enylamine[16] and ethyl chloroformate; benzyl-N-vinylcarbamate;[17] and **benzyl-N-allylcarbamate**, b.p. 104–106° (0.3 mm.) (*Anal.* Calcd. for $C_{11}H_{13}NO_2$: C, 69.04; H, 6.85; N, 7.32. Found: C, 69.33; H, 7.07; N, 7.69.).

General Hydroboration Procedure. In a 1-l., three-necked flask equipped with a pressure-equalizing, 250-ml. dropping funnel, a thermometer, a magnetic stirring assembly, and a nitrogen purge system was placed a freshly prepared solution of diborane gas (2–3 g. in 400 ml. of dry tetrahydrofuran). This solution was cooled in an ice–acetone bath to 0°. To this mixture a solution of the substituted olefin (0.1 mole) in tetrahydrofuran (150 ml.) was added dropwise over 30–45 min. with continuous stirring. The temperature was maintained at less than 5° during the entire procedure and after the addition, the mixture was stirred for an additional 30 min. Borane/olefin mole ratios of 1/8 gave essentially the same yield of the described boronic acids. Methanol (75 ml.) then was introduced dropwise at such a rate as to keep the temperature less than 10° and to prevent excessive foaming.

In the cases of the ethyl N-vinyl- and N-allylcarbamates this mixture was evaporated directly and distilled under water aspirator pressure to give the dimethyl esters XII and XVIII of the corresponding boronic acids. For N-vinyl- and N-cyclohexenylurea, direct evaporation afforded the dimethyl esters V and IX of the boronic acids as crystalline solids recrystallizable from methanol–ether mixtures. Treatment of any of these boronic esters with water and slow evaporation gave the corresponding boronic acids.

(16) M. G. Ettlinger and J. E, Hodgkins, *J. Am. Chem. Soc.*, 77, 1831 (1955).

(17) M. L. Wolfrom, G. H. McFadden, and A. Chaney, *J. Org. Chem.*, **26**, 2597 (1961).

The dimethyl esters of the boronic acids derived from benzyl N-vinyl- and N-allylcarbamates were not isolated as such but were converted by water directly to the corresponding boronic acids XV and XIX. These were obtained by evaporation of the aqueous solution and recrystallized from water. No pure dimethyl ester or boronic acid could be obtained from the hydroboration mixture prepared from N-allylurea. The iminodiethanol derivative of XVII was obtained by adding iminodiethanol (0.1 mole) in dimethylformamide (60 ml.) to the residue remaining after evaporation of the reaction mixture.

The hydroboration of ethyl N-but-3-enylcarbamate was conducted as described above. Direct distillation of the reaction mixture afforded a mixture of the **dimethyl esters of 4-(carbethoxyamido)-butylboronic acid** and **1-methyl-3-(carbethoxyamido)propylboronic acid**, b.p. 102–104° (0.15 mm.). *Anal.* Calcd. for $C_9H_2BNO_4$: C, 49.79; H, 9.28; N, 6.45; B, 4.98. Found: C, 50.01; H, 9.48; N, 6.85; B, 4.68.

Iminodiethanol Derivatives. The boronic acid (or dimethyl ester) (1–2 g.) was dissolved in dimethylformamide (DMF) (7 ml.); and added to a solution of iminodiethanol (1–2 g.) in the same solvent (5 ml.). Usually the derivative crystallized at once. If not, addition of tetrahydrofuran or tetrahydrofuran–ether mixture effected precipitation. These compounds were recrystallized usually from DMF–THF mixtures.

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Bicyclo[1.1.0]butane Chemistry. I. The Synthesis and Reactions of 3-Methylbicyclo[1.1.0]butanecarbonitriles

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Received September 1, 1965

Abstract: The hydrohalogenation–dehydrohalogenation of 3-methylenecyclobutanecarbonitriles provides a facile, high-yield synthesis of 3-methylbicyclo[1.1.0]butanecarbonitriles. The latter react with a broad spectrum of reagents including acids, electron-deficient multiple bonds, nucleophiles, free radicals, and halogens to give cyclobutanes and cyclobutenes. The bicyclobutane ring system is thermally labile leading to a synthesis of substituted butadienes. Catalytic hydrogenation of bicyclobutanes consumes 2 moles of hydrogen leading to open-chain structures. The bicyclobutane ring system is stable to certain transformations of the nitrile group. These reactions are discussed in terms of the scope, conditions, and mechanistic implications.

The report by Wiberg and Ciula[1] of the first authentic[2] bicyclo[1.1.0]butane derivative, ethyl bicyclo[1.1.0]butane-1-carboxylate, has stimulated interest in the synthesis and chemistry of these highly strained structures. Several techniques have been developed for generating bicyclo[1.1.0]butanes including 1,3-dehydrohalogenation,[1,3] intramolecular insertion or addition of a carbene,[4–13] intermolecular addition of carbenes to cyclopropenes or acetylenes,[14–16]

(1) K. B. Wiberg and R. P. Ciula, *J. Am. Chem. Soc.*, **81**, 5261 (1959).

(2) Several reports of bicyclo[1.1.0]butane derivatives have appeared: W. H. Perkin and J. L. Simonsen, *Proc. Chem. Soc.*, **21**, 256 (1905); O. Döbner and G. Schmidt, *Ber.*, **40**, 148 (1907); N. Zelinsky and J. Gutt, *ibid.*, **40**, 4744 (1907); M. Guthzeit and E. Hartman, *J. Prakt. Chem.*, **81**, 329 (1910); R. M. Beesley and J. F. Thorpe, *Proc. Chem. Soc.*, **29**, 346 (1913); *J. Chem. Soc.*, **117**, 591 (1920). In each case, the structures have been revised: W. H. Perkin and J. L. Simonsen, *Trans. Chem. Soc.*, **91**, 816 (1907); R. Willstätter and J. Bruce, *Ber.*, **40**, 3979 (1907); C. K. Ingold, M. M. Parekh, and C. W. Shoppee, *J. Chem. Soc.*, 142 (1936); H. O. Larsen and R. B. Woodward, *Chem. Ind.* (London), 193 (1959).

(3) J. Meinwald, C. Swithenbank, and A. Lewis, *J. Am. Chem. Soc.*, **85**, 1880 (1963).

(4) W. R. Moore, H. R. Ward, and R. F. Merritt, *ibid.*, **83**, 2019 (1961).

(5) D. M. Lemal, F. Menger, and G. W. Clark, *ibid.*, **85**, 2529 (1963).

(6) S. Masamune, *ibid.*, **86**, 735 (1964).

(7) A. Small, *ibid.*, **86**, 2091 (1964).

(8) H. M. Frey and I. D. R. Stevens, *Proc. Chem. Soc.*, 144 (1964).

(9) W. E. Doering and M. Pomerantz, *Tetrahedron Letters*, 961 (1964).

(10) D. M. Lemal and K. S. Shim, *ibid.*, 3231 (1964).

(11) G. L. Closs and R. B. Larrabee, *ibid.*, 287 (1965).

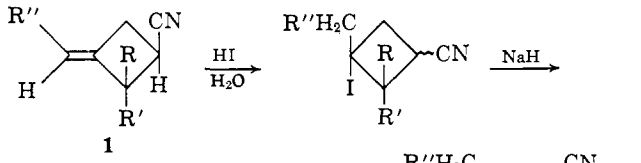
(12) J. A. Smith, H. Shechter, J. Bayless, and L. Friedman, *J. Am. Chem. Soc.*, **87**, 659 (1965).

(13) S. Masamune and N. T. Castellucci, *Proc. Chem. Soc.*, 298 (1964).

(14) W. Mahler, *J. Am. Chem. Soc.*, **84**, 4600 (1962).

the photolysis of dienes,[17,18] 1,3-dehalogenation,[16,19] and cationic rearrangements.[12,20] We now report the synthesis and properties of several bicyclo[1.1.0]butanecarbonitriles.

Synthesis. Hydroiodination–dehydroiodination of several 3-alkylidenecyclobutanecarbonitriles (**1**)[21] leads to 3-alkylbicyclo[1.1.0]butanecarbonitriles (**2**) in good yield. The hydrohalogenations are carried out in aqueous medium, and the dehydrohalogenations are effected with sodium hydride in ether solution. The



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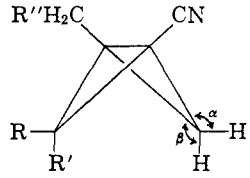


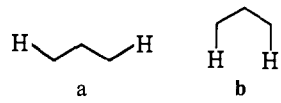
2

1a, R = R′ = R″ = H
b, R = R′ = CH_3; R″ = H
c, R = R′ = H; R″ = CH_3
d, R = R″ = H; R′ = CH_3
e, R′ = R″ = H; R = CH_3

2a, R = R′ = R″ = H (67.3%)
b, R = R′ = CH_3; R″ = H (48.5%)
c, R = R′ = H; R″ = CH_3 (51%)
d, R = R″ = H; R′ = CH_3 (17.5%)[22] + **e**, R′ = R″ = H; R = CH_3 (8.5%)[22]
2d, 20.8%[22] + **2e**, 32.8%[22]

structures **2a–e** are supported by the elemental analyses and molecular weights and confirmed by their spectral properties. In the infrared spectra of **2a–e**, bands are observed at 3070 (cyclopropyl CH_2), 2215 cm^{-1} (nitrile) with no absorption bands in the range 1680–1620 cm^{-1} associated with C=C stretching vibrations.[23] The near-infrared spectrum of **2a** displayed bands at 1.655 and 2.225 μ associated with a methylene group in a cyclopropane ring.[24]

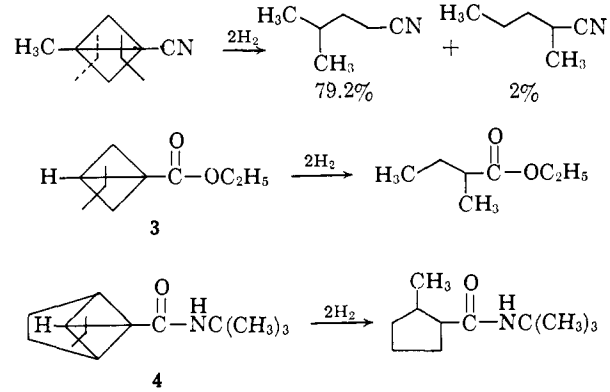
The nmr spectrum (neat) of **2a** consists of a multiplet at τ 7.98 (2 H, half-width 2 cps), a singlet at τ 8.23 (3 H, half-width 1 cps, methyl on quaternary carbon), and a multiplet at τ 8.72 (2 H, half-width 2 cps). The two C^{13} satellites of the low-field peak were doublets with J_{HH} = 6.3 cps and $J_{C^{13}H}$ = 156 cps, of the middle peak were sharp singlets with $J_{C^{13}H}$ = 129 cps, and of the upfield peak were *ca.* singlets (half-width 2 cps) with $J_{C^{13}H}$ = 174 cps. Since long-range coupling is usually stronger for protons in configuration a than the configuration b, the low-field peak is probably due to the *exo* protons.[25] The



unusual occurrence of two protons with different C^{13}–H coupling constants bonded to the same carbon probably indicates that angles α and β are different due to mutual repulsion of the *endo* protons.

