for 4 hr in methanol (25 ml) under a nitrogen atmosphere at which time all of the ketone had been converted to tosylhydrazone as shown by tlc. The solution was concentrated to 5 ml, added at 0° to $NaBH_4$ (40 mg) in methanol (10 ml), stirred for 6 hr at room temperature, and heated at reflux for 1 hr. Removal of solvent and glpc at 170° gave *all-trans*-hydrocarbon X, retention time 18 min 18 sec; mass spectrum *m/e* 318.3285 (M^+, $C_{23}H_{42}$).

6,10-Dimethylundecan-2-one (XI). Ketal III (100 mg) was dissolved in 25 ml of ethanol and hydrogenated over 20 mg of 5% Pd/C. Filtration, addition of dilute phosphoric acid, evaporation of the ethanol, addition of water, extraction into ether, and evaporation of the ether gave saturated ketone XI.

Anal. Calcd for $C_{13}H_{26}O$: C, 78.4; H, 13.3. Found: C, 78.7; H, 13.2.

Synthesis and Polymerization of 1-Bicyclobutanecarbonitriles

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Wilmington, Delaware 19898. *Received March 12, 1970*

Abstract: 1-Bicyclobutanecarbonitrile and its bridge deuterated, 2,2-dimethyl, and 2,2,4,4-tetramethyl derivatives have been synthesized *via* base-induced elimination reactions of the corresponding 3-chlorocyclobutanecarbonitriles or 3-cyanocyclobutyl benzenesulfonates. They readily undergo free-radical or anionic homopolymerizations to form high polymers containing 1,3-cyclobutane links in the chain. The tetramethyl polymer also contains ketenimine links, arising from propagation through N and caused by steric hindrance. Facile copolymerizations with the usual vinyl monomers also occurred, again incorporating cyclobutane rings into the polymer chain. The nature of the substituents at the 3 position determined their effect on polymerizability. The 3-methyl- and 2,2,3-trimethyl-1-bicyclobutanecarbonitriles did not polymerize well with radicals, but anionic polymers could be made. The 3-phenyl derivative also did not polymerize well. On the other hand, 1,3-bicyclobutanedicarbonitrile and 3-chloro-1-bicyclobutanecarbonitrile polymerized and copolymerized well under radical or anionic conditions. 1-Bicyclobutanecarbonitrile dimerized in solution at 80° and trimerized at 150°.

Ring-opening polymerization of compounds containing cyclopropane rings has been explored briefly in the past. Cyclopropane itself has not been reported to polymerize well, and 1,1-dimethylcyclopropane[2] and isopropylcyclopropane[3] give only low polymers. Ketley,[4] Takahashi,[5] Lishanskii,[6] and their colleagues have shown that 1,1-dichloro-2-vinylcyclopropane polymerizes. Several bicyclic compounds containing three-membered rings also undergo polymerization. Pinazzi[7] has described low polymers from bicyclo[*n*.1.0]alkanes and spiropentane is claimed to polymerize.[8] Of direct interest in the present connection, Wiberg and coworkers[9] have shown that methyl and ethyl 1-bicyclobutanecarboxylate polymerize when left at room temperature. This series of articles will explore the synthesis and polymerization of selected bicyclic monomers and show that polymerization of bicyclo[*x*.*y*.0] compounds with opening of a strained single bond constitutes a new area of polymer chemistry. The present article deals with 1-bicyclobutanecarbonitriles.

Synthesis of Monomers. Convenient access to most of the required compounds was provided by cycloaddition of allene or 1,1-dimethylallene to acrylonitrile.[10] Conversion of the resulting methylenecyclobutanecarbonitriles to the corresponding 3-methyl-1-bicyclobutanecarbonitriles has already been described by Blanchard and Cairncross.[11] Alkyl groups at the reaction center usually diminish polymerizability, so we wished to prepare the corresponding compounds lacking the 3-methyl substituent. We used oxidation with sodium metaperiodate–osmic acid[12] for 3-methylenecyclobutanecarbonitrile, and the more reactive ozone for the hindered and less-soluble 2,2-dimethyl compound[10] to obtain 3-oxo-1-cyclobutanecarbonitrile and 2,2-dimethyl-3-oxo-1-cyclobutanecarbonitrile. Exhaustive methylation of either of these compounds using sodium hydride and methyl iodide in *N*-methylpyrrolidone solution gave 2,2,4,4-tetramethyl-3-oxocyclobutanecarbonitrile. Reduction of the three ketones by sodium borohydride in water gave the corresponding alcohols in good yields. 3-Hydroxycyclobutanecarbonitrile was smoothly converted by thionyl chloride to 3-chlorocyclobutanecarbonitrile,[13] while the methylated hydroxynitriles were converted to the corresponding benzenesulfonates using benzenesulfonyl chloride in

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[2] H. Pines, W. D. Huntsman, and V. N. Ipatieff, *J. Amer. Chem. Soc.*, 75, 2315 (1953).

[3] W. Naegele and H. Haubenstock, *Tetrahedron Lett.*, 48, 4283 (1965).

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[5] T. Takahashi, I. Yamashita, and T. Miyakawa, *Bull. Chem. Soc. Jap.*, 37, 131 (1964).

[6] I. S. Lishanskii, A. G. Zak, R. F. Fedorova, and A. S. Khachaturov, *Vysokomol. Soedin.*, 7966 (1965).

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[8] J. Brossas, P. Pinazzi, R. Cheritat, J. Brasse, and A. Pleurdeau, French Patent 1,469,121 (1967).

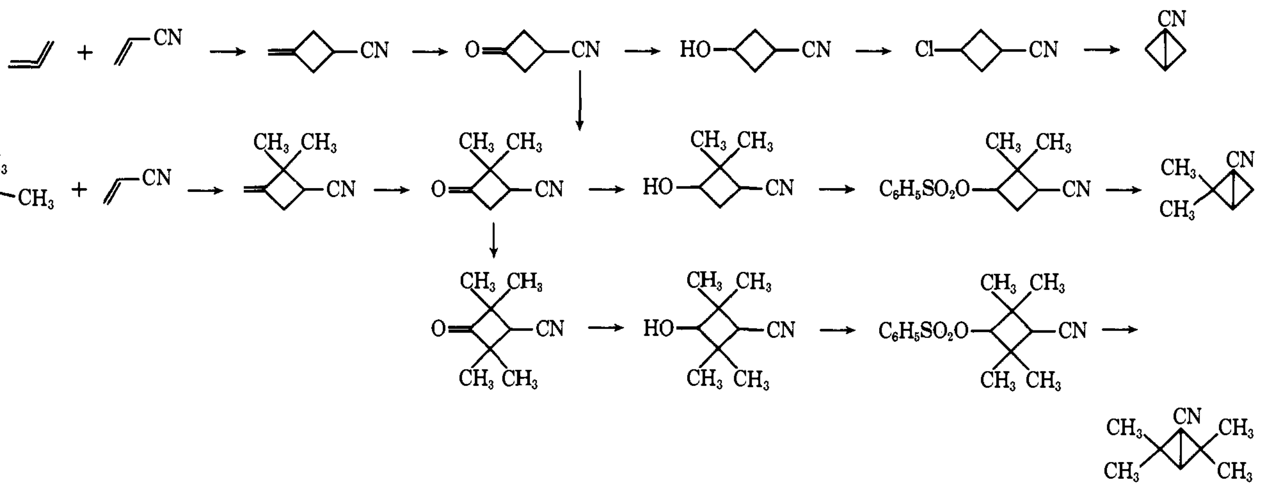
[9] (a) K. B. Wiberg, G. M. Lampman, R. C. Ciula, D. S. Connor, P. Schertler, and J. Lavanish, *Tetrahedron*, 21, 2749 (1965); (b) K. B. Wiberg, *Rec. Chem. Progr.*, 26, 143 (1965).

[10] H. N. Cripps, J. K. Williams, and W. H. Sharkey, *J. Amer. Chem. Soc.*, 81, 2723 (1959). An equal volume of benzene was added to moderate the reaction of allene and acrylonitrile.

[11] E. P. Blanchard and A. Cairncross, *ibid.*, 88, 487 (1966).

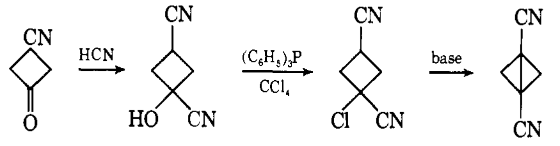
[12] F. F. Caserio, Jr., and J. D. Roberts, *ibid.*, 80, 5837 (1958).

[13] W. A. Neville, D. S. Frank, and R. D. Trepka, *J. Org. Chem.*, 27, 422 (1962).

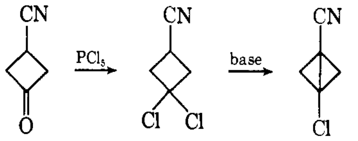


pyridine. Treatment of the chloro- or benzenesulfonyloxy nitriles with strong bases gave the corresponding bicyclobutanes in good yields. Potassium *tert*-butoxide in ether was preferred but sodium hydride or sodium amide in polar solvents could also be used. Although previous investigators have used bromides and iodides in such syntheses, both isomers of the chloronitrile appear to be highly, and about equally, reactive. A recent article[14] described the 2,2,4,4-tetramethylbicyclobutane ester corresponding to our nitrile.

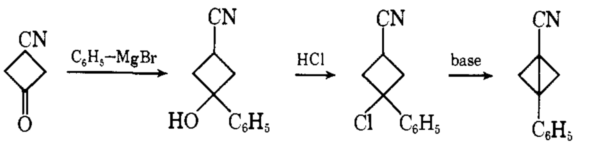
3-Oxocyclobutanecarbonitrile was used to prepare three other bicyclobutanecarbonitriles. Treatment with HCN gave the cyanohydrin which with triphenylphosphine and carbon tetrachloride[15] gave 1-chloro-1,3-cyclobutanedicarbonitrile. This was readily dehydrochlorinated by strong bases to give 1,3-bicyclobutanedicarbonitrile.



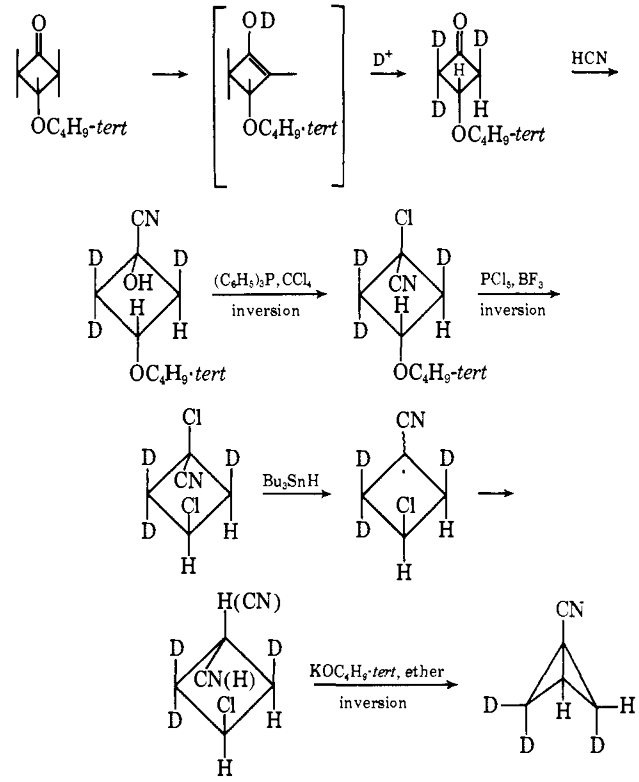
The cyano ketone with PCl$_5$ at 0° reacted preferentially at the carbonyl group to give the 3,3-dichloro derivative, which on dehydrochlorination gave 3-chloro-1-bicyclobutanecarbonitrile.



