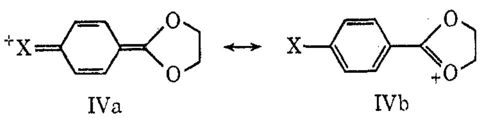

IVa IVb

lated π_y bond orders in the C_2–O bonds summarized in Table I.

It would have been extremely interesting to see if a linear correlation existed between the methylene proton nmr chemical shifts and the σ^+ (or σ) constants of H, CH_3, F, NH_2, OH, and CN in cations **1**–**6**. However, a thorough examination of the literature reveals that the nmr spectra of **1**, **3**, **4**, and **6** have never been recorded and no evidence for the preparation of **3**, **4**, or **6** has appeared.[32] However, the 2-diethylamino[9,10] and the 4,4-dimethyl[33] analogs of **4** and the 4,4-dimethyl[33] analog of **1** have been prepared, and these serve as models in order to compare the nmr δ values with the calculated total positive charge densities at the methylene protons. For those examples where these calculated charge densities could be compared to the measured chemical shifts, a linear correlation exists. As the positive charge on the methylene hydrogens increased, the δ values became increasingly deshielded. The only exception found was ion **5**, where X = OH. The point for **5** fell off the line on a plot of δ *vs.* the total charge density at the methylene protons. The measured value of δ for **5** was shielded about 34 Hz more than expected from the plot. This unexpected phenomenon has been noted twice before. Hart and Tomalia found that the methylene protons of **5** were more deshielded than those of **2** (X = CH_3) and several other 2-alkyl and 2-vinyl substituted cations as well.[9,10] Taft and Ramsey reported that the CH_3O protons, in the analogous acyclic series, were more deshielded in the trimethoxy cation than in the dimethoxymethyl cation. To quote Hart and Tomalia,[9] "a good explanation for these observations is not immediately obvious." However, given this linear correlation of δ *vs.* calculated charge density, one predicts that the methylene protons of **3** (X = F) should appear more deshielded than any other member of this series (δ 630–640 Hz downfield from TMS). The methylene protons of **6** (X = CN) should appear at δ 550–560 Hz.[34]

In conclusion, the INDO calculations have provided a conceptual view of the electron distribution (both π and σ) and the geometry of a series of 2-substituted 1,3-dioxolan-2-ylium ions. While the exact quantities of the calculated properties are subject to the usual criticisms,[19,20] the trends within the series should be realistic.

Registry No.—**1**, 37037-20-0; **2**, 18948-87-3; **3**, 37406-82-9; **4**, 37161-34-5; **5**, 18747-87-0; **6**, 37161-36-7.

[32] Cation **1** was prepared by treating 1,3-dioxolane with trityl tetrafluoroborate by Meerwein, *et al.*, but nmr spectra were not recorded; see H. Meerwein, V. Hederich, H. Morschel, and K. Wunderlich, *Justus Liebigs Ann. Chem.*, **635**, 1 (1960).

[33] C. U. Pittman, Jr., and S. P. McManus, *Tetrahedron Lett.*, 339 (1969).

[34] Experimental studies to test these predictions for **3** and **6** will be performed by S. P. McManus, C. U. Pittman, Jr., *et al.*

Dehydrocyanation of Dinitriles. Preparation of 1-Cyclobutenecarbonitrile by Direct Dehydrocyanation of 1,2-Cyclobutanedicarbonitrile

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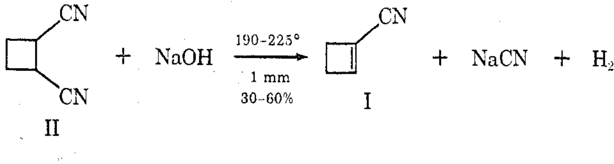
1-Cyclobutenecarbonitrile (I) was synthesized in high purity and good yield directly from 1,2-cyclobutanedicarbonitrile. The chemistry of I was investigated on a comparison basis with acrylonitrile. Dehydrocyanation with alkali appears to have general utility for double-bond formation.