At first, the low chemical shifts for the cyclopropyl and methyl protons of **2a** were disturbing. However, reduction of the nitrile group to aminomethyl (see below) shifts these protons upfield to more normal positions, τ 8.79–9.50 and 8.54. This shift must be due to a change in the electronic character of the bridgehead substituent and not to a difference in the geometry of **2a** and **5**. A change in geometry between **2a** and **5** would alter the H–H and C^{13}–H coupling constants of the cyclopropyl and methyl protons; however, these couplings are essentially the same. The *exo* protons at τ 8.79 are not coupled to the *endo* at 9.50 by more than 1 cps but are coupled to each other by 6.5 cps. The *exo* and *endo* protons have $J_{C^{13}H}$ = 150 and 169 cps.

Hydrogenation. The catalytic reductions of bicyclo[1.1.0]butanes reported are characterized by the consumption of 2 moles of hydrogen. From these cases, two principle patterns evolve, namely (a) destruction of the central and one other cyclopropyl bond,[1,3,4,10] and (b) destruction of two cyclopropyl bonds but not the central bond.[6,9] A third pattern has been reported[16,26] which involves 1,3 reduction. The catalytic reduction of **2a** is no exception in taking up 2 moles of hydrogen (corrected for nitrile reduction) (Figure 1) and follows pattern a above. It is interesting that the major product (79.2%) of **8** is 4-methylvaleronitrile resulting from reduction of the two bonds joining the carbon atom bearing the nitrile group. Wiberg[1] and Meinwald[3] observed reductions of **3** and **4**, respectively, at the carbon not bearing the electron-withdrawing group.

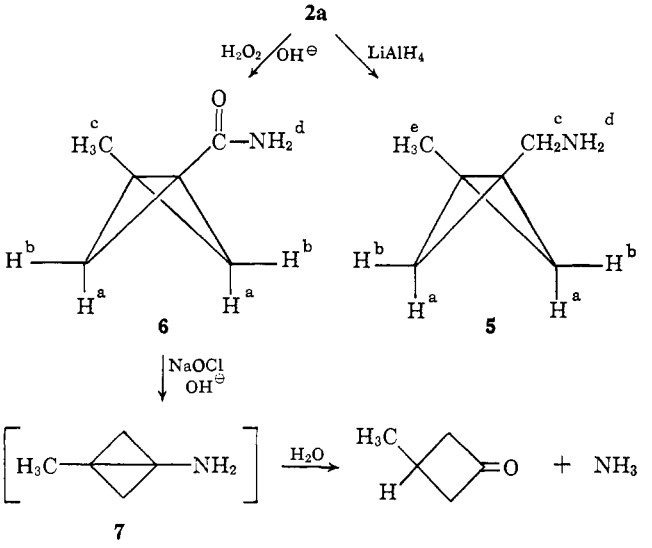


This difference may be due to steric factors, all three reductions occurring at the less hindered site. A low yield (2%) of 2-methylvaleronitrile shows that, indeed, bonds to both bridgehead carbons are reducible. The

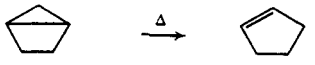
(15) I. A. D'yakonov, M. I. Komendantov, *Zh. Obshch. Khim.*, **31**, 3881 (1961); I. A. D'yakonov, M. I. Komendantov, and V. V. Razin, *ibid.*, **33**, 2420 (1963).
(16) W. E. Doering and J. F. Coburn, Jr., *Tetrahedron Letters*, 991 (1965).
(17) W. G. Dauben and F. G. Willey, *ibid.*, 893 (1962).
(18) R. Srinivasan, *J. Am. Chem. Soc.*, **85**, 4045 (1963).
(19) K. B. Wiberg and G. M. Lampman, *Tetrahedron Letters*, 2173 (1963).
(20) J. Bayless, L. Friedman, J. A. Smith, F. B. Cook, and H. Shechter, *J. Am. Chem. Soc.*, **87**, 661 (1965).
(21) H. N. Cripps, J. K. Williams, and W. H. Sharkey, *ibid.*, **81**, 2723 (1959).
(22) Substantial quantities of 2,3-dimethyl-2-cyclobutene-1-carbonitrile are formed in these reactions.
(23) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, p 34.
(24) W. H. Washburn and M. J. Mahoney, *J. Am. Chem. Soc.*, **80**, 504 (1958); P. G. Gassman, *Chem. Ind.* (London), 740 (1962).
(25) For leading references see (a) A. Rassat, C. W. Jefford, J. M. Lehn, and B. Waegell, *Tetrahedron Letters*, No. **5**, 233 (1964); (b) S. Masamune, *J. Am. Chem. Soc.*, **86**, 735 (1964); (c) E. J. Snyder and B. Franzus, *ibid.*, **86**, 1166 (1964); (d) P. Laszlo and P. R. Schleyer, *ibid.*, **86**, 1171 (1964); (e) A. D. Cross and P. W. Landis, *ibid.*, **86**, 4005 (1964); (f) A. D. Cross, *ibid.*, **86**, 4011 (1964); (g) J. Meinwald, Y. C. Meinwald, and J. N. Baker, *ibid.*, **86**, 4074 (1964).
(26) R. B. Turner, P. Goebel, W. E. Doering, and J. F. Coburn, Jr., *Tetrahedron Letters*, 997 (1965).

products were identified by comparison of their mass spectral patterns with those of synthetic specimens.

Transformations of the Nitrile Group. Chemical reduction of **2a** with lithium aluminum hydride affords 3-methyl-1-aminomethylbicyclo[1.1.0]butane (**5**) in high yield. The bicyclic system survives this reaction as evidenced by the nmr spectrum which shows resonances at τ 9.50 (H^a), 8.79 (H^b), 6.95 (H^c), 9.06 (H^d), and 8.54 (H^e) with areas in the ratio of 2:2:2:2:3, respectively. Another transformation of the nitrile group in **2a** in which the bicyclic ring system is unaffected is the preparation of 3-methylbicyclo[1.1.0]butanecarboxamide (**6**) by treatment of **2a** with alkaline hydrogen peroxide. Structure **6** is supported by the nmr spectrum which has resonances at τ 9.13 (H^a), 8.11 (H^b), 8.76 (H^c), and 5.87 (H^d), with areas in the ratios of 2:2:3:2, respectively. Efforts to convert **6** to the aminobicyclo[1.1.0]-butane **7** led to 3-methylcyclobutanone, possibly *via* the hydrolysis of **7** in a reaction analogous to the hydrolysis of an enamine.



Pyrolysis. Based on the closest homolog, bicyclo-[2.1.0]pentane (**8**),[27] bicyclo[1.1.0]butanes would be expected to thermally isomerize to cyclobutenes and perhaps subsequently to butadiene derivatives. Thus, Criegee and Rimmelin[27] have shown that **8** cleanly isomerizes to cyclopentene at 330°. It was surprising



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to find that pyrolysis of **2a** in the gas phase at 200–340° gave a *single* product, the spectral properties of which were not consistent with a cyclobutene but were consistent with 2-cyano-3-methyl-1,3-butadiene (**9**).[28] Support for structure **9** was found in its Diels–Alder adduct with tetracyanoethylene,[29] 1-methyl-2,4,4,5,5-pentacyanocyclohexene (**10**), which shows no vinyl protons in its nmr spectrum. Confirmation of structure **9** was obtained by catalytic reduction to a mixture of 2,3-dimethylbutyronitrile[30] and trimethylacryloni-

(27) R. Criegee and A. Rimmelin, *Chem. Ber.*, 90, 414 (1957).
(28) A. M. Clifford and J. R. Long, U. S. Patent 2,328,890 (1943).
(29) T. L. Cairns, R. A. Carboni, D. D. Coffman, V. A. Engelhardt, R. E. Heckert, E. L. Little, E. G. McGeer, B. C. McKusick, W. J. Middleton, R. M. Scribner, C. W. Theobald, and H. E. Winberg, *J. Am. Chem. Soc.*, 80, 2775 (1958).
(30) M. L. Sassiver and J. English, *ibid.*, 82, 4891 (1960).