Treatment of 3-oxocyclobutanecarbonitrile with phenylmagnesium bromide followed by aqueous hydrogen chloride and base gave 3-phenyl-1-bicyclobutanecarbonitrile.



The cycloaddition of ketenes to vinyl ethers[15] was used to prepare an extensively bridge-deuterated 1-bicyclobutanecarbonitrile for future spectroscopic studies of the polymer. 3-*tert*-Butoxycyclobutanone, prepared by cycloaddition of ketene to *tert*-butyl vinyl ether, was almost completely deuterated using NaOCH$_3$ in D$_2$O–THF. The little remaining hydrogen was largely cis to *tert*-butoxy, which could be understood on the basis of preferential deuteration of a flat enol on the less-hindered side. Addition of HCN also occurred with CN$^-$ attacking the less-hindered side. The hydroxyl and *tert*-butoxyl were replaced with complete inversion to give only the *cis*-dichloride. Only the chlorine α to cyano in the dichloronitrile was replaced by 1 equiv of tributyltin hydride, as expected because of resonance stabilization of the intervening radical, to give *cis*- and *trans*-3-chlorocyclobutanecarbonitriles. Reaction of the cis–trans mixture with base led to bridge-deuterated 1-bicyclobutanecarbonitrile. The hydrogen visible in the nmr spectrum, other than the bridgehead, was at the exo position.



Another elimination reaction to form 1-bicyclobutanecarbonitrile was the thermolysis of the sodium salt of 1-cyano-3-chlorocyclobutanecarboxylic acid.

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(14) C. Burridge and D. P. G. Hamon, *Chem. Commun.*, 206 (1968).

(15) J. B. Sieja, *J. Amer. Chem. Soc.*, **93**, 130 (1971).

Table I. Homopolymerizations of 1-Cyanobicyclobutanes

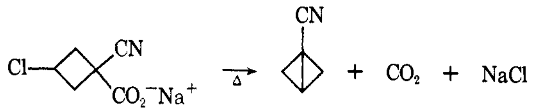
Monomer	Amt, g	Solvent	Initiators	Amt, g	Temp, °C	Time, hr	Yield, %	η_{inh}[a]	Remarks
1-Bicyclobutanecarbonitrile	15.8	H_2O	Standard aqueous slurry		42	9	98	2.63	Dumas nitrogen determination satisfactory for polynitriles. *Anal.* Calcd for ANP: N, 26.40. Found: N, 26.44. The deuterated 1-bicyclobutanecarbonitrile also polymerized to a high yield of high polymer. *Anal.* Calcd for poly(1-bicyclobutanecarbonitrile) $(C_5H_5N)_x$: N, 17.71. Found: N, 17.79
1-Bicyclobutanecarbonitrile	0.95	γ-Butyrolactone	Benzoin methyl ether Isobutyraldehyde	0.04 0.04	28	16	100	1.04	
1-Bicyclobutanecarbonitrile	30	Tetramethylene sulfoxide, 200 ml	Azobisisobutyronitrile	0.1	50	14.5	High	Rigid gel	
1-Bicyclobutanecarbonitrile	30	Tetramethylene sulfoxide, 200 ml	Azobisisobutyronitrile Isobutyraldehyde	0.1 1.0	50	20.3	70	3.00	
1-Bicyclobutanecarbonitrile	1.9	HMPA, 10 ml	1.6% NaH solution in tetramethylene sulfoxide	150 (μl)	−15 60	6 4	79	0.19	
1-Bicyclobutanecarbonitrile	2.4	THF, 27 ml	15% *n*-BuLi solution in hexane	0.4 (ml)	0	2	23	0.21	
3-Methyl-1-bicyclobutanecarbonitrile	1.84	THF, 17.8 ml	15% *n*-BuLi solution in hexane	0.12	0	2	100	1.09 (hexafluoroisopropyl alcohol)	Soluble only in acidic solvents: trifluoroacetic acid, etc.
3-Methyl-1-bicyclobutanecarbonitrile	1.84	THF, 17.8 ml	Sodium naphthalene in THF	1.0 (ml)	0 25	1 18	100	0.37 (trifluoroacetic acid)	
2,2-Dimethyl-1-bicyclobutanecarbonitrile	0.8	None	Azobisisobutyronitrile Black light (max at 3500 Å, Pyrex filter)	Trace	Room temp	17	High	>1.0	
2,2-Dimethyl-1-bicyclobutanecarbonitrile	35	Water	Standard aqueous slurry		50	2.5	30	1.16	Poor conversion due to low water solubility of monomer. *Anal.* Calcd for $(C_7H_9N)_x$: C, 78.46; H, 8.47; N, 13.07. Found: C, 76.11, 76.23; H, 8.63, 8.68; N, 13.66; 13.58
2,2,3-Trimethylbicyclobutanecarbonitrile	6.0	THF, 45 ml	15% *n*-BuLi in hexane	2.0 (ml)	−78 0 Room temp	1 3 16	48	0.06	
2,2,4,4-Tetramethyl-1-bicyclobutanecarbonitrile	1.0	DMSO, 4 ml	Azobisisobutyronitrile Isobutyraldehyde	0.07 0.3 (ml)	55	16	60	0.79 in HFIPA	Gives a slurry; polymer insoluble DMSO. Standard aqueous slurry recipe gives no polymer; monomer insoluble in water. *Anal.* Calcd for N: 10.36. Found: N, 10.0. Contains ketenimine link by ir. Steric hindrance causes propagation at N
2,2,4,4-Tetramethyl-1-bicyclobutanecarbonitrile	1.4	γ-Butyrolactone, 5 ml	Benzoyl peroxide Isobutyraldehyde	0.10 0.3 (ml)	60	5.6	30	1.13 in HFIPA	Polymer shows ketenimine structure by ir, so not due to azo initiator
3-Chlorobicyclobutane-1-carbonitrile	1.14	H_2O, 5 ml	Standard aqueous slurry		50	1	37		Polymer insoluble in all organic solvents; soluble in H_2SO_4
3-Chloro-1-bicyclobutanecarbonitrile	1	*N*-Methylpyrrolidone, 5 ml	Azobisisobutyronitrile		60	24	10		
1,3-Bicyclobutanedicarbonitrile	2	DMSO, 10 ml	Azobisisobutyronitrile		60	3	83	0.73 (H_2SO_4)	Polymer insoluble in all organic solvents. Soluble in H_2SO_4

1,3-Bicyclobutanedicarbonitrile	2	H_2O	Standard aqueous emulsion	50	2	40
1,3-Bicyclobutanedicarbonitrile	1	THF	15% BuLi solution in hexane	0	4.5	60

[a] 0.1% in DMF unless otherwise indicated.

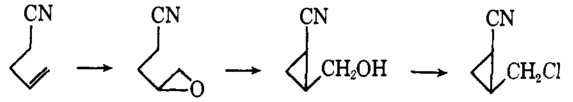
Table II. Copolymerizations of 1-Cyanobicyclobutanes with Vinyl Monomers and with Each Other

Monomer	Amt, g	Comonomer	Amt, g	Solvent	Initiators	Amt, g	Temp, °C	Time, hr	Yield	η_{inh}[a]	Analysis, %
1-Bicyclobutanecarbonitrile	2.5	Acrylonitrile	7.5		Stand. emul rec		50	2	75%	2.34	*Anal.* Found: C, 69.77, 69.81; H, 5.64, 6.00; N, 23.92, 24.17 corresponding to 75 AN/25 CBB
1-Bicyclobutanecarbonitrile	5.0	Acrylonitrile	5.0		Stand. emul rec		50	2	76%	2.92	*Anal.* Found: C, 71.93, 72.19; H, 6.20, 6.20; N, 21.91, 22.04 corresponding to 45–48 AN/55–53 CBB.
1-Bicyclobutanecarbonitrile	7.5	Acrylonitrile	2.5		Stand. emul rec		50	2	76%	2.94	*Anal.* Found: C, 73.39, 73.52; H, 6.13, 6.13; N, 19.59, 19.81 corresponding to 23 AN/77 CBB
1-Bicyclobutanecarbonitrile	4.0	Styrene	99.0	Toluene, 1.0 l.	Azobisisobutyronitrile	1.0	80	24	33.3 g	0.06	Infrared spectrum shows polystyrene, CN group. *Anal.* Found: N, 0.68, 0.89 corresponding 96.2 S/3.8 CBB (by wt.)
1-Bicyclobutanecarbonitrile	4.0	Methyl methacrylate	95.0	H_2O	3% polymethacrylic acid Dipotassium phosphate Azobisisobutyronitrile CH_3OH	8.6 4.3 1.5 50.0 (ml)	80	2.5	80.6 g	2.44	Infrared spectrum shows poly MMA, CN group. *Anal.* Found: N, 0.74, 0.64 corresponding to 95.8 MMA/4.2 CBB.
1-Bicyclobutanecarbonitrile	2.88	Vinyl chloride	1.91	DMSO, 10 ml	Azobisisobutyronitrile	0.01	50	16	3.05 g	0.70	*Anal.* Found: C, 67.57, 67.63, 67.21; H, 5.71, 6.16, 6.21; N, 13.58; Cl, 11.24 corresponding to 20–22 VCl/80–78 CBB
1-Bicyclobutanecarbonitrile	2.88	Vinyl chloride	3.94	DMSO, 10 ml	Azobisisobutyronitrile	0.01	50	16	3.10 g	0.37	*Anal.* Found: C, 62.37, 62.76; H, 5.68, 5.85; N, 11.33; Cl, 18.67 corresponding to 33–35 VCl/67–65 CBB
1-Bicyclobutanecarbonitrile	11.4	2,2-Dimethyl-1-bicyclobutanecarbonitrile	10.4	H_2O, 70 ml	Stand. aqueous slurry		50	2	12.45 g after reprecipitation	4.00	*Anal.* Found: C, 74.06, 74.22; H, 7.08, 7.33; N, 16.15, 16.15 corresponding to 33 DMeCBB/67 CBB
Bicyclobutanecarbonitrile	3	Isobutylene	2.7	DMSO, 10 ml	Azobisisobutyronitrile	0.10	50	16	2.74 g	0.77	*Anal.* Found: C, 76.71, 75.80, 77.28; H, 7.92, 7.57, 7.91; N, 14.79 corresponding to 16–20% isobutylene
Bicyclobutanecarbonitrile	1.5	Methyl methacrylate	1.53	DMSO, 10 ml	Azobisisobutyronitrile Isobutyraldehyde	0.10 1.89 (ml)	50	16	2.50 g	0.32	*Anal.* Found: C, 65.67, 65.92; H, 6.80, 6.69; N, 8.15, 8.29 corresponding to 53–63% MMA.
3-Methylbicyclobutanecarbonitrile	9.0	SO_2	25 (ml)	None	None		−78	1.6	High	0.21	Polymer ground dry and analyzed. Calcd: S, 20.38. Found: S, 20.18. Ir shows polysulfinate structure (doublet at 8.6 and 8.8, no absorption at 7.6 μ), not polysulfone
2,2,3-Trimethyl-1-bicyclobutanecarbonitrile	6.0	3-Methyl-1-bicyclobutanecarbonitrile	4.5	THF, 90 ml	15% n-BuLi in hexane	15 (ml)	−78 0 Room temp	1 3 16	96%	0.06	
2,2,4,4-Tetramethyl-1-bicyclobutanecarbonitrile	0.15	Acrylonitrile	0.85	DMSO, 4 ml	Azobisisobutyronitrile	0.07	55	16	75% (stays in solution)	0.45	*Anal.* Found: N, 23.90 corresponding to 16 TeMeCBB/84 AN



However, thermolysis of 3-cyanocyclobutyl acetate led only to vinyl acetate and acrylonitrile.