1-Cyclobutenecarbonitrile (I) has been prepared by several routes,[1,2] but was not readily available in the required purity for our polymer studies.[3] An unusually facile, good-yield synthesis of high-purity I was devised from the readily available 1,2-cyclobutanedicarbonitrile (II) isomer mixture (acrylonitrile cyclodimer) by contacting the latter in the vapor phase at 190–225° with any of a number of granular bases (Table I). The crude product I contains only traces of starting material and thermal rearrangement product, 2-cyanobutadiene (III),[4] and needs only be purified by simple distillation for use as a high-grade monomer.

This simple and direct synthetic process was almost overlooked because dehydrocyanations are not commonly employed in organic synthesis. Apparently, cyanide ion is not a particularly good "leaving group". Indeed, in seeking routes to I, we took a more classical approach and prepared *cis*- and *trans*-2-chlorocyclobutanecarbonitrile by a laborious literature procedure[5] in order to study their dehydrochlorination. The reaction of either isomer proceeds well at 110–115° to give I in good yield. Substantial improvements in the chloro-



II I

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[1] R. Tietz and W. G. Kenyon, U. S. Patent 3,468,861 (1969).

[2] D. M. Gale, *J. Org. Chem.*, **35**, 970 (1970).

[3] Unpublished work.

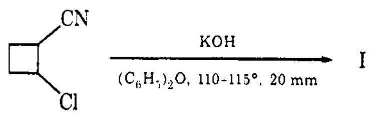
[4] Kinetics of the rearrangement have been published: S. N. Sarner, D. M. Gale, H. K. Hall, Jr., and A. B. Richmond, *J. Phys. Chem.*, **76**, 2817 (1972). Some of the material presented here was issued in the form of a patent: D. M. Gale, U. S. Patent 3,657,313 (1972).

[5] W. A. Nevill, D. S. Frank, and R. D. Trepka, *J. Org. Chem.*, **27**, 422 (1962). These materials can also be prepared directly by cross-cycloaddition of vinyl chloride and acrylonitrile, but in low conversion: D. M. Gale, U. S. Patent 3,642,859 (1972).

Table I

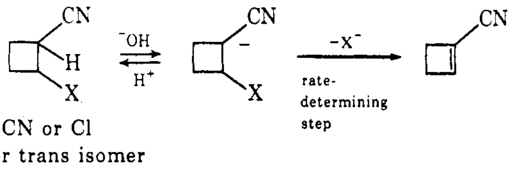
Reaction of 1,2-Cyclobutanedicarbonitrile Vapor with Various Forms of NaOH at 200–225°

Base form	% Converted to I
Soda lime, 8 mesh	32
Soda lime, 20 mesh	42
Sodium hydroxide pellets	40
Ascarite (90% NaOH on asbestos)	59



nitrile synthesis were discovered, but even so the preparation of large quantities of I was time consuming.

Dehydrochlorination, then, proceeded to a similar conversion at a lower temperature than dehydrocyanation, implying a faster rate for the removal of HCl. A carbanion mechanism is called for in each case because each process works well with either *cis*- or *trans*-nitrile starting material.



The loss of X^-, therefore, can be assumed to be rate determining. This mechanism predicts that bases weaker than hydroxide will remove HCN at elevated temperatures as long as anion formation is feasible at that temperature. Furthermore, if the base is sufficiently weak not to react with HCN, a catalytic process should be possible; thus

$$\text{II} + \xrightarrow[\Delta]{\text{basic catalyst}} \text{I} + \text{HCN}$$

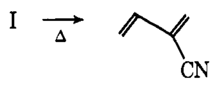
To this end, we studied the reaction of II in the vapor phase with a number of MgO–ZnO catalysts (Table II).