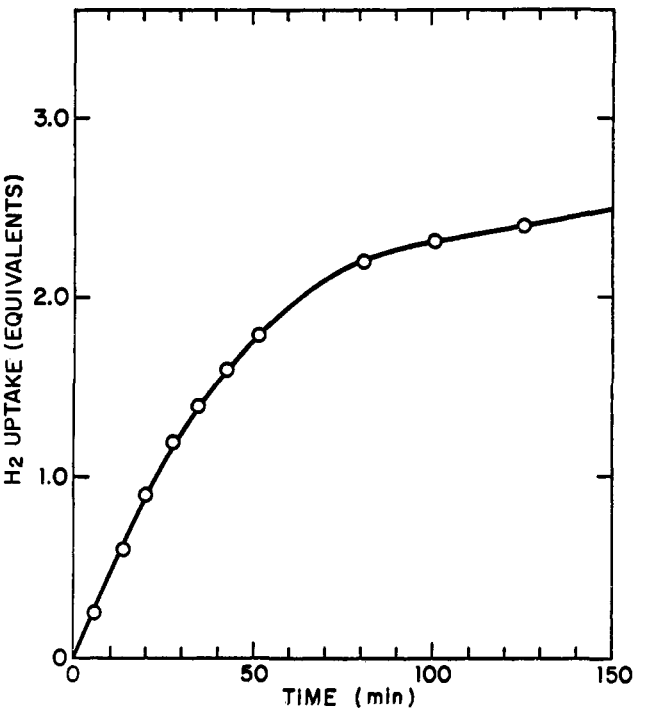
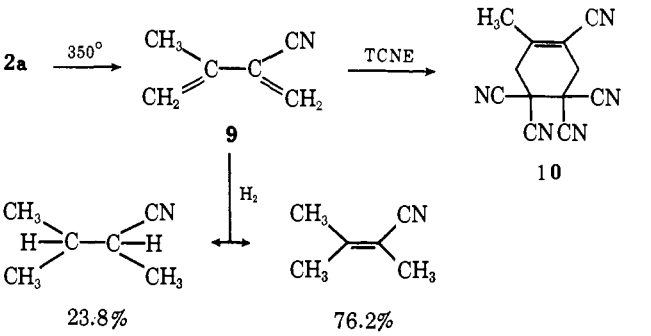


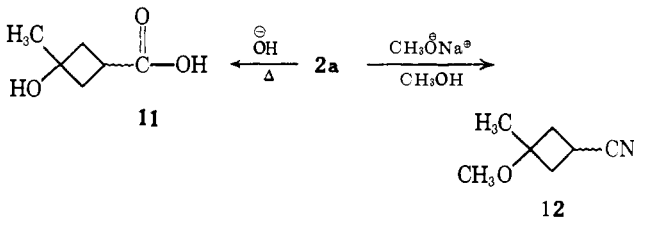
Figure 1. Catalytic reduction of 3-methylbicyclo[1.1.0]butanecarbonitrile.

trile.[31] This is the only ring-opening reaction of bicyclo[1.1.0]butanes in which the central bond is preserved that we have observed. Several other examples of this type of rearrangement have now been reported.[5,7–9,14,16,18]



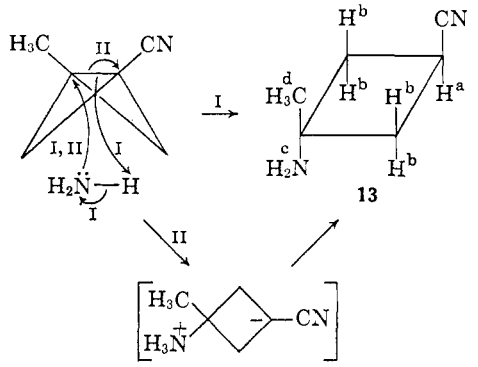
Reaction with Nucleophiles. In attempting to prepare 3-methylbicyclo[1.1.0]butanecarboxylic acid, the nitrile **2a** was saponified by boiling with aqueous sodium hydroxide and subsequently neutralized. We obtained 3-hydroxy-3-methylcyclobutanecarboxylic acid (**11**), which was synthesized for comparison. It seemed reasonable that the addition of water to the central bond could have occurred during the alkaline saponification or in the subsequent acidification (*cf.* Reactions with Acid). The former seems likely in view of the methoxide-catalyzed addition of methanol to **2a** to give a mixture of *cis*- and *trans*-3-methoxy-3-methylcyclobutanecarbonitriles (**12**). 3-Methylbicyclo[1.1.0]butanecarbonitrile (**2a**) also adds nucleophiles in spontaneous reactions not requiring added catalyst. Typical of these reactions is that of **2a** with ammonia which occurs at 100° and affords a *single* isomer of 3-amino-3-

(31) Fr. de Lact, *Bull. Soc. Chim. Belges.*, 38, 163 (1929); *Chem. Abstr.*, 23, 4443 (1929).



11 12

methylcyclobutanecarbonitrile (**13**). Structural support for **13** is found in its nmr spectrum which shows resonances at τ 6.94 (H^a, multiplet), 7.80 (H^b, doublet), 8.38 (H^c), and 8.59 (H^d), with areas of 1:4:2:3, respectively. It is tempting to look upon this stereospecific addition as occurring *via* either a concerted four-center type reaction (I) or a two-step addition–proton transfer process (II), either of which could lead to **13** with nitrile and amino groups *trans*. Proof of this stereochemistry cannot be offered. Additional examples of additions of this type, all of which appear to be stereospecific, include those of **2a** with dimethylamine, aniline, and dipropylamine.



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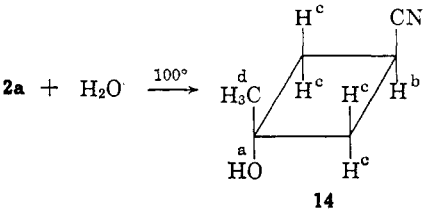
Another example of the uncatalyzed reactions of nucleophiles is the addition of water to **2a**. This reaction affords a single isomer of 3-hydroxy-3-methylcyclobutanecarbonitrile (**14**). It is interesting that this is the same product that results by reacting **2a** with dilute acid (see below). Mechanistic implications similar to those discussed for the addition of amines would predict stereospecific addition of water which could lead to the product with nitrile and hydroxyl groups *trans*.

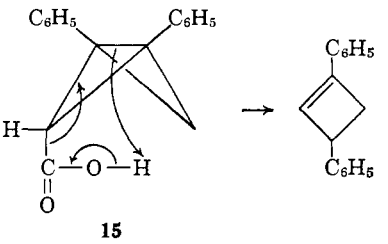


14

Support for structure **14** is found in the infrared spectrum which shows the absence of cyclopropylmethylene groups (3070 cm^{-1}) and the presence of a hydroxyl group (3400 cm^{-1}) and a nitrile group (2215 cm^{-1}). Further evidence is provided by the nmr spectrum which shows resonances centered at τ 5.73 (H^a, singlet), 6.83 (H^b, multiplet), 7.60 (H^c, multiplet), and 8.54 (H^d, singlet) with area ratios of 1:1:4:3, respectively.

Reactions with Acids. The sensitivity of bicyclo[1.1.0]butanes to acids has been pointed out by Moore.[4] 3-Methylbicyclo[1.1.0]butanecarbonitrile (**2a**) is no exception, reacting cleanly and rapidly with 0.1 *N* hydrochloric acid at room temperature to give a single isomer of the hydroxynitrile **14**. This reaction undoubtedly involves initial protonation at C-1[32] on the side opposite the nitrile group followed by hydration of the carbonium ion formed at C-3.

The direction of protonation can be construed from the observation of Masamune[33] that the bicyclobutanecarboxylic acid **15** undergoes facile decarboxylation at 85°, whereas the acid **16** is stable up to 200°. Only the former could involve intramolecular protonation at carbon on the side opposite the phenyl group.



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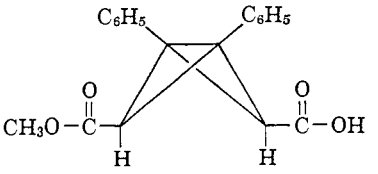
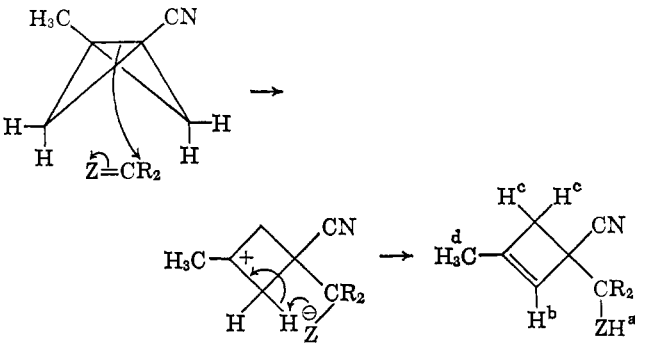


16

Reactions with Electron-Deficient Multiple Bonds. The reaction of **2a** with anhydrous hexafluoroacetone, *sym*-dichlorotetrafluoroacetone, or 1,1-bis(trifluoromethyl)-2,2-dicyanoethylene[34] provides additional examples of electrophilic addition, in this case leading to cyclobutene derivatives **17**, **18**, and **19**, respectively.



17, R = CF_3; Z = O
18, R = CF_2Cl; Z = O
19, R = CF_3; Z = $C(CN)_2$

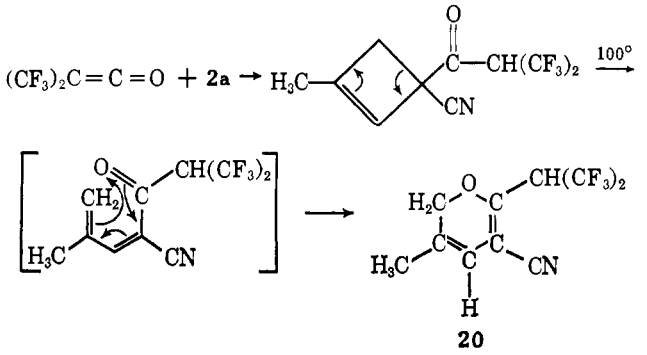
Structures **17** and **18** are supported by, in addition to elemental analysis, the infrared spectra which in each case show bands at 3300 and 3560 (OH), 2250 (CN), and 1650 cm^{-1} (C=C) and the nmr spectra which consist of resonances at τ 2.87 (H^a, singlet), 4.42 (H^b, multiplet), 7.70 (H^c, multiplet), and 8.31 (H^d, multiplet), with area ratios of 1:1:2:3, respectively. Structure **19** receives similar support from its nmr spectrum which has resonances at τ 4.3 (H^a, singlet), 4.02 (H^b, multiplet), 6.63 (H^c, multiplet), and 8.05 (H^a, multiplet), with area ratios of 1:1:2:3, respectively. The

(32) We cannot eliminate the possibility that initial protonation occurs on nitrogen.
(33) S. Masamune, *Tetrahedron Letters*, 945 (1965).
(34) W. J. Middleton, *J. Org. Chem.*, 30, 1402 (1965).

$HC(CN)_2$ proton readily exchanges with deuterium in D_2O.

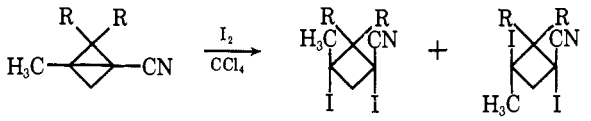
The reaction of **2a** with hexafluoroacetone is essentially instantaneous at 0° and is considered to involve initial approach of hexafluoroacetone at C-1 from the side opposite the nitrile group as in the reactions with acid. Attack from this direction should be sensitive to steric inhibition from *endo* substituents in the 2 or 4 positions since the C^{13}–H coupling constants indicate *endo* H–H repulsion. Support for this direction of attack is found in the observation that introduction of two methyl groups at C-2, and thus one *endo*-CH_3, completely suppresses the reaction of **2b** with hexafluoroacetone. Thus, **2b** was recovered unchanged after contact with hexafluoroacetone in ether at 0° for 4 hr.