The foregoing syntheses of the bicyclobutane ring all involved a 1,3-elimination reaction of a cyclobutane derivative. It was of interest to determine whether the bicyclic structure could be constructed by fusing a new cyclopropane ring to one already present. Epoxidation of 4-pentenenitrile gave the epoxide which on treatment with sodium amide in refluxing tetrahydrofuran gave only 2-(hydroxymethyl)cyclopropanecarbonitrile. Thionyl chloride transformed this without rearrangement into 2-(chloromethyl)cyclopropanecarbonitrile, which, when treated with strong base, gave no 1-bicyclobutanecarbonitrile under conditions where 3-chlorocyclobutanecarbonitrile gave high yields.



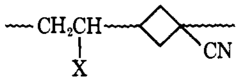
Properties. 1-Bicyclobutanecarbonitriles were colorless liquids, distillable below 1 mm. As discussed further below, they may be polymerized by light and/or air and undergo thermal transformations, but they could be stored almost indefinitely at −80°. At this temperature they were all crystalline; 1-bicyclobutanecarbonitrile melted at −27°.

Homopolymerization. The bicyclobutanecarbonitriles which lack alkyl or aryl substituents at the 3 position readily underwent radical-initiated polymerizations in solution in the presence of chain-transfer agents, in suspension, or in emulsion to give high molecular weight polymers. Qualitatively, bicyclobutanecarbonitrile was as reactive as acrylonitrile. Methyl groups at C-2 and C-4 did not slow the rate of polymerization appreciably.

Anionic polymerizations of these monomers were carried out using butyllithium in tetrahydrofuran, but it was more difficult to obtain high molecular weight, colorless products by this mode of initiation. The 3-methyl-1-bicyclobutanecarbonitriles polymerized under these conditions.

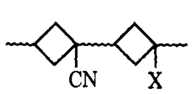
The homopolymer results are given in Table I.

Copolymerizations. 1-Bicyclobutanecarbonitrile copolymerized readily with various vinyl monomers such as styrene and methyl methacrylate under radical conditions to give a new class of high molecular weight copolymers. This represents a new method for incorporating rings into chains of carbon atoms. The polymerizations are described in Table II.



Moreover, 1-bicyclobutanecarbonitriles copolymerized with each other and with other bridgehead-substituted[16] bicyclobutanes to give another new class of high molecular weight copolymers.

The infrared spectrum of the polymers was compatible only with a 1,3-cyclobutane ring: no evidence for cyclopropyl hydrogens could be seen. Also Dr. R. C. Ferguson detected no cyclopropyl hydrogens using a 220-MHz nmr spectrometer. The observation of two methyl nmr signals in solutions of the homopolymer of 3-methyl-1-bicyclobutanecarbonitrile leads to the conclusion that both cis and trans links are present.

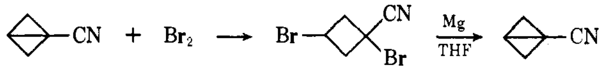


Poly-1-bicyclobutanecarbonitrile melts at 370°, followed immediately by decomposition according to DTA, and stays white and unchanged well above 300° in air. The other cyanopolymers are also high melting (>300°) and thermally stable. Poly-1-bicyclobutanecarbonitrile showed a low degree of crystallinity by X-ray analysis. The cyanopolymers dissolved in polar liquids such as *N,N*-dimethylacetamide, γ-butyrolactone, and *N*-methylpyrrolidone.

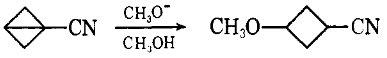
Poly-3-methyl-1-bicyclobutanecarbonitrile possessing an inherent viscosity of 1.0 was amorphous. It was soluble in trifluoroacetic acid and hexafluoro-2-propanol.

Chemical Reactions of 1-Bicyclobutanecarbonitriles. Blanchard and Cairncross have shown that 3-methyl-1-bicyclobutanecarbonitrile exhibits remarkably diverse reactions. We have briefly explored selected reactions with 1-bicyclobutanecarbonitrile.

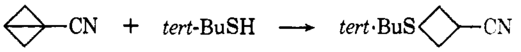
Addition of bromine to 1-bicyclobutanecarbonitrile gave rapidly and quantitatively a 3:1 mixture of *cis*- and *trans*-dibromides. Treatment of this mixture with magnesium in THF regenerated a good yield of 1-bicyclobutanecarbonitrile.



Nucleophiles reacted at the 3 position as expected. Thus, methoxide added to 1-bicyclobutanecarbonitrile to give a 2:1 isomer mixture of 3-methoxycyclobutanecarbonitrile.



Free radicals other than growing polymer chains also added smoothly to the strained central bond of 1-bicyclobutanecarbonitrile. Treatment with *tert*-butyl mercaptan gave approximately equal amounts of *cis*- and *trans*-3-*tert*-butylthiocyclobutanecarbonitrile. At most, 6.5% of the product formed by addition of thiyl radical to the 1 position was observed, in contrast to the results of Blanchard and Cairncross[11] on 3-methyl-1-bicyclobutanecarbonitrile who found addition of thiyl radical predominantly at the 1 position.



Electrophiles added only sluggishly to 1-bicyclobutanecarbonitrile. Thus, hexafluoroacetone, which reacted vigorously with the 3-methyl derivative,[11] barely reacted with 1-bicyclobutanecarbonitrile. It seems reasonable that the 3-methyl substituent stabilizes positive charge in several of the reactions studied previously.

Heating 1-bicyclobutanecarbonitrile neat or in solution at around 80°, in either case in the presence of a

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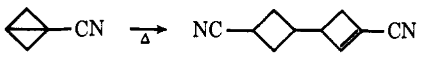
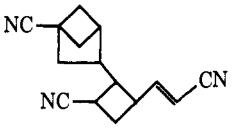
[16] H. K. Hall, Jr., C. Smith, E. Blanchard, Jr., S. Cherkofsky, and J. Sieja, *J. Amer. Chem. Soc.*, 93, 121 (1971).

free-radical inhibitor, gives the tail-to-tail dimer. At higher temperatures, approximately 150°, the formation



of a trimer predominates. The structure, on the basis of ir, nmr, and mass spectra, is thought to be



Experimental Section

Routine Procedures. The following analytical gc columns were used: A, 1 *M* 20% butanediol succinate on 60–80 NAW Chromosorb W at 175°; B, 2-ft 10–20% silicone gum nitrile XE-60 on 60–80 Gas Chromosorb R at 150°; C, 1 *M* 20% fluorosilicon on 60–80 Gas Chromosorb R; D, capillary column, Squalane. A tricyanoethoxypropane column was also found useful with nitriles.

The percentage composition was taken directly from the areas under the peaks.

A wet test meter from American Meter Co. was used to measure H_2 evolution.

Capillary melting points were taken on a Thomas–Hoover apparatus and were corrected by use of standard substances. Melting points when given to 0.1° or mixture melting points were taken on a Thomas–Hoover apparatus whose thermometer had been calibrated against the supplier's standard samples. Those reported to 1° were taken on a Fisher–Johns block.

Nmr spectra were interpreted from intensities (±15%) and reference chemical shifts. Deuteration was used to locate hydroxyls. Because of cis–trans mixtures and complex spectra generally of cyclobutanes, spin–spin splitting was interpretable in only a few cases. The numbers given for multiplets are the centers of the integration trace for the given envelope. All values are in δ units. Spectra were usually run in $DCCl_3$ solution on a Varian A-60 spectrometer. Abbreviations used are: (s) singlet; (d) doublet; (t) triplet; (q) quadruplet; (p) pentuplet; (m) multiplet.

Infrared spectra were determined routinely using a Perkin-Elmer No. 21 instrument. Abbreviations used are: s, strong; m, medium; w, weak.

3-Oxocyclobutanecarbonitrile. A 5-l., four-necked flask fitted with an efficient motor-driven stirrer, an air-cooled reflux condenser, and a thermometer was immersed in a large pail filled with ice. In it were placed 260 g (2.79 mol) of 3-methylenecyclobutanecarbonitrile,[10] 3.5 l. of water, and 250 ml of ether. The mixture was cooled with stirring to 5–8° and 0.50 g of osmic acid (*caution:* very poisonous) was added and rinsed in with a little water. Over 4–5 hr, sodium metaperiodate (1360 g, 6.37 mol) was added in small portions with continued stirring at 5–8°. A gentle nitrogen bleed was applied and the mixture was stirred overnight while the ice was gradually allowed to melt in the pail and the mixture came to room temperature. At this point, the reaction mixture should be a slurry of white salts in an aqueous phase, and no organic phase should be present. When necessary, a little additional water was added to get a filterable slurry. The mixture was filtered, and the salts were washed thoroughly with chloroform and discarded. A continuous liquid–liquid extractor was set up, and the water extract was extracted continuously overnight with the chloroform. The chloroform extract was boiled down and was heated on the steam bath under house vacuum and finally under aspirator vacuum to remove the chloroform. The clear, dark-gray residue was dissolved in 800 ml of tetrahydrofuran, 10 ml of mercury (*caution:* add carefully to avoid breaking the flask) and 17 g of silver carbonate were added, and the mixture was stirred under reflux overnight with a motor-driven stirrer. The flask was wrapped with aluminum foil to protect it from light. The mixture was filtered and the salts and mercury rinsed with tetrahydrofuran. The tetrahydrofuran was evaporated and the residue was distilled through a Claisen head using an oil bath, magnetic stirrer, and full pump vacuum. The product distilled smoothly at 58–62° (0.30 mm) and solidified as a white solid in the receiver. At the very end, the temperature rose to 71° and a yellow solid began coming over. The distillation was terminated before it entered the receiver. The ketone weighed 196 g (74%) and was rather unstable. It should be stored under nitrogen in a freezer. It melted at 49.0–50.0° (lit.[10] mp 50°); ir 5.55 (C=O), 4.45 μ (–CN); nmr δ 3.47 (m).

3-Hydroxycyclobutanecarbonitrile. To a stirred solution of 2.25 g (0.060 mol) of sodium borohydride in 50 ml of water was added with stirring a warm slurry of 19.0 g (0.20 mol) of 3-oxocyclobutanecarbonitrile in 50 ml of water. The reaction was mildly exothermic and judicious ice cooling was used to maintain the temperature at 35°. After the addition was complete, the solution was stirred at room temperature for 4 hr and was extracted continuously overnight with chloroform. The chloroform extract was dried and distilled to give 16.79 g (86.5%) of colorless liquid: bp 70–71° (0.33 mm); ir 2.95 (–OH), 4.46 μ (–CN); nmr δ 2.62 (m, 5 H, ring protons), 4.27 (m, 2 H, C*HOH*).

Anal. Calcd for C_5H_7ON: C, 61.84; H, 7.27; N, 14.42. Found: C, 61.52; H, 7.26; N, 14.18.

The compound was a 70:30 cis–trans mixture as established by gas chromatography on column A.

