-methylcyclobutanecarbonitrile (18).** Fractions of bp 73–76° (17 mm), 7.3 g, consisted largely of one component (2% over-all yield) which was purified by preparative gas chromatography ("CHDMS," cyclohexane dimethanol succinate column) and distillation affording 1.54 g of **18**, bp 63° (7 mm), $n^{25}\text{D}$ 1.4534. This product had a parent mass of 121 in its mass spectrum, nmr absorption [$(CD_3)_2SO$] at τ 3.89–4.35 (1.00 H, four lines), 4.92–5.27 (1.96 H, multiplets), 6.68–7.24 (1.10 H, further split quintet), 7.50–8.20 (4.25, H, further split quintet), and 8.87 (3.01 H, singlet), and infrared absorption at 3110, 2250, 1640, 1000, and 918 cm^{-1}. *Anal.* Calcd. for $C_8H_{11}N$: C, 79.29; H, 9.15; N, 11.56. Found: C, 79.54, 79.66; H, 9.17, 9.23; N, 11.43, 11.38.

C. **4-Methylbicyclo[2.1.1]hexanecarbonitrile (20).** Fractions of bp 70–73.5° (17 mm), 39.1 g, mainly contained a saturated adduct which was freed of impurities (identified in earlier and later fractions) by permanganate oxidation. To a rapidly stirred mixture of distillate (39.1 g) and water (400 ml) at room temperature was added, in small portions, potassium permanganate (20 g) until the purple color persisted for 1 hr. The mixture was extracted with petroleum ether (bp 30–60°), and the petroleum ether was dried over $MgSO_4$, filtered, and evaporated. The residue was distilled affording 29.8 g (11.5%) of **20**, bp 72.5° (10 mm), $n^{24}\text{D}$ 1.4510, mass spectrum parent mass 121, nmr spectrum τ 7.8–8.6 (8 H, multiplet), 8.73 (3 H, singlet), infrared spectrum 2239 cm^{-1}. *Anal.* Calcd for $C_8H_{11}N$: C, 79.29; H, 9.15; N, 11.56. Found: C, 79.54, 79.84; H, 9.11, 9.53; N, 11.48, 11.36. The nitrile (CN) was characterized by conversion to $CONH_2$, mp 210°; CH_2NH_2HCl, mp 222–225°; $CH_2NHCOCH_3$, mp 71–72°; and NH_2HCl, mp 255–256°, with satisfactory analyses and spectra for 1-substituted derivatives of 4-methylbicyclo[2.1.1]hexane.

D. **High-Boiling Products.** Fractions with bp 76° (17 mm) to 50° (0.1 mm), 8.7 g, contained several minor products which were not further investigated. The largest fraction, bp 110–120° (0.16 mm), 109.8 g, was found to be a mixture of several components by gas chromatography. The mixture had a parent mass at 242 and perhaps at 214 in its mass spectrum, infrared absorption (neat) at 2240, 1660, and 1380 cm^{-1}, and nmr absorption (CCl_4) consistent with ethyl groups (A_2B_3 pattern). *Anal.* Found: C, 78.82, 78.42, 78.12; H, 8.60, 8.57, 8.28; N, 14.21, 14.38.

4-Methylbicyclo[2.1.1]hexanecarboxylic Acid (22). A mixture of 4-methylbicyclo[2.1.1]hexanecarbonitrile (**20**) (10.0 g, 83 mmoles), NaOH (10.0 g), and water (10 ml) was heated at reflux overnight, diluted with alcohol (2 ml) (used to wash down the condenser), refluxed for 1 additional hr, and cooled, giving a precipitate which was redissolved by adding 50 ml of water. The solution was extracted with ether, freed of ether with a nitrogen stream, cooled by an ice bath, and acidified with concentrated HCl, giving a precipitate. The product was recovered by filtration and extraction of the filtrate with dichloromethane, air-dried, and sublimed at 100° (0.2 mm), giving 11.4 g (99%) of colorless **22**, mp 61–63°. The acid displayed nmr absorption ($CDCl_3$) at τ −2.34 (1.08 H, singlet), 7.80–8.65 (8.00 H, multiplets), and 8.78 (3.00 H, singlet). *Anal.* Calcd for $C_8H_{12}O_2$: C, 68.54; H, 8.63. Found: C, 68.16; H, 8.58.