When bis(trifluoromethyl)ketene[35] is allowed to react with **2a**, the initially formed product is unstable, thermally rearranging to the pyran **20**. Structure **20** receives support from its H nmr spectrum which displays resonances at τ 4.27 (=CH—, one-proton multiplet), 5.69 (–$CH(CF_3)_2$, one-proton septuplet), 5.20 (–CH_2–, two-proton multiplet), and 8.20 (CH_3–, three-proton multiplet).



20

Halogenation. The addition of iodine to 3-methylbicyclo[1.1.0]butanecarbonitrile **(2a)** or 2,2,3-trimethylbicyclo[1.1.0]butanecarbonitrile **(2b)** occurs readily in carbon tetrachloride solution at room temperature without catalysis. The reaction is not stereospecific as evidenced by the formation of *cis* and *trans* isomers in each case. Thus, **2a** affords two isomers, in the ratio of 81:19, of 1,3-diiodo-3-methylcyclobutanecarbonitrile (**21**) in 82% yield, and **2b** gives a 75% yield of 1,3-diiodo-2,2,3-trimethylcyclobutanecarbonitrile (**22**) as isomers in the ratio of 84:16. Structure **21** (major isomer) is supported by the nmr spectrum which has resonances



2a, R = H
b, R = CH_3

21, R = H
22, R = CH_3

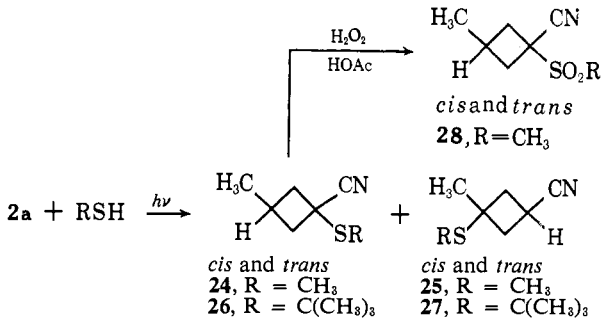
at τ 6.45 (four-proton multiplet) and 7.70 (three-proton singlet). The minor isomer of **21** shows resonances at τ 5.93, 6.21, 6.58, and 6.83 (four protons, multiplets) and 7.62 (three-proton singlet). Similarly, the nmr spectrum of the major isomer of **22** reveals resonances at τ 8.83, 8.28, 7.60 (all singlets), and 6.84 (doublet) with the area ratios of 3:3:3:2, respectively, where the minor isomer displays resonances at τ 8.64, 8.33, 7.65 (all singlets), and 6.90 (multiplet) again with area ratios of 3:3:3:2. Wiberg and Lampman[19] observed the formation of 82% *cis*- and 18% *trans*-1,3-diiodocyclobutane from the addition of iodine to bicyclo[1.1.0]butane. Structural assignment was possible on the basis of symmetry and the resulting simplicity of the nmr spectrum of the *trans* isomer. Unfortunately, an unambiguous assignment cannot be made on this basis in our case because of the asymmetry of both the *cis*- and *trans*-1,3-diiodo-3-methylcyclobutanecarbonitriles **21** and **22**.

The diiodide **21** can be converted to **2a** in modest yield by treatment with sodium hydride in a reaction analogous to the conversion of 1,3-diiodo-1,3-dimethylcyclobutane to 1,3-dimethylbicyclobutane.[16]

The addition of bromine to **2a** leads to 1,3-dibromo-3-methylcyclobutanecarbonitrile (**23**) as a single crystalline isomer; however, the poor yield (25%) negates the possible significance of the stereospecificity. The nmr spectrum of **23** consists of two unsplit resonances at τ 6.48 (four protons) and 7.93 (three protons), entirely consistent with the assigned structure.

Other reported examples of the addition of halogens to bicyclo[1.1.0]butanes include the chlorination of 1,3-bis(trifluoromethyl)-2,2,4,4-tetrafluorobicyclobutane which leads to a mixture of *cis*- and *trans*-1,3-dichloro-1,3-bis(trifluoromethyl)-2,2,4,4-tetrafluorocyclobutanes[14] and the addition of iodine to 1,3-dimethylbicyclo[1.1.0]butane which affords *cis*-1,3-diiodo-1,3-dimethylcyclobutane.[16]

Radical Additions. Thiols add to 3-methylbicyclo[1.1.0]butanecarbonitrile (**2a**) in a radical chain process. In the case of methanethiol, thermal activation at 100° or ultraviolet irradiation at 8° leads to the same product composition, namely a 50:50 mixture of *cis*- and *trans*-3-methyl-1-methylthiocyclobutanecarbonitriles (**24**) (80%) and a 50:50 mixture of *cis*- and *trans*-3-methyl-3-methylthiocyclobutanecarbonitriles (**25**) (20%). *t*-Butyl mercaptan fails to add with thermal activation (100°) but adds readily under ultraviolet irradiation or radical initiation. The products consist of a mixture of *cis*- and *trans*-3-methyl-1-*t*-butylthiocyclobutanecarbonitriles (**26**) (82%) and of *cis*- and *trans*-3-methyl-3-*t*-butylthiocyclobutanecarbonitriles (**27**) (18%). In **26** and **27**, one isomer predominates (55:45). The structural assignments are supported by the elemental analyses and are confirmed by the spectral characteristics which are presented in the Experimental Section.



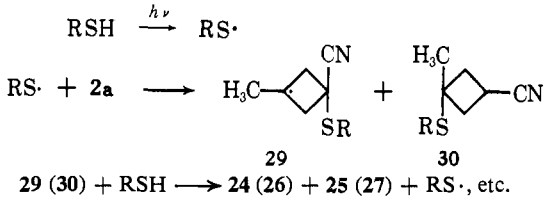
cis and *trans*
24, R = CH_3
26, R = $C(CH_3)_3$

cis and *trans*
25, R = CH_3
27, R = $C(CH_3)_3$

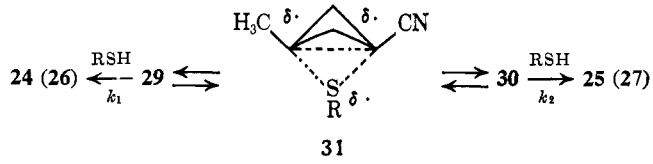
3-Methylbicyclo[1.1.0]butanecarbonitrile (**2a**) does not display a maximum in the ultraviolet region and is recovered unchanged after ultraviolet irradiation in hexane solution. It seems reasonable that the photo-

(35) I. L. Knunyants, Yu. A. Cheburkov, and M. D. Bargamova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **8**, 1389 (1963).

lytic addition of thiols involves as the initiation step the formation of a thiyl radical. This thiyl radical then attacks **2a** at either C-1 or C-3 to give the propagating radicals **29** and **30**, respectively, which subsequently react with the thiol to provide a new thiyl radical and the products **24–27**. We were surprised to find that the predominant products from this reaction were those



formed *via* **29**. This would appear to be the lesser stabilized radical in the pair **29** and **30**. One rationalization is that an equilibrium exists between **29** and **30** and that **29** reacts more rapidly with thiol than does **30** ($k_1 > k_2$). The recent synthesis of bicyclo[1.1.1]-pentane[36] coupled with the bulk of a sulfur atom makes a bridging equilibrium *via* a radical such as **31** reasonable.



Alternative explanations include consideration of steric effects which might predict addition of the bulky thiyl radical at C-1 rather than C-3 or electronic effects which predict addition of an electrophilic thiyl radical at C-1. At the present time, we cannot substantiate any of these explanations.

Experimental Section[37]

3-Methylenecyclobutanecarbonitrile (1a). The reaction, in a 1-l. stainless steel shaker tube, of allene (80 g) and acrylonitrile (250 ml) in benzene (250 ml) with 2.5 g of phenothiazine as inhibitor was carried out at 200° for 8 hr. Distillation gave **1a** (27%) which had bp 73° (30 mm) and n^{25}D 1.4579 (lit[21] bp 64–65° (21 mm), n^{25}D 1.4595).

2,2-Dimethyl-3-methylenecyclobutanecarbonitrile (1b). This nitrile was prepared in 19.4% yield from 1,1-dimethylallene (132 g, 1.94 moles)[38] and acrylonitrile (250 ml) in benzene (250 ml) with phenothiazine (2 g) as inhibitor by the procedure described for **1a**. The product **1b** isolated by fractionation had bp 107.5° (100 mm), n^{25}D 1.4492 (lit[21] bp 111° (100 mm), n^{25}D 1.4503).

***cis*- (1e) and *trans*-2-Methyl-3-methylenecyclobutanecarbonitrile (1d) and 3-Ethylidenecyclobutanecarbonitrile (1c).** In a 1-l. stainless steel shaker tube, phenothiazine (2.5 g), anhydrous benzene (250 ml), acrylonitrile (250 ml, *ca.* 202 g, 3.80 moles), and methylallene (98% pure from Columbia Chemical Co.) (25 g, 0.46 mole) were reacted at 200° and autogenous pressure for 8 hr. The combined product from six such runs was distilled to give 211.2 g (74%) of cycloadducts, bp 72–85° (23 mm), n^{24}D 1.4612. Gas chromatographic analysis of the cycloadducts showed a 20:14:41 mixture. The product was carefully fractionated through a 13-mm Podbielniak column.

A. ***trans*-2-Methyl-3-methylenecyclobutanecarbonitrile (1d).** The fraction, bp 72.5° (24 mm), n^{24}D 1.4525, 29.7 g, was characterized as *trans*-2-methyl-3-methylenecyclobutanecarbonitrile[39] by infrared absorption (neat) at 3110, 2250, 1688, 1380, and 890 cm^{-1} and nmr absorption (CCl_4) at τ 5.20 (2.00 H, multiplet), 6.35–7.70 (3.96 H, multiplets), and 8.77 (3.12 H, doublet, J = 7 cps). *Anal.* Calcd for C_7H_9N: C, 78.46; H, 8.47; N, 13.07. Found: C, 78.80, 78.84; H, 8.56, 8.66; N, 12.85, 12.80.