3-Chlorocyclobutanecarbonitrile. A 500-ml four-necked flask was equipped with a mechanical stirrer, thermometer, 250-ml addition funnel without a pressure equalizing side arm, and an efficient condenser. From the top of the condenser was arranged in series an ice-cooled trap, a calcium sulfate drying tower, a Nujol bubbler, and a gas scrubber. To the flask was added 97 ml (1.36 mol) of thionyl chloride. To the funnel was added a solution of 5 ml of dimethylformamide in 97 g (1 mol) of 3-hydroxycyclobutanecarbonitrile. The contents of the funnel were added to the flask over 45 min at about 55°. The mixture was then heated to 100–105° for 1 hr until no more sulfur dioxide was evolved. The mixture was cooled and distilled to give 93.9 g (81%) of product containing trace amounts of DMF and about 1% of a low boiler: bp 48–51° (1.9 mm); 98° (28 mm); ir 4.44 μ (–CN); nmr δ 2.87 (m, 5 H, ring protons), 4.68 (m, 1 H, CHCl).

Anal. Calcd for C_5H_6NCl: C, 51.96; H, 5.23; Cl, 30.68. Found: C, 52.04; H, 5.59; Cl, 30.70.

The purity was 97.9% as established by gas chromatography on column A. Column B resolved this to an 83:17 mixture of cis–trans isomers.

1-Bicyclobutanecarbonitrile. A 1-l. glass flask fitted with a stirrer, condenser, and nitrogen bleed was dried with a heat gun and cooled under nitrogen. Under a nitrogen atmosphere, there was placed in the flask 62.4 g (0.54 mol) of 3-chlorocyclobutanecarbonitrile and 600 ml of ether. The mixture was stirred and cooled to 12°, at which temperature 66.0 g (0.588 mol) of potassium *tert*-butoxide was added portionwise over 8 min. Stirring at 12° was continued for 15 min. About 20 g of powdered solid carbon dioxide was added, and then water was added 1 ml at a time until the salts coagulated (not >5 ml). About 10 g of magnesium sulfate and 0.40 g of phenothiazine were added. The reaction mixture was filtered cold under nitrogen pressure through diatomaceous earth using a coarse sintered-glass filter, followed by three rinses of fresh ether. Ether was evaporated from the filtrate under house or gentle water vacuum at 35–45°. The residue along with additional phenothiazine was redried if necessary and transferred to a distillation flask fitted with a Vigreux head. The remaining ether was removed with the bath at 25° without cooling water in the condenser. When the pressure decreased to 8 mm, cooling of the condenser with water and of the receiver with ice–methanol was begun. Almost all the *tert*-butyl alcohol was removed in this way. The distillate was examined by gc to ensure that no bicyclobutanecarbonitrile was present. When it was, the inhibitor was added, alcohol was evaporated, and the residue was returned to the distillation flask. With the bath at <35°, about 35 g (82.0%) of bicyclobutanecarbonitrile of high purity distilled at <1 mm into a Dry Ice chilled receiver: ir 4.44, 4.49 (–CN), 3.19 3.25, 3.38 μ (C–H); nmr δ 1.23 (m, 2 H, endo H's), 2.22 (m, 2 H, exo H's), 2.52 (m, 1 H, bridgehead H) (bp 38° (4 mm) ≈99.5% pure on column C).

Anal. Calcd for C_5H_5N: C, 75.92; H, 6.37; N, 17.71; mol wt, 79.1. Found: C, 76.14; H, 6.64; N, 17.41; 17.49 (Pregl); mol wt 75 (cyroscopic in benzene).

Water wash is best avoided in the work-up. 1-Bicyclobutanecarbonitrile is either fairly soluble in water or reacts with excess alkali. Conventional addition, wherein chloronitrile is added to excess base, causes the addition of *tert*-butoxide to 1-bicyclobutanecarbonitrile. Inverse addition as described gives much higher yields, and a slight excess of base can be tolerated.

1-Cycanocyclobutane-1-carboxylic Acid. A quantity of 30.6 g (0.2 mol) of 1-cyano-1-carbethoxycyclobutane[17] was stirred at room temperature with a solution of 8.5 g (0.21 mol) of sodium hydroxide in 200 ml of water. After 4 hr the solution was completely homogeneous. The aqueous solution was extracted with ether to remove any neutral impurities, and these extracts were discarded. The aqueous solution was acidified with concentrated hydrochloric acid, then extracted (six 100-ml portions) with ether. The ether extracts were dried and evaporated (using vacuum pump to remove last traces of solvent) to give 24.2 g (97%) of white crystals: mp 61–66°; ir 4.48 (–CN), 5.88 (C=O), 3–4 μ (OH of acid); nmr δ 2–3 (m, 6 H, all ring H's), 10.8 (s, 1 H, acid H).

Anal. Calcd for $C_6H_7NO_2$: C, 57.59; H, 5.64; N, 11.20. Found: C, 57.45; H, 5.63, 5.79; N, 11.15, 11.17.

3-Chloro-1-cyanocyclobutane-1-carboxylic Acid. A solution of 16.25 g (0.13 mol) of 1-cyanocyclobutane-1-carboxylic acid in 75 ml of water was stirred magnetically under a sunlamp at room temperature while chlorine was bubbled through the solution for ~7 hr. The two-phase mixture was then flushed with nitrogen until colorless. The mixture was extracted (six 100-ml portions) with chloroform, and the chloroform extracts were dried, filtered, and evaporated to give 19 g (91%) of white paste. This material was recrystallized from 40 ml of benzene to give 6.7 g (32%) of white crystals: mp 122–151.5°; ir 3–4 (OH of acid), 5.77 (C=O of acid), 4.46 μ (–CN); nmr δ 2.6–3.5 (m, 4 H, CH_2's), 4.7 (p, 1 H, CHCl), 12.1 broad singlet (1 H), acid H.

Anal. Calcd for $C_6H_6NO_2Cl$: C, 45.20; H, 3.79; N, 8.78; Cl, 22.20. Found: C, 45.52; H, 3.80; N, 8.57; Cl, 22.55.

Decarboxylation of 3-Chloro-1-cyanocyclobutane-1-carboxylic Acid. A 0.32-g sample of 3-chloro-1-cyanocyclobutane-1-carboxylic acid was heated at 165–170° in a Pyrex tube under nitrogen for 1 hr. Evolution of gas began at about 150° and after 1 hr at 170° had stopped completely. The gc of the amber liquid showed three peaks, two of which accounted for 95% of the area and corresponded to both isomers of 3-chlorocyclobutanecarbonitrile by retention time. The third, minor peak—about 5%—corresponded to 3,3-dichlorocyclobutanecarbonitrile, which probably resulted from the presence of a small amount of dichlorination product in 3-chloro-1-cyanocyclobutane-1-carboxylic acid. Neither isomer of 2-chlorocyclobutanecarbonitrile was observed by gc analysis on column B. The liquid was distilled in a microdistillation set-up to give 0.12 g (50%) of colorless 3-chlorocyclobutanecarbonitrile, bp 90–105° (13 mm).

Sodium 3-Chloro-1-cyanocyclobutane-1-carboxylate. A quantity of 1.81 g (0.0113 mol) of 3-chloro-1-cyanocyclobutane-1-carboxylic acid dissolved in 5 ml of ethanol and 20 ml of water was titrated with 10% sodium hydroxide solution to a pH of 8–9 (~4.4 ml required). The aqueous solution was then evaporated to a constant weight of 2.05 g (100%) of off-white powder, mp 96–104°, vigorous evolution of gas at 135°.

Decarboxylative Elimination of Sodium Chloride from Sodium 3-Chloro-1-cyanocyclobutane-1-carboxylate. A microdistilling tube containing 0.9 g (5 mmol) of sodium 3-chloro-1-cyanocyclobutane-1-carboxylate was evacuated to 0.1 mm and the receiver was chilled in Dry Ice. The solid was heated at 170–180° for 1 hr. The material which distilled was 0.1–0.15 g (25–38%) of colorless liquid. The gc (column B) and nmr spectra showed this material to be a 3:1 mixture of 1-bicyclobutanecarbonitrile and 3-chloro-1-bicyclobutanecarbonitrile. The latter compound apparently was formed from a small amount of sodium 3,3-dichloro-1-cyanocyclobutane-1-carboxylate present in the starting material.

Thermolysis of 3-Cyanocyclobutyl Acetate. 3-Cyanocyclobutyl acetate was prepared by acetylation of 3-hydroxycyclobutanecarbonitrile.

Anal. Calcd for $C_7H_9NO_2$: C, 60.42; H, 6.52; N, 10.07. Found: C, 60.50; H, 6.24; N (modified Dumas), 9.97, 9.68.

This material was pyrolyzed over 20 mesh quartz in an Inconel pyrolysis tube at temperatures from 200 to 500°. The main products were vinyl acetate and acrylonitrile. Acetaldehyde and carbon dioxide were also noted. A little higher boiling material containing carbonyl, cyano, and olefinic groups appeared. 1-Bicyclobutanecarbonitrile could not be detected.

4,5-Epoxypentane-1-nitrile. *m*-Chloroperbenzoic acid (237 g, ~1.1 mol) and dry chloroform (1000 ml) were mixed with stirring at 18°. 4-Pentene-1-nitrile (74.1 g, 0.913 mol) was added, causing the temperature to increase to 35°. The solution was cooled in an ice bath for 1 hr; however, upon removal of the ice bath the temperature increased to 42°. After having been stirred overnight, the solution was filtered and the precipitate washed with 100 ml of chloroform. The combined filtrates were concentrated on a rotary evaporator, diluted with 100 ml of benzene, cooled, refiltered, and concentrated. The crude product was distilled (86–103°, 0.5–2 mm) in a molecular still until a solid began to sublime. The product was redistilled in a spinning-band column to give 59.7 g of epoxide: bp 47–49° (0.25–0.4 mm) (67.3% yield); ir 4.45 μ (–CN); nmr δ 1.9–2.6 (m).

Anal. Calcd for C_5H_7ON: C, 61.84; H, 7.27. Found: C, 61.69, 62.00; H, 7.22, 7.41.

2-(Hydroxymethyl)cyclopropanecarbonitrile. Sodium amide was prepared from 2.3 g (0.1 mol) of sodium and 200 ml of liquid ammonia. The liquid ammonia was poured from the cylinder into a 250-ml, three-necked flask equipped with a mechanical stirrer and a Dry Ice condenser. A small portion of the sodium metal was added to give a blue solution. A crystal of $Fe(NO_3)_3 \cdot H_2O$ was added after 0.5 min which turned the solution dark gray. The remaining sodium was added over 15 min, and excess ammonia was allowed to evaporate while it was gradually replaced with 200 ml of THF. The solution was allowed to stand overnight. The last traces of ammonia were driven off by heating the solution to a gentle reflux with a gentle nitrogen bleed.

4,5-Epoxypentanenitrile (9.71 g, 0.10 mol) was added to the sodium amide (0.10 mol) over 45 min with rapid evolution of ammonia. The solution was stirred for another 25 min, until weak ammonia evolution indicated complete reaction. An ice bath was used to cool the solution to 25°, and 75 ml of saturated ammonium chloride was added with stirring. The organic layer was separated. The aqueous layers were extracted with five 100-ml portions of ether; the extracts were dried and concentrated on a rotary evaporator. The crude product was distilled in a molecular still to yield 4.72 g (48.6%) of 2-(hydroxymethyl)cyclopropanecarbonitrile: bp 73° (0.20 mm); ir 2.95 (–OH), 4.45 μ (CN); nmr δ 1.27 (m, 4 H, ring protons), 3.48 (m, 2 H, CH_2OH), 3.99 (s, 1 H, –OH). The compound consisted of two isomers to the extent of 18.4 and 80.3% on column C.

Anal. Calcd for C_5H_7ON: N, 14.42. Found: N, 14.07, 14.39.

A second experiment on an 0.41 *M* scale gave a 78.3% yield of 2-(hydroxymethyl)cyclopropanecarbonitrile, bp 92° (0.7 mm). Gc analysis (column C) showed it to be 18.4% of one isomer and 80.3% of the other.