Table II

Reactions of II with Various Basic Catalysts

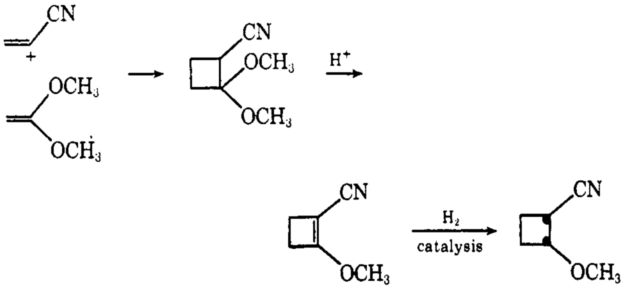
Catalyst	Temp, °C	Pressure, mm	Convn to I, %	Convn to III, %
ZnO:MgO (1:4)	298–303	0.6–0.9	23.7	4.9
ZnO:MgO (3:1)	300	0.5–2.0	12.5	3.3
ZnO:MgO (1:1)	300	0.5–2.0	16.7	3.0

Although I is formed to some extent at 225°, best conversions were generally obtained at about 300°. The higher temperatures required may reflect greater difficulty in forming the anion or difficulty in freeing the base from HCN. Loss of CN^- is probably no longer rate determining. Because of the higher temperatures generally employed for the catalytic process, I was usually contaminated with III; the catalytic dehydrocyanation, therefore, was less desirable as a laboratory process than the stoichiometric dehydrocyanation. The conversion of I to III occurs readily with heat alone.[4] The formation of III from II over basic catalysts at 400° has been reported.[6] The true catalytic nature of the second II to I process was demonstrated by quantitative analysis of HCN corresponding to II converted with the 1:3 MgO–ZnO catalyst.

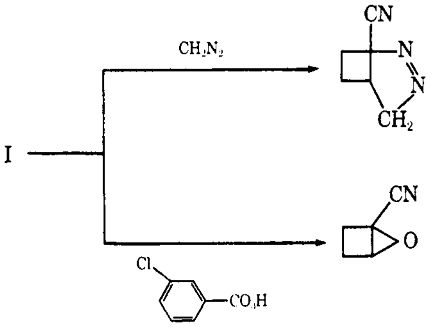


III

Chemistry of I.—It was of interest to briefly examine the chemistry of I because of its structural relationship to acrylonitrile (AN). Like AN, compound I underwent the Ritter reaction with *tert*-butyl alcohol, addition of methoxide ion, and addition of a mercaptal radical and bromine. In the case of methoxide addition, the trans isomer was favored over the cis by 8:1. Stereochemical assignments were made by stereospecific synthesis of *cis*-2-methoxycyclobutanecarbonitrile as well as by spectral evidence.



Compound I also underwent two reactions not known for AN.



Direct epoxidation was also demonstrated for methacrylonitrile; this suggests that the presence of an α hydrogen may explain the inability of AN to be directly epoxidized. The 1,3 cycloaddition of diazomethane probably to form an azo intermediate (characterization incomplete owing to the explosive nature of the material) perhaps occurs with AN, but again due to the presence of an α hydrogen the isolated product is 2-pyrazoline-3-carbonitrile.[7]

Dehydrocyanation *vs.* Dehydrochlorination in Other Systems.—In order to determine the possible general utility of dehydrocyanation, we studied the elimination of HX in several representative systems.

Dehydrochlorination, well known for its utility in double-bond formation, occurred in both reactions type A and B, although cyclobutanecarbonitrile (reaction B) was formed only in trace quantities (Table III). Dehydrocyanation, on the other hand, worked well with only reaction C, another example of utilizing a vicinal dinitrile starting material. These results sug-

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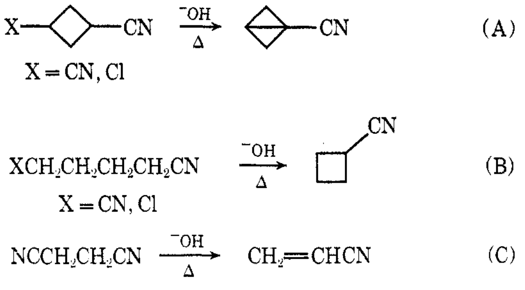
(6) Grasselli, *et al.*, U. S. Patent 3,347,902 (1967).