B. ***cis*-2-Methyl-3-methylenecyclobutanecarbonitrile (1e).** The fraction, bp 81.5° (24 mm), n^{24}D 1.4573, 24.7 g was characterized as *cis*-2-methyl-3-methylenecyclobutanecarbonitrile (**1e**) by infrared absorption (neat) at 3100, 2245, 1688, 1380, and 885 cm^{-1} and nmr absorption (CCl_4) at τ 5.18 (2.00 H, multiplet), 6.5–7.5 (4.18 H, multiplets) and 8.71 (3.22 doublet, J = 7 cps). *Anal.* Calcd for C_7H_9N: C, 78.46; H, 8.47; N, 13.07. Found: C, 78.43, 78.29; H, 8.45, 8.35; N, 12.89, 12.89.

C. 3-Ethylidenecyclobutanecarbonitrile (1c). The fraction, bp 89.0° (24 mm), n^{24}D 1.4654, 60 g, was characterized as 3-ethylidenecyclobutanecarbonitrile by infrared absorption (neat) at 3070, 2245, 1712, 1380, and 857 cm^{-1} and nmr absorption (CCl_4) at τ 4.80 (1.0 H, multiplet), 7.00 (5.2 H, multiplet), and 8.49 (3.1 H, multiplet). *Anal.* Calcd for C_7H_9N: C, 78.46; H, 8.47; N, 13.07. Found: C, 78.21, 78.18; H, 8.40, 8.21; N, 13.03, 12.94.

3-Methylbicyclo[1.1.0]butanecarbonitrile (2a). To 56% hydriodic acid (4000 g) stirred and cooled with an ice bath was added 3-methylenecyclobutanecarbonitrile (848 g, 9.13 moles) over a period of 1 hr. The mixture was allowed to stir at room temperature for 16 hr. The lower organic phase was separated, and the aqueous phase extracted with methylene chloride (200 ml). The combined organic phase was extracted successively with water (two 400-ml portions), aqueous sodium thiosulfate (200 ml), and water (two 400-ml portions), and then dried over anhydrous magnesium sulfate. The mixture was filtered, and the filtrate was freed of solvent and starting material by evaporation at 50° (0.1 mm) to leave 1466 g (72.8%) of crude 3-iodo-3-methylcyclobutanecarbonitrile. This crude iodonitrile was added with stirring to a slurry of sodium hydride–mineral oil dispersion (315 g of 54% by weight NaH) in ether (5200 ml). The mixture was stirred at 25° for 16 hr, at reflux for 7 hr and finally at 25° for 16 hr (hydrogen evolution had essentially ceased after the 7 hr at reflux). The mixture was treated with methanol (100 ml) and then water (1000 ml). The ether phase was separated and the aqueous phase extracted with ether (two 100-ml portions). The combined ether phase was dried over anhydrous magnesium sulfate, filtered, and distilled to give 3-methylbicyclo[1.1.0]butanecarbonitrile (**2a**) (572 g, 92.5%) which had bp 95–96.5° (100 mm), n^{25}D 1.4521. *Anal.* Calcd for C_6H_7N: C, 77.38; H, 7.58; N, 15.04. Found: C, 77.48, 77.21; H, 7.79, 7.64; N, 15.02, 15.29.

2,2,3-Trimethylbicyclo[1.1.0]butanecarbonitrile (2b). To 56% hydriodic acid (635 g) stirred and cooled with an ice bath was added 2,2-dimethyl-3-methylenecyclobutanecarbonitrile (171 g, 1.425 moles) over a period of 1 hr. The mixture was stirred for 16 hr at 25°, and then the upper organic phase was separated, and the aqueous phase was extracted with methylene chloride (50 ml). The combined organic phase was extracted successively with sodium chloride solution (100 ml), aqueous sodium thiosulfate solution (100 ml), and sodium chloride solution (100 ml). The organic phase was dried over anhydrous magnesium sulfate, filtered, and distilled through a 12-in. Vigreux column to give 229 g (64.7%) of crude 2,2,3-trimethyl-3-iodocyclobutanecarbonitrile, bp 81–83° (1 mm). This crude iodide (229 g, 0.925 mole) was added to a slurry of sodium hydride–mineral oil dispersion (41 g of 56% by weight NaH, 0.955 mole NaH) in ether (1000 ml), and the mixture was stirred at room temperature until hydrogen evolution ceased. Work-up as described for **2a** above gave 2,2,3-trimethylbicyclo-[1.1.0]butanecarbonitrile (**2b**) (82.5 g, 75%) as a colorless liquid, bp 72–73° (15 mm), n^{25}D 1.4585. *Anal.* Calcd for $C_8H_{11}N$: C, 79.29; H, 9.15; N, 11.56. Found: C, 79.34; H, 9.47; N, 11.77.

***endo*- (2d) and *exo*-2,3-Dimethylbicyclo[1.1.0]butanecarbonitrile (2e).** To 55–58% hydriodic acid (150 ml) cooled with an ice bath was added with vigorous stirring *trans*-2-methyl-3-methylenecyclobutanecarbonitrile (28.1 g, 0.262 mole). The mixture was stirred at 0° for 1 hr and at 25° for 2 hr. The layers were separated, and the aqueous layer was extracted with methylene chloride. The combined organic and methylene chloride layers were rinsed with 100 ml of water, decolorized with dilute sodium thiosulfate, dried over $MgSO_4$, filtered, concentrated, and stripped of starting

(36) K. B. Wiberg, D. S. Connor, and G. M. Lampman, *Tetrahedron Letters*, 531 (1964).

(37) Melting and boiling points are uncorrected.

(38) Ya. I. Ginzburg, *J. Gen. Chem. USSR*, 10, 513 (1940); *Chem. Abstr.*, 34, 7843 (1940).

(39) This and its *cis* isomer were produced in a 2:1 ratio by the reaction of allene and *trans*-crotononitrile at 200° for 8 hr, but in very low yield.

material by stirring at 25° (0.25 mm), to give 46.6 g (76%) of pale brown liquid. The product composition was determined from its nmr spectrum to be 75% with iodo and nitrile *trans* (methyl groups at lower field) and 25% *cis*. To a mixture of 54% sodium hydride–mineral oil dispersion (10.0 g, 0.22 mole NaH) and anhydrous ether (180 ml) was added under nitrogen with stirring 3-iodo-3-methyl-*trans*-1-cyano-2-methylcyclobutane (46.6 g, 0.198 mole). After stirring for 3 days at room temperature, the mixture was cooled with an ice bath and cautiously quenched with 35 ml of water. The ether layer was separated, dried with $MgSO_4$, filtered, and concentrated. The residue was distilled at 65–75° (19 mm) to give 15.8 g (74%) colorless liquid. Careful distillation did not separate the products. The product composition was determined from its nmr spectrum to be 54% 2,3-dimethyl-2-cyclobutene-1-carbonitrile, 31% *endo*- (**2d**) and 15% *exo*-2,3-dimethylbicyclo[1.1.0]butanecarbonitrile (**2e**). The cyclobutene was separated from the bicyclobutanes by preparative gas chromatography (using the cyanoethoxy derivative of pentaerythritol).

The 2,3-dimethyl-2-cyclobutene-1-carbonitrile fraction was identified by infrared absorption (neat) at 2257 and 1631 cm^{-1}, nmr absorption (CCl_4) at τ 6.72 (1.03 H, multiplet), 7.41 (2.02 H, multiplet), and 8.32 (area 6.00, narrow multiplet), and its mass spectrum with a parent peak at *m/e* 107 (749.2) with the peak at 108 having the correct isotopic abundance for C_7H_9N (58.2). *Anal.* Calcd for C_7H_9N: C, 78.46; H, 8.47; N, 13.07; mol wt, 107.15. Found: C, 77.77, 77.29; H, 8.53, 8.36, 8.27; N, 13.62, 13.86.

The fraction containing the bicyclobutanes could not be further separated by gas chromatography. The identification of the two components was achieved by comparing the nmr and infrared spectra of this mixture and the one for the *cis* isomer. *endo*-2,3-Dimethylbicyclo[1.1.0]butanecarbonitrile (**2d**) (82% of the mixture) exhibited nmr absorption (CCl_4) at τ 7.15–7.55 (1 H, multiplet), 7.84 (1 H, four lines, J = 2.5, 4.0 cps), 8.05 (1 H, doublet, J = 2.5 cps), 8.30 (3 H, singlet), and 9.08 (3 H, doublet, J = 6.0 cps). *exo*-2,3-Dimethylbicyclo[1.1.0]butanecarbonitrile (**2e**) (18% of the mixture) exhibited nmr absorption (CCl_4) at τ 8.09 (1 H, doublet, J = 1.5 cps), 8.37 (1 H, singlet), 8.53 (1 H, coupled to CH_3 at 8.83 by 6.0 cps), 8.83 (3 H, multiplet), and 8.87 (1 H, doublet, J = 1.5 cps).

When *cis*-2-methyl-3-methylenecyclobutanecarbonitrile was substituted in the above reaction, 3-iodo-3-methyl-*cis*-1-cyano-2-methylcyclobutane was obtained in 75% yield. Its nmr spectrum indicated that 59% of the material had iodo and nitrile *cis* (3-methyl group at higher field). *Anal.* Calcd for $C_7H_{10}NI$: C, 35.76; H, 4.29; N, 5.96; I, 53.99. Found: C, 36.89; H, 4.31; N, 6.13; I, 50.97. This iodide was dehydroiodinated by the same procedure used for the *trans* isomer to give 13.8 g (81%) of colorless liquid, bp 65–75° (17 mm). The product consisted of 13% 2,3-dimethyl-2-cyclobutene-1-carbonitrile and 34% *endo*- and 54% *exo*-2,3-dimethylbicyclo[1.1.0]butanecarbonitrile. The cyclobutene was removed by preparative gas chromatography leaving a 56:44 mixture of *exo* and *endo* isomers.

3-Ethylbicyclo[1.1.0]butanecarbonitrile (2c). To 55% hydriodic acid (100 ml) cooled in an ice bath was added 3-ethylidenecyclobutanecarbonitrile (21.4 g, 0.20 mole) with vigorous stirring. The mixture was allowed to warm to room temperature and was stirred overnight. The organic layer was separated, and the aqueous layer was extracted with methylene chloride. The combined organic and methylene chloride layer was rinsed with water, decolorized with 10% sodium thiosulfate, dried over $MgSO_4$, filtered, concentrated, and degassed at 25° (0.3 mm) to give 39.1 g (83.3%) of 3-iodo-3-ethylcyclobutanecarbonitrile.