Potassium *tert*-butoxide in ether gave a low yield of the same hydroxynitrile.

2-(Chloromethyl)cyclopropanecarbonitrile. 2-(Hydroxymethyl)cyclopropanecarbonitrile (4.0 g, 0.04 mol) was added with stirring to 12 ml of thionyl chloride at 0°. The heterogeneous mixture was heated at 80° for 1.0 hr with stirring and then poured onto 100 g of ice. The crude mixture was extracted with two 50-ml portions of methylene chloride, washed with one 50-ml portion of water and two 50-ml portions of saturated $NaHCO_3$, and dried over $MgSO_4$. After concentration on the rotary evaporator the crude product was distilled to give 2.4 g (50.3%) of product; bp 95–99° (11 mm); ir 4.45 μ (CN); nmr δ 1.39 (m, 4 H, ring H's), 3.51 (m, 2 H, CH_2Cl).

Anal. Calcd for C_5H_6NCl: Cl, 30.68; N, 12.10. Found: Cl, 30.44; N, 11.39, 11.47. Experiments with thionyl chloride and pyridine in boiling chloroform and with thionyl chloride in DMF gave the same chloride in good yields.

No separation into isomers was achieved by use of a variety of gc columns.

Reaction of 2-(Chloromethyl)cyclopropanecarbonitrile with Bases. Reaction of the above chloride with potassium *tert*-butoxide or sodium amide in tetrahydrofuran gave only a little olefin and a little recovered chloride. No 1-bicyclobutanecarbonitrile was observed, although the conditions are known to convert 3-chlorocyclobutanecarbonitrile to 1-bicyclobutanecarbonitrile in high yield. Of incidental interest was the fact that the recovered chloride had an altered spectrum from that of starting material, indicating selective destruction of one isomer.

Polymerization of 1-Bicyclobutanecarbonitrile in an Aqueous Slurry. To a stirred mixture of 15.8 g of 1-bicyclobutanecarbonitrile in 100 ml of degassed distilled water, blanketed under nitrogen, were added a solution of 0.100 g of potassium persulfate in 3 ml of water and a solution of 0.0344 g of sodium bisulfite in 1 ml of water. Polymerization as noted by opalescence and curd formation began immediately. The mildly exothermic reaction, maximum temperature 42°, proceeded through a soft mush, a soft sheet on the walls, a solid sheet, and a thick white slurry. Total

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(17) (a) W. J. Bailey and J. J. Daly, Jr., *J. Amer. Chem. Soc.*, 81, 5397 (1959); (b) Dictionary of Organic Compounds, Oxford University Press, London, 1967, p 772.

reaction time was 9 hr. The slurry was filtered and washed with water. It was blended with 400 ml of water, filtered, and washed. This was repeated with water and then with methanol. Drying under nitrogen in a vacuum oven at 80° gave 15.4 g (98%) of white polymer, η_{inh} (*N*-methylpyrrolidone) 2.63.

Anal. Calcd for $(C_5H_5N)_x$: N, 17.71. Found (Dumas): N, 17.79.

The polymer was soluble in hexafluoro-2-propanol, in sulfuric acid, and in dialkyl amides, sulfoxides, and sulfones. By DTA it melted at 377°, followed by exothermic decomposition.

The infrared spectrum of the polymer was consistent with the assigned structure. No indication of a strained cyclopropane C–H bond was seen. The CH center of gravity, 2955 cm^{-1}, was too high for aliphatic C–H and CH_2, but low for a cyclopropane, and was consistent with a four-membered ring. The nitrile frequency was also consistent. Similarly the 220-Mcps nmr spectrum showed only 1,3 linkages to be present.

Bridge Deuteration of 3-*tert*-Butoxycyclobutanone. A mixture of 60 g of ketone, 300 ml of D_2O, 50 ml of THF, and 400 mg of $NaOCH_3$ was stirred for 30 min. The mixture was extracted with ether, dried over $MgSO_4$, filtered, and distilled to give 17.5 g of deuterated ketone, bp 57° (6 mm), which analyzed for >95% tetradeuteration. No deuterium exchange at the 3 position was detected.

Bridge-Deuterated 1-Chloro-3-*tert*-butoxycyclobutanecarbonitrile. A mixture of 35 g of deuterated ketone, 10 g of HCN, and 50 μl of triethylamine was stirred at 35–40° for 2 hr. The solution was taken up in 252 ml of CCl_4 and 77.3 g of triphenylphosphine was added. The solution was heated to 60° and allowed to cool to 40° with the mantle in place. It was then heated at 75° for 2 hr. Triphenylphosphine oxide precipitated gradually. The solution was evaporated and the solids were extracted with ether. A total of 17 g of chloro derivative (bp 45° at 0.25 mm) was distilled from the ether extract. By heating the residual solid under reduced pressure, an additional 16 g of product was obtained.

Bridge-Deuterated 1,3-Dichlorocyclobutanecarbonitrile. The deuterated 1-chloro-3-*tert*-butoxynitrile, 32.6 g, was added to 51 g of PCl_5 followed by 300 μl of BF_3·etherate. The mixture was heated to 40° (mild exothermic reaction), an additional 15 g of PCl_5 was added, and the reaction was heated to reflux for 4.5 hr. The cooled reaction mixture was decomposed with ice and water and the product extracted into ether, dried, and distilled. Careful redistillation gave 15.1 g of bridge-deuterated 1,3-dichlorocyclobutanecarbonitrile, bp 74–77° (18 mm) $n^{26}\text{D}$ 1.476–1.478. Nmr showed 90–95% tetradeuteration.

3-Chlorocyclobutanecarbonitrile by Reduction of 1,3-Dichlorocyclobutanecarbonitrile. A mixture of 4.5 g (0.03 mol) of 1,3-dichlorocyclobutanecarbonitrile, 9.7 g of tributyltin hydride, and $\sim$10 mg of Vazo was heated with magnetic stirring in an oil bath. When the temperature reached 50°, the reaction became exothermic and a small amount of material was lost through the condenser. After the exotherm was over, the mixture was stirred at 100° for 3 hr. The gc (column C) chromatogram showed the presence of $\sim$1% starting material, less than 1% 1-chlorocyclobutanecarbonitrile and cyclobutanecarbonitrile, and approximately 98% of a mixture of the cis and trans isomers of 3-chlorocyclobutanecarbonitrile. The mixture was distilled to give 2.7 g (77%) of 3-chlorocyclobutanecarbonitrile, bp 73–76° (7 mm), and 7.6 g (78%) of tributyltin chloride, bp 92–100° (0.1 mm).

Bridge-Deuterated 3-Chlorocyclobutanecarbonitrile. In a 50-ml three-necked flask with thermometer, condenser, and magnetic stirring bar, under nitrogen, was placed 13.9 g (0.09 mol) of bridge-deuterated 1,3-dichlorocyclobutanecarbonitrile. The liquid was stirred in an oil bath at 100°. A pinch of Vazo was added and 26.2 g of tributyltin hydride was added dropwise over 0.5 hr. During the addition the temperature of the mixture rose to 130° then gradually dropped back to 100°. Gas chromatography showed about 15% starting material left, so 5 g of tributyltin hydride was added. Stirring at 100° was continued for another 2 hr. At this time less than 2% of starting material was observed by gc. The solution was transferred to a single-necked flask and distilled through a 4-in. Vigreux column to give 8.6 g (80%) of bridge-deuterated 3-chlorocyclobutanecarbonitrile, bp 70–80° (7 mm), which was >98% pure by gc and which was approximately a 2:1 mixture of cis and trans isomers. Further distillation afforded 29.0 g of tributyltin chloride, bp 82–99° (0.05 mm).

Bridge-Deuterated 1-Bicyclobutanecarbonitrile. To a chilled (8°) solution of bridge-deuterated 3-chlorocyclobutanecarbonitrile (8.48 g, 0.074 mol) in 80 ml of anhydrous ether was added 9.5 g (0.085 mol) of potassium *tert*-butoxide over 3 min. After stirring for 15 min, the mixture was chilled and Dry Ice, phenothiazine, 1 ml of water, and $MgSO_4$ were added. The mixture was filtered through a pressure funnel, under N_2, and concentrated on the rotary evaporator. An attempt was made to distill the crude product at 8 mm (bath = 50°), but the product began to polymerize. After more phenothiazine was added, the product was distilled ($\sim$28°, 0.3 mm) with Dry Ice cooling, giving a 2.8-g (49%) yield.

The mass spectrum was consistent with the assigned structure. The nmr peaks were much sharper than in the case of undeuterated 1-bicyclobutanecarbonitrile, as expected. The absorptions lay at δ 2.41 (s, 1 H, bridgehead), 2.08 (s, 0.77 H, exo), and 1.17 (s, 0.2 H, endo).

2,2-Dimethyl-3-oxocyclobutanecarbonitrile. A solution of 28.0 g (0.23 mol) of 2,2-dimethyl-3-methylenecyclobutanecarbonitrile in 300 ml of dichloromethane was ozonized at −78° for 5.5 hr, at which time it turned blue. Excess ozone was blown out with nitrogen. The solution was dripped into a stirred mixture of 20 g of zinc dust and 200 ml of 1:1 acetic acid–water. The mixture was heated to 100° with stirring to remove dichloromethane, cooled, filtered, and extracted with ten 100-ml portions of chloroform. The extracts were washed with one 100-ml portion of 10% aqueous potassium iodide solution, six 100-ml portions of 10% sodium bicarbonate, and one 100-ml portion of water, dried over $MgSO_4$, filtered, and rotevaporated. Four such batches when combined weighed 145.3 g. Distillation through a Claisen head gave 85.5 g (75.2%) of ketone: bp 82–90° (10 mm); $n^{25}\text{D}$ 1.4516; >99% pure by gc; melting at about 28°; ir 5.55 (C=O), 4.45 (CN), 7.20, 7.29 μ ($C(CH_3)_2$); nmr δ 1.3, 1.4 (7 H, 2s, $C(CH_3)_2$ plus CHCN), 3.36 (2 H, m, $CH_2C(=O)$).

Anal. Calcd for C_7H_9ON: C, 68.27; H, 7.37. Found: C, 68.12; H, 7.21.

2,2-Dimethyl-3-hydroxycyclobutanecarbonitrile. To a stirred solution of 1.70 g (0.18 equiv) of sodium borohydride in 50 ml of water was added 18.9 g (0.153 mol) of 2,2-dimethyl-3-oxocyclobutanecarbonitrile. The exothermic reaction was maintained at 35–45° with water cooling. The addition required 17 min, and the reaction mixture was stirred for an additional 3 hr. The oily upper layer was taken up by extraction five times with 60-ml portions of chloroform. The organic layers were dried and distilled to give 17.9 g (95.5%) of a waxy colorless solid: bp 70° (0.25 mm); ir 2.94 (OH), 4.45 (CN), 7.19, 7.27 μ ($C(CH_3)_2$); nmr δ 1.17 (6 H, 4s of two isomers, $-CH_3$), 2.34 (3 H, m, CH_2CHCN), and 3.90 (2 H, m, HCOH).

Anal. Calcd for $C_7H_{11}ON$: C, 67.17; H, 8.86; N, 11.19. Found: C, 66.44, 66.82; H, 8.25, 8.53; N, 11.13.