Pyrolysis of 4-Methylbicyclo[2.1.1]hexanecarbonitrile (20). Compound **20** was injected into a helium stream and swept through a 12 × $^3/_8$ in. pyrolysis chamber packed with 8–20 mesh quartz chips into a gas chromatograph. The sample was in the pyrolysis chamber approximately 15–20 sec. At 350°, a trace of pyrolysis product was observed, at 400° 15% of a single product, at 450° 50% conversion to products of which one accounted for 99%, and at 500° 85% conversion to products of which one accounted for 97%. The pyrolysate at 500° was collected. It was identified as 2-cyano-5-methyl-1,5-hexadiene (**21**) by strong infrared absorption (neat) at 3080, 2225, 1650, 1620, 1380, 935, and 890 cm^{-1}, and nmr absorption (CCl_4) at τ 4.30 (2.0 H, doublet), 5.2–5.4 (2.0 H, poorly resolved multiplet), 7.71 (4.0 H, singlet), and 8.28 (3 H, singlet).

1-Hydroxymethyl-4-methylbicyclo[2.1.1]hexane (23). To a stirred mixture of lithium aluminum hydride (6.1 g, 0.161 mole) in 210 ml of anhydrous ether under nitrogen was added a solution of 4-methylbicyclo[2.1.1]hexanecarboxylic acid (**20**) (11.3 g, 0.081 mole) in 120 ml of ether at a rate that maintained a gentle reflux. After the addition was complete, the mixture was heated at reflux for 1 hr., cooled with an ice bath, cautiously treated with 3.2 ml of water, then with 5.0 ml of 6 *N* NaOH, and finally with 18.3 ml of water, giving a granular precipitate. The granular solid was removed by filtration and rinsed with ether. The combined ether solution was dried over $MgSO_4$, filtered, and concentrated, and the residue was distilled to give 8.9 g (87%) of **23**, bp 80° (19 mm), $n^{24}\text{D}$ 1.4614. The product had nmr absorption (CCl_4) at τ 6.47 (2 H, singlet), 6.53 (1 H, singlet), 8.48 (3.91 H, broad singlet), and 8.81, 8.65–9.05 (6.87 H, singlet and multiplet), and infrared absorption (neat) at 3500, 1375, and 1030 cm^{-1}. *Anal.* Calcd for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 75.91; H, 11.36.

1-Hydroxymethyl-4-methylbicyclo[2.1.1]hexane *p*-Toluenesulfonate (24). To an ice bath cooled, stirred solution of 1-hydroxymethyl-4-methylbicyclo[2.1.1]hexane (**23**) (8.9 g, 71 mmoles) in 27 ml of anhydrous pyridine was added *p*-toluenesulfonyl chloride (15.0 g, 79 mmoles). A precipitate soon formed. After standing overnight at 0°, the mixture was poured into 250 ml of ice–water and extracted with ether. The ether solution was rinsed with cold 2 *N* HCl, cold water, cold 2% $NaHCO_3$, and cold water, dried over $MgSO_4$, filtered, and concentrated to give 19.3 g (97%) of colorless **24**, mp 61–64°. An analytical sample was prepared by filtering a CCl_4 solution and precipitating the product with petroleum ether, mp 66–67°. The product had nmr absorption (CCl_4) at τ 2.24, 2.38, 2.57, 2.81 (4.00 H, AB pattern), 6.02 (1.98 H, singlet), 7.58 (3.16 H, singlet), 8.50 (4.13 H, broad singlet), and 8.84, 8.65–9.05 (7.33 H, singlet and multiplet). *Anal.* Calcd for $C_{15}H_{20}SO_3$: C, 64.25; H, 7.19; S, 11.44. Found: C, 64.08, 63.92; H, 7.16, 7.26; S, 11.6.