To a stirred suspension of 54% sodium hydride–mineral oil dispersion (8.14 g, 0.183 mole of NaH) in 150 ml of anhydrous ether under dry nitrogen was added 3-iodo-3-ethylcyclobutanecarbonitrile. Gas evolution was brisk for the first few minutes then dropped off abruptly. After 5 days of stirring, the mixture was cooled with an ice bath and cautiously quenched with 30 ml of water. The ether layer was dried with $MgSO_4$, filtered, concentrated, and the residue was distilled crudely at 45° (3 mm) to give 14.0 g (79%) of 3-ethylbicyclo[1.1.0]butanecarbonitrile contaminated with 10% 3-ethylidenecyclobutanecarbonitrile (**1c**) and two other components. Fractional distillation gave a fairly pure cut (93%), bp 61° (11 mm), $n^{25}D$ 1.4565. *Anal.* Calcd for C_7H_9N: C, 78.46; H, 8.47; N, 13.07. Found: C, 77.67, 77.50, 77.15; H, 8.50, 8.52, 8.53; N, 13.13, 13.14.

3-Ethylbicyclo[1.1.0]butanecarbonitrile (**2c**) had infrared absorption (neat) at 3070, 2230 (very strong), and 935 cm^{-1} and nmr absorption (CCl_4) at τ 7.6–8.1 (4.00 H, *ca.* quartet and singlet) and 8.7–9.0 (4.75 H, *ca.* triplet and singlet).

Catalytic Reduction of 2a. A. Microdetermination (Figure 1). A solution of **2a** (0.398 g, 0.00428 mole) in alcohol (20 ml) containing 5% Pd–C catalyst (0.1 g) was reduced at 25° and 1 atm for 126 min. During this time, 239.5 ml of hydrogen was consumed, and at the end of the reduction (the last 25 min) the rate of H_2 uptake equalled 0.35 ml/min. Filtration of the reduction mixture gave a solution which was alkaline to moist pH paper, indicating reduction of the nitrile group. Based on this final rate, it can be estimated that 0.35 × 126 = 44 ml of H_2 was used in the reduction of the nitrile group. Therefore, 239.5 − 44 = 195.5 ml (0.00872 mole) of hydrogen was consumed in the reduction of C–C bonds. This is equivalent to 2.03 moles of H_2/mole of **2a**. Analysis of the product mixture by gpc revealed one major product (79.2%), the remainder being divided between eight other products.

B. Product Identification. A solution of 4.65 g of **2a** in alcohol (50 ml) containing 5% Pd–C catalyst (0.25 g) was reduced in a Parr shaker at 40 psi hydrogen pressure for 2 hr. Filtration and distillation gave 2.5 g of product, bp 152–155°. The major product was collected by gpc and shown to be 4-methylvaleronitrile by comparison of its infrared and nmr spectra with those of a synthetic sample. 2-Methylvaleronitrile was identified by comparison of its mass spectral cracking pattern with that of a synthetic specimen.

2-Methylvaleronitrile.[40] To a slurry of sodium hydride–mineral oil dispersion (12.7 g, 6.35 g of NaH, 0.265 mole) in tetrahydrofuran (150 ml) was added propionitrile (13.75 g, 0.25 mole) and 1-iodopropane (42.5 g, 0.25 mole). The mixture was heated at reflux for 16 hr, cooled, and methanol (10 ml) was added. Distillation of the solvent and product at 1 mm into a Dry Ice–acetone-cooled receiver and subsequent fractionation gave 2-methylvaleronitrile (8.8 g, 36%), bp 148° (micro) and $n^{25}D$ 1.3999.

4-Methylvaleronitrile. This nitrile was prepared in 12.5% yield from acetonitrile (10.25 g), isobutyl bromide (34.3 g), and sodium hydride–mineral oil dispersion (12.7 g, 50% by weight NaH, 6.35 g, 0.265 mole) in tetrahydrofuran (150 ml) by the procedure described for 2-methylvaleronitrile. 4-Methylvaleronitrile had bp 159° (micro), $n^{25}D$ 1.4045 (lit[41] bp 155–156°, $n^{22}D$ 1.4048).

1-Aminomethylbicyclo[1.1.0]butanecarbonitrile (5). To an ice–water-cooled, stirred solution–slurry of lithium aluminum hydride (10 g, 0.253 mole) in diethyl ether (500 ml.) was added 3-methylbicyclo[1.1.0]butanecarbonitrile (18.6 g, 0.2 mole). The mixture was stirred and cooled in an ice bath for 2 hr, heated at reflux for 0.5 hr, and then recooled in an ice–water bath. Cautious addition of 10.4 ml of H_2O was followed by the addition of 8 ml of 6 *N* NaOH and finally 36.8 ml of water. The ether phase was decanted from the resulting granular precipitate, and this precipitate was washed with 400 ml of ether. The combined ether phase was dried over $MgSO_4$, filtered, and the ether was distilled through an 18-in. helices-packed column. Fractionation of the residue through a semimicro spinning-band column gave 12.01 g (62%) of product which had bp 60–63° (94 mm), $n^{25}D$ 1.4528–1.4539.

To a solution of this amine (2.5 g, 0.026 mole) in ether (100 ml) was added with ice bath cooling phenyl isocyanate (2.5 ml). An immediate exothermic reaction resulted in a mass of white crystals. The crystals were collected and purified by recrystallization from aqueous ethanol to give 4.47 g of 1-[3-phenylureiodomethyl]-3-methylbicyclo[1.1.0]butane, mp 153.5°. *Anal.* Calcd for $C_{13}H_{16}N_2O$: C, 72.19; H, 7.46; N, 12.95. Found: C, 71.98; H, 7.53; N, 12.75.

3-Methylbicyclo[1.1.0]butanecarboxamide (6). The general procedure was that employed for the preparation of toluamide.[42]

To a stirred solution of alcohol (50 ml), 30% H_2O_2 (40 ml) and 3-methylbicyclo[1.1.0]butanecarbonitrile (9.3 g, 0.1 mole) cooled in an ice–water bath was added 6 *N* NaOH (4 ml). The solution was stirred at 0° for 1 hr and then warmed to 50–60° for 2 hr. The ethanol was evaporated at reduced pressure and the aqueous phase was extracted with three 125-ml portions of ethyl acetate followed by two 125-ml portions of hot ethyl acetate. The extracts were combined, dried over $MgSO_4$, and filtered, and the filtrate was concentrated at reduced pressure. The colorless, crystalline residue was recrystallized from ethyl acetate to give 7.4 g (66%) of product as colorless plates, mp 144–144.5° dec. *Anal.* Calcd for C_6H_9NO: C, 64.84; H, 8.16; N, 12.60. Found: C, 64.44; H, 7.89; N, 12.41.

(40) P. A. Levene and L. A. Mikeska, *J. Biol. Chem.*, **84**, 577 (1929).
(41) H. A. Bruson and T. W. Riener, U. S. Patent 2,458,337 (1949); *Chem. Abstr.*, **43**, 3440 (1949).
(42) C. R. Noller, "Organic Syntheses," Coll Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p 586.

Reaction of 3-Methylbicyclo[1.1.0]butanecarboxamide (6) with Alkaline Sodium Hypochlorite. Into a cold solution of sodium hydroxide (12 g, 0.3 mole) in water (100 ml) was bubbled chlorine (3.5 ml liquid). To the resulting solution was added 3-methylbicyclo[1.1.0]butanecarboxamide (5.5 g, 0.05 mole). The mixture was stirred at 0° for 4 hr and then warmed to 50° whereupon an oil separated. The solution was steam distilled and the distillate was made alkaline with 6 *N* NaOH, extracted with ether, and concentrated to leave a yellow oil. Distillation of this oil through a spinning-band column resulted in 1.5 g of a product, bp 111°, $n^{25}D$ 1.4159. Infrared spectroscopy revealed a carbonyl band at 1775 cm^{-1} (cyclobutanone), and the compound formed a 2,4-dinitrophenylhydrazone which had mp 106–107° (lit[43] bp 111–113°, $n^{25}D$ 1.4140, mp of 2,4-dinitrophenylhydrazone, 108.5–109.5°).

Pyrolysis of 3-Methylbicyclo[1.1.0]butanecarbonitrile (2a). A 200-ml flask equipped with magnetic stirrer and heating mantle was charged with 105 g of 3-methylbicyclo[1.1.0]butanecarbonitrile and then surmounted with a 14 × 200 mm pyrolysis tube packed with 60–100 mesh quartz chips. The upper outlet of the pyrolysis tube led to a Dry Ice–acetone-cooled receiver. The pyrolysis tube was externally heated to 350 ± 5°, and the system was evacuated to 1 mm. The pyrolysate (103 g) which collected in the receiver (*solid at −78°*) was analyzed by gas chromatography and found to be 98% pure 2-cyano-3-methyl-1,3-butadiene (**9**). It had $n^{25}D$ 1.4618 (lit[28] $n^{31}D$ 1.4545). The diene dimerized and polymerized on storage at room temperature.

1,4,4,5,5-Pentacyano-2-methylcyclohexene (10). To a solution of tetracyanoethylene (2.56 g, 0.02 mole) in ethyl acetate (20 ml) was added 2-cyano-3-methyl-1,3-butadiene (2.5 ml). A pale yellow color developed. After standing 48 hr the solvent was evaporated and the residue was recrystallized from alcohol to give 1.7 g (38.5%) of **10** as miniature, white needles, mp 186.5–187° dec. *Anal.* Calcd for $C_{12}H_7N_5$: C, 65.15; H, 3.19; N, 31.66. Found: C, 65.02; H, 3.17; N, 31.60.

Catalytic Reduction of 2-Cyano-3-methyl-1,3-butadiene (9). A solution of **9** (0.33 g, 0.0036 mole) in ethyl ether (10 ml) containing 0.1 g of PtO_2 was reduced at atmospheric pressure until the hydrogen uptake (149 ml, 0.0067 mole) ceased. Filtration and distillation gave a crude product which consisted of 2,3-dimethylbutyronitrile (23.8%) and trimethylacrylonitrile (76.2%). The former was identified by its inseparability on a capillary gas chromatogram from a synthetic sample. The latter was identified similarly and also by comparison of its infrared spectrum with that of a synthetic sample.

2,3-Dimethylbutyronitrile. This nitrile was prepared in 25% yield from propionitrile (13.75 g, 0.25 mole), 2-iodopropane (42.5 g, 0.25 mole), and sodium hydride–mineral oil dispersion (12.7 g, 50% by weight NaH, 0.26 mole of NaH) in tetrahydrofuran (150 ml) by the procedure described for 2-methylvaleronitrile. The 2,3-dimethylbutyronitrile had bp 145° (micro), $n^{25}D$ 1.3993 (lit[30] $n^{25}D$ 1.3992).