2,2-Dimethyl-3-cyanocyclobutyl Benzenesulfonate. To a solution of 16.0 g (0.128 mol) of 3-hydroxy-2,2-dimethylcyclobutanecarbonitrile in 90 ml of pyridine at 0° was added 26.0 g (0.147 mol) of benzenesulfonyl chloride during 17 min with stirring. The reaction mixture was stirred at 0° for an additional hour and left at 0° overnight. It was poured into 600 g of ice and water and stirred for 40 min. The mixture was neutralized with 250 ml of cold 6 *N* hydrochloric acid and extracted three times with 200-ml portions of ether. The combined organic layers were washed with 50 ml of saturated potassium chloride solution, dried, and evaporated. The residue was stirred at 60° and 2 mm for 3 hr to leave 30.4 g (89.5%) of 2,2-dimethyl-3-cyanocyclobutyl benzenesulfonate.

Anal. Calcd for $C_{13}H_{15}NO_3S$: C, 58.85; H, 5.70. Found: C, 59.24; H, 5.98.

Crystallization from hexane–ethyl acetate (2:1) at 0° gave the crystalline benzenesulfonate in good yield: mp 72–74°; ir 4.48 (CN), 7.31, 8.42 μ ($-SO_2O-$); nmr δ 1.09 (3 H, s, CH_3), 1.28 (3 H, s, CH_3), 2.45 (3 H, m, CH_2CHCN), 4.50 (1 H, m, $CHOSO_2$), 7.68 (5 H, m, phenyl H's).

Anal. Found: C, 58.89; H, 5.80, 5.73.

2,2-Dimethyl-1-bicyclobutanecarbonitrile. All operations were carried out under dry nitrogen. To a solution of 5.0 g (0.0189 mol) of crystalline 2,2-dimethyl-3-cyanocyclobutyl benzenesulfonate in 100 ml of ether was added with stirring 2.12 g (0.0189 mol) of potassium *tert*-butoxide. After the mixture had been stirred for 5.3 hr at room temperature, the initial thick sludge had become a thin slurry, samples of which dissolved in water. To the mixture were added 0.3 g of 2,5-di-*tert*-butylquinone, about 5 g of Dry Ice, and dropwise, 3 ml of water to form a granular precipitate. Magnesium sulfate was added, and the mixture was filtered under nitrogen pressure through Celite, which was rinsed with fresh ether. The filtrate was concentrated and distilled to give 1.52 g (75.0%) of 2,2-dimethyl-1-bicyclobutanecarbonitrile: bp 50–51° (9 mm); ir 4.53 (CN), 7.21, 7.34 μ ($C(CH_3)_2$); nmr δ 0.95 (3 H, s, CH_3), 1.33 (3 H, s, CH_3), 1.85 (1 H, s, bridgehead H), 2.29 (2 H, s, CH_2).

Anal. Calcd for C_7H_9N: C, 78.46; H, 8.47. Found: C, 78.18; H, 8.84.

An equally satisfactory work-up involved adding sufficient water to the reaction mixture to dissolve the precipitated salts, separating the ether layer, washing, drying, and distilling.

2,2,4,4-Tetramethyl-3-oxocyclobutanecarbonitrile from 3-Oxocyclobutanecarbonitrile. Sodium hydride, 20 g (0.448 mol) of a 54% dispersion in mineral oil, was cleaned under nitrogen with two 200-ml portions of pentane. It was covered with 100 ml of *N*-methylpyrrolidone. To this suspension was added with stirring a solution of 9.51 g (0.10 mol) of 3-oxocyclobutanecarbonitrile in 70 g (0.493 mol) of methyl iodide over 2.2 hr with mild cooling to maintain the temperature at 25–30°. At the end of the addition, 8.43 l. of gas had been evolved. The mixture was stirred overnight with a large pan of water around the flask. This precaution was necessary as heat is evolved slowly and steadily for some time after addition is complete. After this 14-hr period, the total volume of gas was 12.64 l. The semisolid reaction mixture was poured onto 400 ml of water and ice and extracted five times with 200-ml portions of pentane. The combined organic layers were back-washed with 50 ml of saturated potassium chloride solution, dried, and distilled. The semicrystalline distillate, bp 40° (0.25 mm), weighed 6.99 g. Two recrystallizations from 10-ml portions of pentane at −80° and two recrystallizations from 15-ml portions of pentane at −35° gave 3.00–4.15 g (19.8–27.4%) of 2,2,4,4-tetramethyl-3-oxocyclobutanecarbonitrile: mp 57–59°; ir 4.46 (CN), 5.63 (C=O), 7.24, 7.30 μ ($C(CH_3)_2$); nmr δ 1.4 and 1.34 (12 H, 2 s, *exo-* and *endo-*CH_3), 2.84 (1 H, s, CHCN).

Anal. Calcd for $C_9H_{13}ON$: C, 71.49; H, 8.67. Found: C, 71.40, 71.75; H, 8.67, 8.74.

2,2,4,4-Tetramethyl-3-oxocyclobutanecarbonitrile *via* 2,2-Dimethyl-3-oxocyclobutanecarbonitrile. A slurry of 35.8 g (0.80 mol) of 53% dispersion NaH (cleaned with pentane under N_2) in 0.225 l. of *N*-methylpyrrolidone was stirred with cooling at 20–25°. The ketone, 43.1 g (0.35 mol) in 127.8 g (0.90 mol) of methyl iodide, was added dropwise over a 90-min period with water cooling at 20–25°. The reaction started immediately to give 20.1 l. of H_2 as measured by a wet test meter. The solid reaction mixture was placed on 800 ml of ice and water, extracted with 0.8 l. of pentane, 0.1 l. of ether, and then three portions of [0.4 l. of pentane + 0.1 l. of ether]. After washing one 0.1-l. portion of H_2O, the organic layer was dried and concentrated to give a crystalline solid. A second run using 42.0 g (0.295 mol) of the ketone gave 15.4 l. of H_2 and the crystalline solid. The solids were combined and recrystallized from 0.15 l. of boiling hexane to yield 54.3 g (52.9%) of 2,2,4,4-tetramethyl-3-oxocyclobutanecarbonitrile.

2,2,4,4-Tetramethyl-3-hydroxycyclobutanecarbonitrile. To a stirred, nitrogen-swept solution of 2.0 g (0.0528 mol) of sodium borohydride in 50 ml of water, was added 6.00 g (0.0397 mol) of 2,2,4,4-tetramethyl-3-oxocyclobutanecarbonitrile. The solution was stirred at 25° for 4.5 hr and then extracted with four 100-ml portions of ether. The ether layer was washed with 25 ml of saturated KCl solution, dried over magnesium sulfate, and concentrated on a rotary evaporator. The 4.6 g of nice crystals obtained from the ether layer was sublimed at 80–120° (0.3 mm) to yield 4.3 g (70.5%) of 2,2,4,4-tetramethyl-3-hydroxycyclobutanecarbonitrile: mp 111.3–116.3°; ir 4.48 (CN), 2.94 μ (OH); nmr δ 1.18, 1.20, 1.28 (12 H, three singlets, CH_3's of two isomers), 2.41 (1 H, s, CHCN), 3.18 (1 H, s, C*H*OH), 3.65 (1 H, s, OH).

Anal. Calcd for $C_9H_{15}ON$: C, 70.55; H, 9.87; N, 9.14. Found: C, 70.91, 70.56; H, 9.79, 9.85; N, 8.98, 9.10.

2,2,4,4-Tetramethyl-3-cyanocyclobutyl Benzenesulfonate. To an ice-chilled solution of 4.55 g (0.030 mol) of 2,2,4,4-tetramethyl-3-oxocyclobutanecarbonitrile in 30 ml of pyridine was added 6.82 g (0.0386 mol) of benzenesulfonyl chloride over 16 min with vigorous stirring. The solution was kept in ice for 5.5 hr and then left at 5° for 40 hr. The solution was poured into a beaker of excess ice water with magnetic stirring. The resulting crystalline solid was filtered, triturated, and rinsed well with water. The solid was pump dried over P_2O_5 to give 4.80 g of solid, mp 94–96°. The infrared spectrum showed $C_6H_5SO_2O$ to be present and no OH. The solid was recrystallized from 15 ml of hexane plus 3 ml of ethyl acetate and filtered while hot. With cooling, nice soft crystals formed which were filtered and pumped dry. The yield was 3.70 g (42%) of crystals which melted from 97.7 to 98.7°; ir 4.47 (CN), 6.28 (aromatic), 7.34, 8.42 μ ($-SO_2O-$); nmr δ 1.1 and 1.24 (12 H, 2 singlets, *exo-*, *endo-*methyls), 3.00 (1 H, s, CHCN), 4.25 (1 H, s, CHOS), 7.70 (5 H, m, phenyl).

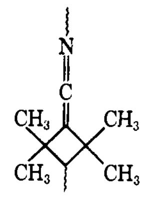
Anal. Calcd for $C_{15}H_{19}O_3NS$: C, 61.47; N, 6.53. Found: C, 61.58; N, 6.52.

A second run was carried out using crude 2,2,4,4-tetramethyl-3-hydroxy-1-cyclobutanecarbonitrile obtained by reduction of 15.4 g of oxonitrile with 26.5 g of benzenesulfonyl chloride and 75 ml of pyridine. The product crystallized well in water. The solid was pumped dry in a desiccator over P_2O_5 to yield 24.7 g (81.7%) of 2,2,4,4-tetramethyl-3-cyanocyclobutyl benzenesulfonate, mp 85–87°. The mixture of hydroxynitrile isomers appeared to give a better yield.

2,2,4,4-Tetramethyl-1-bicyclobutanecarbonitrile. All operations were carried out under dry nitrogen. At −10°, potassium *tert*-butoxide (2.58 g, 0.023 mol) was added in portions, with no visible reaction, over 10 min to a solution of 2,2,4,4-tetramethyl-3-cyanocyclobutyl benzenesulfonate (5.87 g, 0.02 mol) in 60 ml of ether. The mixture was allowed to come to room temperature with stirring, stirred for 2.0 hr, and cooled in an ice bath. Phenothiazine, Dry Ice, and water (8 ml) were added. The ether layer was separated. The salts were extracted with ether (25 ml). The ether layers were washed with two 10-ml portions of saturated KCl solution. After being dried over $MgSO_4$, the mixture was concentrated on the rotary evaporator and distilled from phenothiazine into a Dry-Ice chilled receiver to yield 1.28–1.47 g (47.4–54.3%), bp 25–26° (0.2 mm), 40° (0.35 mm). Perhaps a little was lost because of the low pressure: ir 4.54 (CN), 7.24 μ (CCH_3); nmr δ 1.33, 1.35 (12 H, two singlets, CH_3's), 2.03 (1 H, s, bridgehead H).

Anal. Calcd for $C_9H_{13}N$: C, 79.95; H, 9.69. Found: C, 78.85, 78.82; H, 9.71, 9.59.

An unusual absorption at 4.99 μ in the infrared spectrum of the polymer from 2,2,4,4-tetramethylbicyclobutanecarbonitrile was ascribed to a ketenimine structure.



3-Methyl-1-bicyclobutanecarbonitrile. This compound was available from the work of Blanchard and Cairncross.[11] As a matter of incidental interest, the dipole moment was determined in benzene. The following data were obtained: $n^{25}D$ 1.4532, $d^{25}{}_4$ 0.9108, MR_D 27.649, found, 27.440, P_∞ 332.88, 3.86 μ.

3,3-Dichlorocyclobutanecarbonitrile. In a 500-ml, three-necked flask fitted with a mechanical stirrer were placed 87.2 g (0.42 mol) of phosphorus pentachloride and 100 ml of carbon tetrachloride. The mixture was stirred in an ice–methanol bath at −10 to 0°. To the mixture was added over 1 hr a solution of 38 g (0.4 mol) of 3-oxocyclobutanecarbonitrile in 50 ml of carbon tetrachloride and 200 ml of benzene. The mixture was stirred another 3 hr at −10 to 0°, then was poured into 500 g of ice water. The aqueous mixture was extracted (five 100-ml portions) with chloroform; the chloroform extracts were back-washed (three 100-ml portions) with water, dried, filtered, and evaporated. The residue was distilled twice at reduced pressure to give, after a fair amount of forerun, 17.9 g (30%) of product as a colorless liquid, bp 38–40° (0.1 mm), shown to be *ca.* 98–99% pure by gc (column A). The product crystallized at Dry Ice temperature and on warming melted at *ca.* 20°; ir 4.46 μ (CN); nmr δ 3.3 (m, all H's have approximately the same chemical shift).