1,4-Dimethylbicyclo[2.1.1]hexane (25). To a stirred mixture of lithium aluminum hydride (6.1 g, 0.161 mole) in 100 ml of anhydrous ether under nitrogen was added a solution (19.3 g, 0.0699 mole) of 1-hydroxymethyl-4-methylbicyclo[2.1.1]hexane *p*-toluenesulfonate (**24**) in 120 ml of anhydrous ether at a rate that maintained a gentle reflux. The reaction was fairly exothermic. After the addition was complete, the mixture was heated at reflux for 2 hr, cooled with an ice bath, and cautiously treated with 3 ml of water, giving a granular precipitate. The granular solid was removed by filtration and rinsed with ether. The combined ether solution was dried with $MgSO_4$, filtered, and distilled to give 4.4 g (57%) of **25** as a colorless liquid, bp 91°, $n^{24}\text{D}$ 1.4159–1.4179. The product exhibited nmr absorption (CCl_4) at τ 8.51 (4.0 H, multiplet with half-width of 3.2 cps), 8.84 (6.0 H, singlet with half-width of 1.2 cps), and 8.91 (4.2 H, multiplet with half-width >4 cps), and infrared absorption (neat) at 1380 cm^{-1}. *Anal.* Calcd for C_8H_{14}: C, 87.19; H, 12.81; mol wt, 110. Found: C, 87.26, 86.80, 86.63; H, 13.45, 12.77, 12.77; mass spectrum, parent 110.

Thermal Dimerization of 3-Methylbicyclo[1.1.0]butanecarbonitrile (1). Compound **1** (27.9 g, 0.3 mole) under nitrogen was heated at 150 ± 5° for 64 hr. Distillation of the product afforded 6.8 g (24%) of unreacted **1**, bp 41° (8 mm) and 10.6 g (38%) of colorless oil, bp 76–96° (0.1 mm). The high-boiling fraction consisted of at least five significant components. The ones amounting to 63 and 29% of the mixture were purified by fractional distillation and preparative gas chromatography (Asphaltine on Chromosorb). The most abundant dimer was recrystallized from *n*-hexane as a colorless, moist solid, mp 47–50°, and tentatively identified as 2-isopropenyl-4-methylbicyclo[2.1.1]hexane-1,2-dicarbonitrile (**27**) on the basis of infrared absorption (CCl_4) at 3120, 2240, 1660, 1387, and 907 cm^{-1}, and nmr absorption (CCl_4) at τ 4.81 (2.08 H, multiplet), 7.98 (9.08 H, multiplet), and 8.76 (3.00 H, singlet). *Anal.* Calcd for $C_{12}H_{14}N_2$: C, 77.38; H, 7.58; N, 15.04. Found: C, 77.57; H, 7.50; N, 14.91, 14.55.

Refluxing this dimer with 20% alcoholic KOH afforded a diamide, recrystallized from ethyl acetate, mp 194.5–195.0°. *Anal.* Calcd for $C_{12}H_{18}N_2O_2$: C, 64.84; H, 8.16; N, 12.60. Found: C, 64.96; H, 8.45; N, 12.48. Refluxing this dimer with 20% aqueous NaOH afforded an amide-acid, mp 165–174°. *Anal.* Calcd for $C_{12}H_{17}O_3N$: C, 64.55; H, 7.68; N, 6.27; mol wt, 223. Found: C, 64.50; H, 7.54; N, 5.80; neut equiv, 210.

The second most abundant dimer was recrystallized from carbon tetrachloride as colorless crystals, mp 70.0–70.7°, and tentatively identified as 2,4-dimethyl-2-(*trans*-2-cyanovinyl)bicyclo[2.1.1]hexanecarbonitrile (**28**) on the basis of infrared absorption at 2235, 2225, 1630, 1380, and 980 cm^{-1}, and nmr absorption (CCl_4) at τ 3.05 (0.90 H, doublet, J = 17 cps), 4.43 (0.93 H, doublet, J = 17 cps), 8.0–8.5 (6.00 H, multiplets), 8.60 (3.06 H, singlet), and 8.78 (3.03 H, singlet). *Anal.* Calcd for $C_{12}H_{14}N_2$: C, 77.38; H, 7.58; N, 15.04. Found: C, 77.50, 77.71, H, 7.75, 7.85; N, 15.15, 15.37.