Trimethylacrylonitrile. This compound was prepared in poor yield by the dehydration of 1-hydroxy-1,2-dimethylbutyronitrile[44] according to the procedure of de Lact.[31] A sample of trimethylacrylonitrile isolated by gpc had bp 159°, and $n^{25}D$ 1.4429 (lit[31] bp 157–157.4°, $n^{20}D$ 1.4455).

Alkaline Saponification of 2a. To a solution of potassium hydroxide (8.4 g, 0.15 mole) in water (30 ml) was added 3-methylbicyclo[1.1.0]butanecarbonitrile (9.3 g, 0.1 mole), and the mixture was heated at reflux for 3 hr. The clear solution was acidified with sulfuric acid to pH 2 and then continuously extracted with ether for 24 hr. The ether extract was dried over magnesium sulfate and filtered, and the ether was evaporated. The residual oily crystals were recrystallized from 1,2-dichloroethane to give 3-hydroxy-3-methylcyclobutanecarboxylic acid (4.71 g, 36.2%) as colorless needles, mp 152–153°. *Anal.* Calcd for $C_6H_{10}O_3$: C, 55.37; H, 7.75. Found: C, 55.43; H, 7.58.

3-Hydroxy-3-methylcyclobutanecarboxylic Acid (11). To hydriodic acid (90 g, 55% solution) cooled in an ice bath was added with stirring 3-methylenecyclobutanecarboxylic acid.[21] After 1.5 hr, ice–water (200 ml) was added, and the crystalline, crude 3-iodo-3-methylcyclobutanecarboxylic acid (33 g, 69%) was collected on a filter. This crude iodo acid (33 g, 0.14 mole) was added to a solution of sodium hydroxide (11 g, 0.28 mole) in water (150 ml) at 0°. After 2 hr the mixture was acidified to pH 2 and worked up as described above to give 11.5 g (64.5%) of the subject hydroxy acid which had mp 151–153°, and a mixture melting point with the product from the saponification of **2a** of 151–153°.

Sodium Methoxide Catalyzed Addition of Methanol to 2a. To a solution of sodium methoxide (13.5 g 0.25 mole) in absolute methanol (50 ml) was added 3-methylbicyclo[1.1.0]butanecarbonitrile (9.3 g, 0.1 mole). The mixture was stirred at room temperature under N_2 for 63 hr, and then 300 ml of water was added. Extraction with three 75-ml portions of ether, drying the ether extract over $MgSO_4$, filtration, and distillation resulted in 6.87 g (55%) of *cis*- and *trans*-3-methyl-3-methoxycyclobutanecarbonitrile (**12**) which had bp 89–95° (22 mm), $n^{25}D$ 1.4382–1.4385. *Anal.* Calcd for $C_7H_{11}ON$: C, 67.17; H, 8.86; N, 11.19. Found: C, 67.30; H, 8.93; N, 11.47.

Thermal Addition of Ammonia to 2a. A Carius tube was charged with 3-methylbicyclo[1.1.0]butanecarbonitrile (4.65 g, 0.05 mole) and ammonia (1.7 g, 0.1 mole), sealed under vacuum, and heated at 100° for 21 hr. Distillation of the product gave 4.1 g (74.5%) of 3-amino-3-methylcyclobutanecarbonitrile, bp 48–49° (0.3 mm), $n^{25}D$ 1.4616. This amine formed a picrate which had mp 230–232° after recrystallization from aqueous–ethanol. *Anal.* Calcd for $C_{12}H_{13}N_5O_7$: C, 42.48; H, 3.86. Found: C, 42.30; H, 3.87.

Thermal Addition of Di-n-propylamine to 2a. A mixture of **2a** (4.65 g, 0.05 mole) and di-*n*-propylamine (5.05 g, 0.05 mole) was heated at gentle reflux for 24 hr during which time the temperature rose from 110 to 153°. Distillation gave 7.54 g (77.7%) of 3-methyl-3-(di-*n*-propylamino)cyclobutanecarbonitrile bp 88–90° (0.3 mm), $n^{25}D$ 1.4577. *Anal.* Calcd for $C_{12}H_{22}N_2$: C, 74.17; H, 11.41; N, 14.42. Found: C, 74.16; H, 11.28; N, 14.12.

Thermal Addition of Aniline to 2a. A mixture of 5.0 ml of aniline and 5.0 ml of **2a** was heated at 147° for 15 hr and then distilled to give 4.6 g (50%) of 3-anilino-3-methylcyclobutanecarbonitrile, bp 115° (0.1 mm), $n^{25}D$ 1.5545. *Anal.* Calcd for $C_{12}H_{14}N_2$: C, 77.38; H, 7.58; N, 15.04. Found: C, 77.10; H, 7.83; N, 14.99.

Thermal Addition of Dimethylamine to 2a. By the procedure described above for ammonia, a mixture of **2a** (28 g, 0.3 mole) and dimethylamine (22 g, 0.5 mole) was heated at 100° for 15 hr. Distillation gave 39.2 g (95%) 3-dimethylamino-3-methylcyclobutanecarbonitrile, bp 122° (80 mm), $n^{25}D$ 1.4622. *Anal.* Calcd for $C_8H_{14}N_2$: C, 69.52; H, 10.21; N, 20.27. Found: C, 69.83; H, 10.34; N, 20.30.

Thermal Addition of Water to 2a. To water (10 ml) was added 3-methylbicyclo[1.1.0]butanecarbonitrile (1.84 g, 0.02 mole), and the mixture was heated at reflux with stirring. After 3.5 hr the aqueous phase was analyzed by gpc and revealed a single product along with some unchanged **2a**. Evaporation of the water, recrystallization from ether–petroleum ether (bp 30–60°) of the residue, and subsequent sublimation gave 3-hydroxy-3-methylcyclobutanecarbonitrile as colorless crystals, mp 54°.

Acid-Catalyzed Addition of Water to 2a. To 50 ml of 0.1 *N* hydrochloric acid was added 3-methylbicyclo[1.1.0]butanecarbonitrile (1.84 g, 0.02 mole), and the mixture was stirred at 25°. A mildly exothermic reaction occurred resulting in a clear aqueous solution. Analysis by gpc revealed a single product. Work-up as described above gave 3-hydroxy-3-methylcyclobutanecarbonitrile (1.9 g, 85%), mp 54.5°. *Anal.* Calcd for C_6H_9NO: C, 64.84; H, 8.16; N, 12.60. Found: C, 64.94; H, 8.15; N, 12.41.

Reaction of 2a with Hexafluoroacetone. Into an ice bath cooled solution of 3-methylbicyclo[1.1.0]butanecarbonitrile (4.65 g, 0.05 mole) in ether (50 ml) was bubbled a stream of hexafluoroacetone carried by N_2. A Dry Ice–acetone-cooled condenser was used to prevent the escape of the hexafluoroacetone. The mixture was stirred at room temperature for 1 hr, and then the ether was evaporated. The crystalline residue was recrystallized from ether–petroleum ether to give 10.64 g (82%) of **24** as colorless needles, mp 89–89.5°. *Anal.* Calcd for $C_9H_7NOF_6$: C, 41.71; H, 2.72; N, 5.41; F, 43.99. Found: C, 41.87; H, 2.94; N, 5.61; F, 44.09.

Reaction of 2a with *sym*-Dichlorotetrafluoroacetone. To a solution of 3-methylbicyclo[1.1.0]butanecarbonitrile (9.3 g, 0.1 mole) in ether (100 ml) was added *sym*-dichlorotetrafluoroacetone (20 g, 0.1 mole). The solution was allowed to stand 3 hr at 25° and then the ether was evaporated. The residual crystals were recrystallized from CCl_4 to give 13.8 g (47.2%) of the alcohol **25** which had mp 88–89.5°. *Anal.* Calcd for $C_9H_7NOCl_2F_4$: C, 37.01; H, 2.42; N, 4.80; Cl, 24.28; F, 26.02. Found: C, 37.25; H, 2.58; N, 4.78; Cl, 24.52; F, 25.78.

Reaction of 2b with Hexafluoroacetone. In the manner described for **2a** above, the reaction of 2,2,3-trimethylbicyclo[1.1.0]butanecarbonitrile (6.05 g, 0.05 mole) in ether (50 ml) with hexafluoro-

(43) F. F. Caserio, Jr., and J. D. Roberts, *J. Am. Chem. Soc.*, 80, 5827 (1958).

(44) A. J. Ultée, *Ber.*, **39**, 1858 (1906).

acetone (10 g) for 4 hr at 0° gave on work-up 6.0 g (99%) of recovered **2b**.

Reaction of 2a with 1,1-Bis(trifluoromethyl)-2,2-dicyanoethylene. To a solution of **2a** (2.33 g, 0.025 mole) in ether (25 ml) was added 1,1-bis(trifluoromethyl)-2,2-dicyanoethylene. After standing for 24 hr, the ether was evaporated to leave an oil which crystallized to the relatively unstable 3-methyl-1-cyano-1-[β,β,dicyano-α,α-bis(trifluoromethyl)ethyl-2-]cyclobutene-1-carbonitrile, mp 97–98°. *Anal.* Calcd for $C_{12}H_7N_3F_8$: C, 46.91; H, 2.30; N, 13.68; F, 37.11. Found: C, 47.07; H, 2.44; N, 14.38; F, 36.79.

Reaction of 2a with Bis(trifluoromethyl)ketene. To bis(trifluoromethyl)ketene (35.2 g, 0.198 mole) at −40° in a flask with a Dry Ice condenser was added 3-methylbicyclo[1.1.0]butanecarbonitrile (18.4 g, 0.198 mole). The mixture was allowed to warm to room temperature. After 1 hr at room temperature, the H′ nmr spectrum of the mixture showed that the reaction was 65–70% complete and that the resulting mixture was complex. The reaction was completed by heating the mixture on a steam bath. The red-brown mixture was extracted several times with hot *n*-hexane. The hexane solution was concentrated, and the residue was sublimed at 100° (0.12 mm) to give 21.2 g (39.6%) of colorless crystalline 3-methyl-5-cyano-6-bis(trifluoromethyl)methyl-2H-pyran. An analytical sample, which was provided by recrystallization from *n*-hexane and sublimation, melted at 71.5–73.5°. The product was characterized by infrared absorption (CCl_4) at 2220, 1730 (weak), 1670, and 1610 cm^{-1}; ultraviolet absorption at $\lambda_{max}^{isooctane}$ 298 mμ (ε 4370); nmr absorption (CCl_4) at τ 4.27 (1.00 H, multiplet), 5.20 (1.97 H, multiplet), 5.69 (1.12 H, septuplet), and 8.20 (3.04 H, multiplet); and a mass spectrum with a parent ion at 271. *Anal.* Calcd for $C_{10}H_7NOF_6$: C, 44.29; H, 2.60; N, 5.17; F, 42.04. Found: C, 44.43, 44.78; H, 2.79, 2.88; N, 5.20, 5.51, 5.74; F, 41.65, 41.50.