Anal. Calcd for $C_5H_5NCl_2$: C, 40.03; H, 3.36; N, 9.34; Cl, 47.27. Found: C, 39.97; H, 3.74; N, 8.93, 9.01; Cl, 46.84.

3-Chlorobicyclobutanecarbonitrile. In a 1-l., three-necked flask flamed out and under nitrogen were placed 15 g (0.1 mol) of 3,3-dichlorocyclobutanecarbonitrile and 400 ml of ether. The solution was stirred in an ice–methanol bath at −10°. To the stirred solution was added 16.5 g (0.15 mol) of potassium *tert*-butoxide over 15 min. The reaction mixture was stirred at −10° for 2 hr. Then 100 mg of 2,5-di-*tert*-butyl-*p*-quinone, 10 g of Dry Ice, 2 ml of water, and 10 g of magnesium sulfate were added. The mixture was filtered through Celite (rinsing several times with ether), and the ether filtrate was evaporated to give *ca.* 9 g of yellow liquid. Distillation gave only one fraction, bp 36.5–37° (1.9 mm), 6.3 g (55%) of a colorless liquid which crystallized at Dry Ice temperature. Analysis by gc (column A) showed the product was *ca.* 98% pure: ir 4.50 μ (CN); nmr δ 1.9 (2 H, m), 2.64 (2 H, m).

Anal. Calcd for C_5H_4NCl: C, 52.88; H, 3.55; N, 12.34; Cl, 31.23; mol wt, 113 (Cl = 35). Found: C, 52.72; 53.15, 52.84; H, 3.77, 3.79, 3.68; N, 11.52, 11.60, 11.65, 12.06; Cl, 30.70; mol wt, 113 (Cl = 35) (mass spectrum).

1-Chloro-1,3-cyclobutanedicarbonitrile. In a 1-l. four-necked flask with long condenser, mechanical stirrer, and thermometer, were placed 87 g (3.2 mol) of liquid hydrogen cyanide (**caution!**) and 285 g (3 mol) of 3-oxocyclobutanecarbonitrile (melted to a liquid for easier transfer). The solution was stirred in an ice bath. Cautiously, 0.1-ml portions of triethylamine were added until a temperature rise was noted (1.4 ml of triethylamine was required). The temperature rose very quickly and reached 82°, even with Dry Ice–acetone cooling. The hydrogen cyanide refluxed near the top of the condenser. The reaction gradually subsided and the temperature returned to 25°. Addition of more triethylamine caused no further exotherm. The yellow, fairly viscous liquid was stirred at room temperature for 3 hr. The crude cyanohydrin was then added all at once to a stirred solution of 786.9 g (3 mol) of triphenylphosphine in 2 l. of carbon tetrachloride in a 5-l. three-necked flask. The mixture was refluxed overnight. The cooled viscous solution was poured into ~5-l. of boiling ether. The resulting precipitate was filtered off to give 678 g (81%) of triphenylphosphine oxide. The ether filtrate was evaporated and the residue was distilled through a 6-in. vacuum-jacketed Vigreux column to give 250 g of colorless liquid, bp 92 (0.5 mm) to 115° (4.5 mm). The gc (column C) showed the presence of some starting ketone, so the material was distilled through a 3-ft spinning-band column. After a forerun which contained ketone, the product was collected to give 187 g (45%) of colorless glassy solid: bp 88–90° (0.55 mm), pure by gc (~1:1 mixture of both isomers); ir 4.43 μ (CN); nmr δ 2.8–3.8 (m).

Anal. Calcd for $C_6H_5N_2Cl$: C, 51.26; H, 3.59; N, 19.93; Cl, 25.22. Found: C, 51.45, 51.72; H, 3.68, 3.83; N, 19.91, 19.82; Cl, 25.19.

Preparative gc of a mixture similar to that obtained above resulted in the isolation of both isomers of 1-chloro-1,3-cyclobutanedicarbonitrile. The material represented by the earlier gc peak (7.9 min, at 174° on column A) was collected and recrystallized from petroleum ether (bp 30–60°) to give colorless rods: mp 62.5–63.5°; ir 4.45 (–CN), 7.00 and 7.06 μ (d); nmr δ 2.9–3.6 (m). The material represented by the later gc peak (9.8 min, at 174° on column A) was collected and recrystallized from petroleum ether to give colorless feathery crystals: mp 61.0–61.5°; ir 4.44 (–CN) 7.02 (s), 9.4 μ (d); nmr δ 2.8–3.7 (m).

Anal. Calcd for $C_6H_5N_2Cl$: C, 51.26; H, 3.59; N, 19.93; Cl, 25.22. Found (early peak): C, 50.97, 50.74; H, 3.69, 3.63; N, 19.70, 19.62. Found (later peak): C, 50.99, 51.40; H, 3.15, 3.33; N, 20.05, 20.05; Cl, 25.24.

1,3-Bicyclobutanedicarbonitrile. A 250-ml, three-necked flask fitted with reflux condenser and magnetic stirring bar was flamed out under nitrogen. To the flask were added 2.6 g (0.0185 mol) of 1-chloro-1,3-cyclobutanedicarbonitrile and 100 ml of ether. The solution was stirred in an ice–methanol bath at −10° and 2.5 g (0.022 mol) of potassium *tert*-butoxide was added in ten portions over 15 min. The reaction mixture was stirred for an additional hour at −10°. To the mixture was added 1.5 g of Dry Ice, 0.4 ml of water, 2 g of magnesium sulfate, and 200 mg of inhibitor (2,5-di-*tert*-butyl-*p*-quinone). The mixture was filtered through Celite. The Celite was rinsed several times with ether. The combined filtrate was evaporated to give a white solid, which was dissolved in chloroform (some insoluble white powder was filtered off) and transferred to a short-path distillation set-up. Distillation gave 0.95 g (50%) of a light-yellow solid, bp 69° (0.25 mm). Analysis by gc (column C) and nmr showed the presence of about 3 mol % of inhibitor, so the sample was recrystallized from benzene–petroleum ether to give shiny colorless platelets, mp 51.5–52.5°. The uv spectrum exhibited an absorption at 207 μ (ε 6800) in acetonitrile; ir 4.47 μ (CN); nmr δ 1.81 (2 H, m), 2.73 (2 H, m).

Anal. Calcd for $C_6H_4N_2$: C, 69.22; H, 3.87; N, 26.91; mol wt, 104. Found: C, 68.46, 68.55, 68.70, 69.02, 69.06; H, 3.52, 3.58, 3.94, 3.98, 4.10; N, 26.94, 27.08; mol wt, 104 (mass spectrum).

3-Hydroxy-3-phenyl-1-cyclobutanecarbonitrile. To 110 ml of ethereal phenylmagnesium bromide (3 *M*, 0.33 mol) at −5° was added under nitrogen 200 ml of purified THF. To this cooled (−5 to 0°) solution was added 25 g (0.263 mol) of 3-oxocyclobutanecarbonitrile in 100 ml of THF. After addition was completed (1.5 hr), the contents were heated to 30° for 20 min. The mixture was cooled and acidified with 10% hydrochloric acid. The layers were separated, and the aqueous phase was extracted with ether (four 75-ml portions). The combined organic phase was washed with brine and dried over magnesium sulfate. Removal of solvent gave an oil which partially crystallized on standing. An infrared spectrum of the crude product showed strong absorption at 2.9 (OH), medium absorption at 4.45 (CN), and medium absorption at 5.55, 5.80, and 6.0 μ. The semisolid was taken up in benzene which was then cooled in ice with stirring. Hexane was added slowly, and the crystals which formed were filtered off. The filtrate was concentrated and the process repeated until no more crystals were obtained. The oily residue might contain an additional product, but has not been investigated further. The solid material was recrystallized from benzene to give 11.8 g of hydroxynitrile: mp 89–90°; ir 2.77, 2.90, 4.45 μ ($CHCl_3$); nmr δ 7.37 (5 H, s), 3.45 (OH, 1 H, s); 2.5–3.1 (5 H, m).

Anal. Calcd for $C_{11}H_{11}ON$: C, 76.27; H, 6.40; N, 8.09. Found: C, 75.81; H, 6.20; N, 8.04.

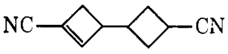
3-Chloro-3-phenyl-1-cyclobutanecarbonitrile. A mixture of 100 ml of benzene, 100 ml of concentrated hydrochloric acid, and 9.2 g (0.053 mol) of 3-hydroxy-3-phenyl-1-cyclobutanecarbonitrile was shaken vigorously in a separatory funnel for 3–4 min. The layers were separated, and the aqueous phase was washed with benzene (one 50-ml portion). Cold water (100 ml) was added to the aqueous phase, and the resulting solution was extracted with benzene (25 ml). The combined organic phase was extracted with water (two 100-ml portions) and brine (two 50-ml portions) and then dried over magnesium sulfate. Removal of solvent gave 10.0 g (100%) of dry, white solid. Recrystallization from ether–hexane gave coarse, white crystals: mp 55–69°; nmr δ 7.31, 7.35 (5 H, s, both isomers), 2.80–3.30 (5 H, m).

Anal. Calcd for $C_{11}H_{10}NCl$: C, 68.91; H, 5.26; N, 7.31; Cl, 18.50. Found: C, 69.28; H, 5.19; N, 7.44; Cl, 18.52.

3-Phenyl-1-bicyclobutanecarbonitrile. A solution of 3.18 g (0.0165 mol) of 3-chloro-3-phenyl-1-cyclobutanecarbonitrile in 30 ml of THF was added at 25° over 30 min to a slurry of 1 g (0417 mol) of sodium hydride (washed free of mineral oil) in 20 ml of THF containing one drop of *tert*-butyl alcohol. The mixture was stirred vigorously at 25° for 24 hr and then cooled. The excess hydride was destroyed with water (20 ml), and the layers were separated. The aqueous phase was extracted four times with ether. The combined organic phase was washed with water and brine, and then dried over magnesium sulfate. Removal of solvent gave an oil which crystallized on scratching. Recrystallization from ether–hexane and finally from hexane gave fine, white needles: mp 45–46°; ir 4.48, 4.53 μ (KBr); uv $\lambda_{max}^{cyclohexane}$ 242 mμ (11,700); nmr δ 7.22 (5 H, s), 2.47 (2 H, t, exo, splitting = 1 cps), 1.37 (2 H, t, endo, splitting = 1 cps).

Anal. Calcd for $C_{11}H_9N$: C, 85.12; H, 5.85; N, 9.02. Found: C, 86.02; H, 6.07; N, 9.00, 9.30.

Dimerization of 1-Bicyclobutanecarbonitrile to 3-(3-Cyanocyclobutyl)-1-cyclobutenecarbonitrile. In a 50-ml, round-bottomed flask under nitrogen were placed 3.95 g (0.05 mol) of 1-bicyclobutanecarbonitrile, 100 mg of inhibitor (2,5-di-*tert*-butyl-*p*-quinone), and 25 ml of cyclohexane. The solution was refluxed for 70 hr. The mixture was added to 150 ml of ether, and the solution was decanted away from some ether-insoluble oil. The solvents were evaporated, and the residue was dissolved in 5 ml of benzene and added to a column of 75 g of Florisil. Elution with benzene to mixtures of benzene and methylene chloride gave 0.81 g (20.5%) (after recrystallization from ether) of white needles, mp 73–75°. A sublimation and three recrystallizations gave material with mp 76.5–77.5°; ir, 4.47, 4.50 (CN), 6.30 μ (C=C); nmr δ 2.0–3.4 (9 H, m) and 6.82 (1 H, s, C=CH).