Cycloaddition of 3-Methylbicyclo[1.1.0]butanecarbonitrile (1) and Styrene. Compound **1** (9.3 g, 0.10 mole), freshly distilled styrene (10.4 g, 0.10 mole), and a trace of hydroquinone were heated at 150 ± 5° for 4 hr. Fractionation of the product through a semimicro, spinning-band column gave 9.3 g (48%) of 2-phenyl-4-methylbicyclo[2.1.1]hexanecarbonitrile (**32**) as a colorless oil, bp 106–109° (1 mm), n^{25}D 1.5350–1.5360. Infrared and ultraviolet spectra of the product showed a small amount of hydroquinone. The product displayed infrared absorption (neat) at 2230, 1380, 745, and 695 cm^{-1}, and nmr absorption (CCl_4) at τ 2.58 (4.9 H, narrow multiplet), 6.38 (0.9 H, multiplet), 7.5–8.5 (6.6 H, multiplets), and 8.81 (3.0 H, singlet). *Anal.*[18] Calcd for $C_{14}H_{15}N$: C, 85.23; H, 7.66; N, 7.10. Found: C, 84.33; H, 7.52; N, 7.38.

2-Phenyl-4-methylbicyclo[2.1.1]hexanecarboxylic Acid (34). A mixture of 2-phenyl-4-methylbicyclo[2.1.1]hexanecarbonitrile (**32**) (3.8 g, 19.3 mmoles), 25 ml of alcohol, and 25 ml of 6 *N* NaOH was heated at reflux for 72 hr. The alcohol was evaporated. The aqueous phase was extracted with ether, acidified, and extracted with ether. The second ether extract was dried over $MgSO_4$, filtered, and concentrated. The residue was recrystallized from hexane, giving 2.45 g (57%) of **34** as colorless needles, mp 103–105°. The acid displayed nmr absorption ($CDCl_3$) at τ −2.01 (1.02 H, singlet), 2.71 (5.03 H, singlet), 6.29 (0.90 H, multiplet), 7.6–8.5 (5.88 H, multiplets), and 8.81 (3.00 H, singlet). *Anal.* Calcd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 77.73, 77.64; H, 7.36, 7.34.

Cycloaddition of 3-Methylbicyclo[1.1.0]butanecarbonitrile (1) and *p*-Methoxystyrene. Compound **1** (9.3 g, 0.10 mole), *p*-methoxystyrene (13.4 g, 0.10 mole), and a trace of hydroquinone were heated at 150 ± 5° for 20 hr. Distillation of the product gave 10.8 g (48%) of 2-(*p*-methoxyphenyl)-4-methylbicyclo[2.1.1]hexanecarbonitrile (**33**) as a viscous oil, bp (superheating) 125–135° (1 mm), n^{25}D 1.5387. The product had infrared absorption (neat) at 2230, 1380, and 832 cm^{-1}, and nmr absorption (CCl_4) at τ 2.83 (4.0 H, AB pattern), 6.23 (4.0 H, large singlet over small multiplet), 7.5–8.5 (7.0 H, multiplet), and 8.79 (3.0 H, singlet). *Anal.*[18] Calcd for $C_{15}H_{17}NO$: C, 79.26; H, 7.54; N, 6.16. Found: C, 79.54, 79.57; H, 7.61, 7.62; N, 7.73, 7.88.

2-(*p*-Methoxyphenyl)-4-methylbicyclo[2.1.1]hexanecarboxylic Acid (35). A mixture of 2-(*p*-methoxyphenyl)-4-methylbicyclo[2.1.1]hexanecarbonitrile (**33**) (4.54 g, 20 mmoles), 25 ml of alcohol, and 25 ml of 6 *N* NaOH was heated at reflux for 9 days. Work-up as described before for **34** gave 2.84 g (60%) of **35** as pale yellow microcrystals, mp 106–108°. The product had nmr absorption ($CDCl_3$) at τ −2.00 (0.99 H, singlet), 2.94 (4.00 H, AB pattern), 6.25 (4.02 H, large singlet over a multiplet), 7.6–8.5 (6.00 H, multiplets), and 8.79 (3.10 H, singlet). *Anal.* Calcd for $C_{15}H_{18}O_3$: C, 73.15; H, 7.37. Found: C, 73.13, 73.20; H, 7.37, 7.40.