Addition of Iodine to 2a. To a stirred solution–slurry of iodine (12.7 g, 0.05 mole) in CCl_4 (100 ml) was added 3-methylbicyclo-[1.1.0]butanecarbonitrile (5.0 g, 0.054 mole). After stirring for 3 hr the mixture was filtered, and the solvent was evaporated. Recrystallization of the residue from methanol resulted in 14.3 g (82.5%) of 1,3-diiodo-3-methylcyclobutanecarbonitrile (**21**) as large plates, mp 90–91.5°. *Anal.* Calcd for $C_6H_7NI_2$: C, 20.73; H, 2.02; N, 4.04. Found: C, 20.91; H, 2.11; N, 3.72.

Reaction of 1,3-Diiodo-3-methylcyclobutanecarbonitrile with Sodium Hydride. To a stirred suspension of 53.4% sodium hydride–mineral oil dispersion (0.90 g, 20 mmoles) in 10 ml of dry THF was added 1,3-diiodo-3-methylcyclobutanecarbonitrile (3.47 g, 10 mmoles). Immediately a little heat and a gas were evolved. An attempt at heating at reflux was stopped due to excessive foaming. After 1.5 hr, the volatile components were transferred to a Dry Ice trap by heating the mixture to 50° (1.0 mm). In addition to THF, the distillate contained four other components in the ratio 6:2:76:16. The larger component had the same retention time as 3-methylbicyclo[1.1.0]butanecarbonitrile (**2a**).

In a similar experiment, distillation gave a product which had bp 43–44° (12 mm), $n^{25}D$ 1.4505, and displayed an infrared spectrum essentially identical with pure **2a**.

Addition of Bromine to 2a. To an ice-cold solution of 3-methylbicyclo[1.1.0]butanecarbonitrile (9.3 g, 0.1 mole) in CCl_4 (50 ml) was added a solution of bromine (16.0 g, 0.1 mole) in CCl_4 (50 ml). The bromine color rapidly discharged and a small hygroscopic precipitate was removed by filtration. Concentration of the filtrate left an oil which crystallized from methanol in large crystals to give 5.2 g of product. Evaporation of the methanol and distillation of the residual oil gave an additional 1.5 g of crude product, bp 85–100° (10 mm), which crystallized. The combined solid was recrystallized from methanol to give 6.35 g (25%) of the dibromide, mp 56–57.6°. *Anal.* Calcd for $C_6H_7NBr_2$: C, 28.47; H, 2.79; N, 5.53; Br, 63.21. Found: C, 28.69; H, 2.77; N, 5.52; Br, 63.08.

Addition of Iodine to 2b. To a stirred solution–slurry of I_2 (5.0 g) in CCl_4 (50 ml) was added 2,2,3-trimethylbicyclo[1.1.0]-butanecarbonitrile (2.42 g, 0.02 mole). The mixture was stirred for 4 hr, the solvent was evaporated, and the residue was recrystallized from methanol to give 4.7 g (75%) of the diiodide **22** as colorless crystals, mp 84–85°. *Anal.* Calcd for $C_8H_{11}NI_2$: C, 25.62; H, 2.96; N, 3.74; I, 67.69. Found: C, 25.92; H, 3.11; N, 3.83; I, 68.18.

Addition of Methanethiol to 2a. Thermal Addition. A Carius tube was charged with **2a** (4.65 g, 0.05 mole) and methanethiol (10 g). The tube was sealed under vacuum and then heated at 100° for 39 hr. Distillation gave 6.15 g (87%) of product as two cuts. Cut 1, bp 32° (0.5 mm), was a mixture of *cis*- and *trans*-1-methylthio-3-methylcyclobutanecarbonitriles (**24**). Cut 2, bp 55–57° (0.5 mm), was a mixture of *cis*- and *trans*-3-methylthio-3-methylcyclobutanecarbonitriles (**25**). Gas chromatographic analysis using a Golay R (polyglycol) column revealed each cut to consist of two peaks of equal area. *Anal.* Calcd for $C_7H_{11}NS$: C, 59.55; H, 7.85; N, 9.92; S, 22.67. Cut 1 Found: C, 59.43; H, 7.68; N, 10.29; S, 22.78. Cut 2 Found: C, 59.55; H, 7.82; N, 10.19; S, 22.70.

Structure **24** (cut 1) is supported by the H nmr spectrum which reveals resonances at τ 8.92 (three-proton doublet, J = 6.3 cps), 7.00–7.50 (one-proton multiplet due to the $HCCH_3$ grouping), 7.79 and 7.80 (three-proton singlets) due to the *cis*- and *trans*-SCH_3, and 7.54–7.81 (four-proton multiplet) due to the cyclobutylmethylene groups. The C-methyl groups in *cis* and *trans* **24** displayed identical chemical shifts in pyridine, trifluoroacetic acid, carbon tetrachloride, benzene, methylene chloride, and hexadeuterioacetone solutions. Oxidation of **24** to the *cis* and *trans* sulfones **28** was effected with hydrogen peroxide in acetic acid (see below). The H nmr spectrum of **28** revealed two methyl doublets (J = 9.5 cps) at τ 8.74 and 8.84. Unlike **24**, the *cis* and *trans* isomers of **25** (cut 2) could be separated by gpc. Their individual H nmr spectra support the formulation **25**, but a differentiation between the *cis* and *trans* forms has not been made. Thus, the isomer of **25** which has the shorter gpc retention time has resonances at τ 8.47 (three-proton singlet CCH_3), 8.00 (three-proton singlet, SCH_3), 7.53–7.70 (four-proton multiplet, cyclobutylmethylene groups), and 6.55–7.00 (one-proton multiplet, HCCN). The H nmr spectrum of the slower moving isomer of **25** has resonances at τ 8.52, 7.92, 7.43–7.68, and 6.68–7.07 corresponding in area and multiplicity, respectively, with the faster moving isomer.

Photolytic Addition. A solution of **2a** (4.65 g, 0.05 mole) in methanethiol (25 ml) contained in a quartz tube was irradiated with a low-pressure mercury resonance lamp for 40 min. Distillation gave 6.35 g (90%) of product which was identical with the product mixture above as judged by gas chromatographic analysis.

***cis*- and *trans*-1-Methylsulfonyl-3-methylcyclobutanecarbonitriles (28).** To an ice bath cooled, stirred solution of **24** (0.705 g, 0.05 mole) in a mixture of glacial acetic acid (2.5 ml) and acetic anhydride (2.5 ml) was added 30% hydrogen peroxide (1.35 ml). The solution was stirred for 3 hr at 0° and 36 hr at 25°. Distillation at reduced pressure in a micro still gave 0.70 g (81%) of **28** as a colorless oil. *Anal.* Calcd for $C_7H_{11}NO_2S$: N, 8.09; S, 18.48. Found: N, 8.42; S, 18.91.

Addition of *t*-Butyl Mercaptan to 2a. Photolytic Addition. A solution of **2a** (28 g, 0.3 mole) in *t*-butyl mercaptan (150 ml) was irradiated with a low-pressure mercury resonance lamp for 4.5 hr. Analysis using gpc revealed 82% of *cis*- and *trans*-1-*t*-butylmercapto-3-methylcyclobutanecarbonitrile (**26**) and 18% *cis*- and *trans*-3-*t*-butylmercapto-3-methylcyclobutanecarbonitrile (**27**). Distillation gave 42 g (76.5%) of product as two cuts. Cut 1 (**26**) had bp 60° (1 mm). Cut 2 (**27**) had bp 79–95° (1 mm). *Anal.* Calcd for $C_{10}H_{17}NS$: C, 65.54; H, 9.35; N, 7.64; S, 17.46. Cut 1 Found: C, 65.52; H, 9.25; N, 7.48; S, 17.73.

The *cis* and *trans* isomers of **26** were not separable by preparative gpc. The H nmr spectrum of the mixture was consistent with the formulation. Thus, resonances were observed at τ 8.76 and 8.85 (three-proton doublets, J = 6 cps) and 7.05–7.25 (one-proton multiplet) due to the $HCCH_3$ grouping, 8.55 and 8.47 (nine-proton singlet) due to the *cis*- and *trans*-$SC(CH_3)_3$ groupings; and 7.25–8.05 (four-proton multiplet) due to the cyclobutylmethylene groups.

Cut 2 was separated into two components by preparative gpc and each analyzed: Cut 2-1 Found: S, 17.72; N, 7.34. Cut 2-2 Found: S, 17.36; N, 7.48.

The *cis* and *trans* isomers of **27** (cut 2) were separated by gpc, but again a differentiation between the two isomers has not been made. The H nmr spectrum of the component of **27** with the shortest retention time has resonances at τ 8.22 (three-proton singlet) due to the $SCCH_3$ grouping; 8.64 (nine-proton singlet) due to the $SC(CH_3)_3$ grouping, 7.33–7.60 (four proton multiplet) due to the cyclobutylmethylene groups, and 6.45–6.96 (one-proton multiplet) due to the NCCH grouping. The H nmr spectrum of the isomer of **27** displaying the longer retention time on gpc had resonances at τ 8.31, 8.64, 7.15–7.60, and 6.67–7.09 corresponding in area and multiplicity, respectively, with the faster moving isomer.

Radical Initiation. A solution of **2a** (4.65 g, 0.05 mole), *t*-butyl mercaptan (7 ml), and α,α′-azodiisobutyronitrile (0.5 g, 0.003 mole) was heated at reflux for 4 hr and then distilled to give 8.82 g (96.5%) of product, bp 38.2–65° (0.16 mm). Gpc analysis revealed the mixture to have the same composition as that obtained in the photochemical experiment.