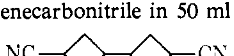


Anal. Calcd for $C_{10}H_{10}N_2$: C, 75.92; H, 6.37; N, 17.71. Found: C, 76.00, 76.22; H, 6.54, 6.16; N, 17.93, 17.87.

Mass spectrum showed expected molecular ion at *m/e* 158. Most intense peak in mass spectrum at *m/e* 105 due to loss of $CH_2=CH-CN$.

A second material was eluted later than the above dimer to give 70 mg of white crystals, mp 116–117°. This material was shown to be a trimer of 1-bicyclobutanecarbonitrile in a yield of about 2%. It was found that this trimer could be more conveniently prepared at higher temperatures, as in a later preparation.

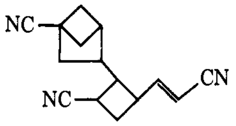
3,3′-Dicyanobicyclobutyl. A solution of 3.7 g of 3-(3-cyanocyclobutyl)-1-cyclobutenecarbonitrile in 50 ml of THF was hydrogenated over palladium-on-carbon for 6 hr at 25°. The solution was filtered through Celite and the filtrate was evaporated to give



3.4 g (92%) of light-yellow liquid which crystallized when scratched. The nmr spectrum of this crude material showed no vinyl hydrogens. The crude product was recrystallized from ether to give 2.4 g of white powder in two crops: mp 58–64°; ir 3.33, 3.38, and 3.48 (sat. CH) 4.47 μ (–CN); nmr δ 2.8–3.3 (2 H, m) and 1.5–2.8 (10 H, m).

Anal. Calcd for $C_{10}H_{12}N_2$: C, 74.96; H, 7.55; N, 17.49. Found: C, 75.18, 75.41, 75.64; H, 7.84, 8.00, 8.00; N, 17.40, 17.56, 17.67.

Trimerization of 1-Bicyclobutanecarbonitrile to 3-[2-Cyano-4-(2-*trans*-cyanovinyl)cyclobutyl]bicyclo[2.1.1]hexane-1-carbonitrile. In a 50-ml, round-bottomed flask under nitrogen were placed 7.9 g of 1-bicyclobutanecarbonitrile, 25 mg of inhibitor (2,5-di-*tert*-butyl-*p*-quinone), 30 mg of ruthenium trichloride, and 20 ml of hexamethylphosphoramide. With magnetic stirring, the mixture was heated at 150° for 20 hr. Most of the solvent was removed by vacuum distillation. The residue was dissolved in 75 ml of benzene and filtered to remove some insoluble material. The benzene solution was concentrated and chromatographed on 45 g of Florisil, eluting with benzene and methylene chloride mixtures, to give 3.5 g of yellow crystals. This material was recrystallized from methanol to give 2.50 g (32%) of colorless crystals: mp 117–118°; ir 4.47 (CN), 6.02 (C=C), 10–10.5 μ (*trans*-HC=CH); nmr δ 1.5–3.6 (13 H, m), 5.5 (1 H, d), 6.3 (1 H, q).



Anal. Calcd for $C_{15}H_{15}N_3$: C, 75.92; H, 6.37; N, 17.71. Found: C, 75.56, 75.51; H, 6.19, 5.81; N, 17.74, 17.79.

In the mass spectrum, both the molecular ion and several fragments were consistent with the proposed structure. Note: in another preparation without ruthenium trichloride, similar results were obtained. Therefore, dimerization seems to predominate at lower temperatures (80°) while trimerization predominates at higher temperatures (150°).

3-(*tert*-Butylthio)cyclobutanecarbonitrile. 1-Bicyclobutanecarbonitrile (3.95 g, 0.05 mol) and 0.5 g of azobisisobutyronitrile were dissolved in 10 ml of *tert*-butyl mercaptan. The magnetically stirred solution was refluxed under nitrogen for 3 hr, then allowed to stand at room temperature overnight. Distillation gave 3.9 g (50%) of colorless liquid, bp 70–85° (0.6 mm). Gc analysis on column D showed two major peaks in area percentages of 42.7 and 46.3%. The rest of the material was divided among nine peaks with area percentages varying from 0.1 to 6.5%. Preparative, gc gave the two major components as colorless liquids, isomer A (42.7%, retention time 5.4 min) and isomer B (46.3%, retention time 7.4 min). From the nmr spectra, it is possible to say that both isomers have the *tert*-butylthio group in the 3 position, but assignments of cis and trans stereochemistry cannot be made; ir, 4.47 (CN), 7.18, 7.32 μ ($C(CH_3)_3$).

Anal. Calcd for $C_9H_{15}NS$: C, 63.85; H, 8.93; N, 8.28; S, 18.94. Found (isomer A): C, 62.34, 62.28; H, 8.63, 8.61; N, 8.58, 8.56; S, 16.62. Found (isomer B): C, 62.16, 62.47; H, 8.70, 8.96; N, 8.58, 8.59; S, 18.21.

Addition of Carbon Tetrabromide to 1-Bicyclobutanecarbonitrile. In a 100-ml, round-bottomed flask were placed 3.95 g (0.05 mol) of 1-bicyclobutanecarbonitrile, 33 g (0.1 mol) of carbon tetrabromide, and 25 ml of carbon tetrachloride. The reaction mixture was stirred at reflux under irradiation by a GE sunlamp for 4 hr. The carbon tetrachloride was removed by rotary evaporation, and the carbon tetrabromide sublimed off under full pump vacuum. The residue was distilled to give 4.4 g (21%) of pale-yellow liquid, bp 119–132° (0.6–0.7 mm), which crystallized on standing to give nearby white crystals, mp 60–67°. Attempts to separate the four possible isomers by gc failed.

Anal. Calcd for $C_6H_5NBr_4$: C, 17.54, H, 1.22; N, 3.41; Br, 77.82. Found: C, 18.48, 18.16, 18.50; H, 1.55, 0.79, 1.25; N, 3.52, 3.39, 3.49; Br, 76.27.

1,3-Dibromocyclobutanecarbonitrile. To a magnetically stirred solution of 15.8 g (0.2 mol) of 1-bicyclobutanecarbonitrile in 100 ml of carbon tetrachloride at room temperature was added over 1 hr a solution of 32 g (0.2 mol) of bromine in 200 ml of carbon tetrachloride. The bromine color discharged as rapidly as the bromine solution was added for at least 90% of the reaction. After the addition was completed, the resulting light-orange solution was rotary evaporated to give 47.3 g (99%) of white crystalline solid. Gc analysis showed the presence of only two peaks in approximate ratios of 3:1. Preparative gc on column B at 125° gave two white solids, isomer A (major, 67–74% of mixture, retention time 25.8 min), mp 66.5–67.5°, and isomer B (minor, 33–26% of mixture, retention time 31.2 min), mp 88.5–89.5°. On the basis of the nmr spectra, the *cis*-dibromo structure was assigned to isomer A and the *trans*-dibromo structure to isomer B. It was found in other preparations that the major cis isomer could be obtained pure by several recrystallizations of the product mixture from methanol: isomer A (cis) ir 4.48 μ (CN); nmr δ 2.9–3. (4 H, m), 4.53 (pentuplet, 1 H) isomer B (trans) ir 4.47 μ (CN); nmr δ 3.38 (4 H, d, $-CH_2-$), 4.77 (pentuplet, 1 H, CHBr).

Anal. Calcd for $C_5H_5NBr_2$: C, 25.13; H, 2.11; N, 5.86; Br, 66.89. Found (isomer A): C, 25.10; H, 2.37; N, 5.92; Br, 66.18. Found (isomer B): C, 24.35; H, 2.10; N, 5.99; Br, 66.67.

1-Bicyclobutanecarbonitrile from Dibromide. In a 50-ml, three-necked flask with reflux condenser and stirring bar was placed 0.7 g (0.03 mol) of magnesium turnings. The flask was flamed out under nitrogen, and 5 ml of THF was added. To the stirred mixture was added a solution of 5 g (0.02 mol) of 1,3-dibromocyclobutanecarbonitrile in 10 ml of THF. The mixture was stirred at room temperature for 3 hr. The reaction mixture was poured into water and extracted with ether containing a trace of 2,5-di-*tert*-butyl-*p*-quinone as inhibitor. The ether extracts were back washed with water, dried, filtered, and evaporated to give 1.0 g of pale-yellow liquid. The nmr spectrum of this material was essentially identical with that of 1-bicyclobutanecarbonitrile, except for trace amounts of THF and inhibitor.

3-Methoxycyclobutanecarbonitrile. To a stirred solution of 5.4 g of sodium methoxide (0.1 mol) in 15 ml of methanol under nitrogen was added over 0.5 hr a solution of 3.95 g (0.05 mol) of 1-bicyclobutanecarbonitrile in 10 ml of methanol. The reaction mixture was stirred at room temperature for another 5 hr. Then water (100 ml) was added, and the mixture was extracted (three 50-ml portions) with ether. The ether extracts were combined and washed once with water, dried over magnesium sulfate, filtered, and evaporated. The residue was distilled to give 2.19 g (40%) of colorless liquid, bp 80–90° (24 mm). Gc analysis (column C) showed two major peaks in area percentages of 66.9 and 31.5%. Preparative gc on column C at 125° gave two colorless liquids, isomer A (major, retention time 4.5 min), and isomer B (minor, retention time 6.0 min): isomer A ir 4.48 (CN), 8.87, 8.98 μ (C–O); nmr δ 2.0–2.7 (4 H, m, ring CH's), 3.14 (1 H, m, CHCN), 3.25 (3 H, s, CH_3O), 4.20 (1 H, m, CHO); isomer B ir, 4.44 (CN), 8.81 μ (–CO); nmr δ 2.0–3.0 (5 H, m, ring CH_2's plus CHCN), 2.23 (3 H, s, CH_3O), 3.95 (1 H, m, CHO).

Anal. Calcd for C_6H_9NO: C, 64.84; H, 8.15; N, 12.60. Found (isomer A): C, 64.24; H, 8.52; N, 12.35, 12.48. Found (isomer B): C, 64.50; H, 8.30; N, 12.19, 12.26.

Polymerization Recipe. In a nitrogen-flushed 4-oz screw cap bottle was placed 10 g of the monomer mixture. The following solutions were added in order: (1) 35 ml of oxygen-free distilled water; (2) 6.25 ml of potassium persulfate solution (1.0 g in 125 ml of oxygen-free distilled water); (3) 2.5 ml of ferrous ammonium sulfate solution in dilute sulfuric acid (16 ml of 0.1 *N* sulfuric acid, 0.004 g of ferrous ammonium sulfate hexahydrate in 80 ml of oxygen-free distilled water); (4) 1.0 ml of soap solution (1.0 g of sodium lauryl sulfate in 10 ml of oxygen-free distilled water); and (5) 6.0 ml of sodium metabisulfite solution (2.0 g of sodium metabisulfite in 100 ml of oxygen-free distilled water). The bottle was capped and taped and rotated in a water bath at 50° for 2 hr. The mixture was blended with saturated sodium sulfate solution or steamed, then filtered, and reblended several times with water and then finally with methanol. The white powdery polymers were dried in a vacuum oven at 80°.

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