Cycloaddition of 3-Methylbicyclo[1.1.0]butanecarbonitrile (1) and 1-(N,N-Dimethylamino)cyclopentene. **1** (9.3 g, 0.10 mole) and 1-(N,N-dimethylamino)cyclopentene (11.1 g, 0.10 mole) were heated starting at 110° to finally 170° over 5 hr. Distillation gave 13.3 g of product, bp 85–120° (2 mm). This crude product was added to a solution of picric acid (20 g) in alcohol (400 ml). The precipitate was filtered, recrystallized from alcohol, filtered, rinsed with alcohol and ether, and air dried, giving material, mp 199–200°. To the picrate and water (100 ml) were added ether (100 ml) and 6 *N* NaOH (20 ml). The aqueous layer was extracted with ether, and the combined ether phases were extracted with 0.6 *N* NaOH, dried over $MgSO_4$, filtered, and concentrated. The residue was distilled twice through a short-path still (1 mm) to give 7.21 g of colorless oil, n^{25}D 1.4968, bp 285° (micro). The product was characterized as 2-(N,N-dimethylamino)-2,3-trimethylene-4-methylbicyclo[2.1.1]hexanecarbonitrile (**36**) by infrared absorption (neat) at 2230 and 1380 cm^{-1}, and nmr absorption (CCl_4) at τ 7.57 (5.9 H, singlet), 7.1–8.5 (12.0 H, multiplets), and 8.87 (3.0 H, singlet). *Anal.* Calcd for $C_{13}H_{20}N_2$: C, 76.42; H, 9.87; N, 13.71. Found: C, 76.22, 76.14; H, 9.93, 9.96; N, 13.32, 13.29.

Thermolysis of *exo*- and *endo*-2,3-Dimethylbicyclo[1.1.0]butanecarbonitrile (46). Mixtures of *exo*- and *endo*-2,3-dimethylbicyclo[1.1.0]butanecarbonitrile (**46**) were dissolved in nitrobenzene, sealed in nmr tubes under vacuum, analyzed for initial concentrations by nmr, heated at 160 ± 1° in a constant temperature oil bath, quenched in ice periodically, and analyzed directly by nmr. The concentrations of both isomers diminished throughout. The broad nmr absorption of the products did not include much in the vinyl region.

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(18) The presence of thermal dimers of 3-methylbicyclo[1.1.0]butanecarbonitrile, which are not separated by this distillation, cause high nitrogen and low carbon values.

Methylcyclopropenone and Related Compounds[1]

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Abstract: Reaction of lithium trichloromethide at −100° with various acetylenes produces substituted cyclopropenones after hydrolysis. Using this procedure, methyl-, propyl-, dimethyl-, and (previously known) dipropylcyclopropenone have been prepared in moderate yields; attempts to produce cyclopropenone from the reaction with acetylene failed. A facile base-catalyzed exchange of the ring hydrogen in propylcyclopropenone has been observed; the acidity of this proton can be related in part to hybridization effects, as reflected in the nmr chemical shift and C^{13} coupling constant. The basicities of methyl- and dimethylcyclopropenones were measured, H_0 at half-protonation being −5.0 and −1.5, respectively. Methylcyclopropenone is slowly cleaved by sodium hydroxide to a mixture of methacrylic and crotonic acids. Pyrolysis of methylcyclopropenone at 200° affords propyne and carbon monoxide, but heating at 100° produces a dimeric lactone.

In the years since the synthesis of diphenylcyclopropenone[2] a number of other substituted cyclopropenones have been prepared.[3] However, to date neither the parent compound nor a monosubstituted derivative has been reported, although such compounds would be of considerable interest. In our laboratory a number of attempts to synthesize such compounds

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