(7) Terent'ev and Gurvich, *Sb. Statei Obshch. Khim., Akad. Nauk SSSR*, 1, 404 (1953); see also "The Chemistry of Acrylonitrile," 2nd ed, American Cyanamid Co., New York, N. Y., 1959.

TABLE III

YIELD OF NITRILES FORMED BY DEHYDROCHLORINATION OR DEHYDROCYANATION WITH BASE

Process	Reaction conditions	Base employed	Yield of nitrile, %
A, X = Cl	115°, boiling toluene	85% KOH	40; recovered some starting material
A, X = CN	225°, 1 mm	Ascarite	None, recovered starting material
A, X = CN	225°, 250°, 300°, 1 mm	Soda lime	Trace
B, X = Cl	225°, 1 mm	Ascarite	Trace
B, X = CN	225°, 1 mm	Ascarite	None
C	250°, 1 mm	Ascarite	70; recovered some starting material



gest that dehydrocyanation might be general for vicinal double bond formation, and the method of choice only when warranted by starting material considerations.

Experimental Section

Cyclobutenecarbonitrile (I). A. By Dehydrocyanation of 1,2-Cyclobutanedicarbonitrile (II) with Ascarite.—A vertical quartz tube 50 cm long and 2.5 cm in diameter, packed 20 cm of its length with Ascarite, was heated with a 30-cm-long cylindrical furnace to 200° for 2 hr in an air stream until most of the water and absorbed gases were removed. The temperature was maintained at 225° and was recorded by a thermocouple well inserted at the top of the bed. The dinitrile II (10 g) was added in a melt dropwise over 2 hr and product I was collected in a series of traps cooled in solid carbon dioxide-acetone. The entire system was evacuated during the reaction at the best vacuum that could be maintained by an efficient oil pump (0.5–2 mm). A 59% conversion to I was obtained (determined by quantitative gc analysis on a silicone gum nitrile column at 150° or with a butanediol succinate column at 100°). An average contact time of II was about 0.41 sec. Trap-to-trap distillation of the contents (after separating the layers) of the traps gave 99.5% pure I (55% yield not corrected for II left in the tube).

Table I gives results with other bases treated as above. In each case, I was further purified by distillation in a low temperature (Dry Ice cooled) Vigreux column, bp 40° (20 mm). A free-radical inhibitor such as hydroquinone or phenothiazine was added to the pot to prevent polymerization.

Scale-up of the above procedure was accomplished by using a horizontally fixed 7.5-cm-diameter quartz tube (reactor) connected by an elbow joint to a vertical 2.5-cm quartz tube (vaporizer). Heating tapes were used to ensure the absence of cool spots between two split tube furnaces surrounding the tubes. Using predried 12-mesh soda lime (860 g), 133 g of II added over 24 hr at a reactor tube temperature of 194–197° (0.4–14 mm) led to 30.8 g of 95% pure I and 56 g of recovered II (33.5 g of II thus left in the reactor unaccounted for). Similarly, 860 g of Ascarite was used to form the reactor bed; 71 g of II was added at 197° (0.4–2.0 mm) over 13 hr, giving 24.2 g of crude I and 10 g of recovered II. Crude I (95 g) was collected from a number of these scale-up runs and distilled through a low-temperature still. Pure I (>99.5%) weighing 72.1 g was obtained. Isolated yields (corrected for recovered II) for both soda lime and "Ascarite" were therefore about 39%.

As noted in ref 1, pure I had a refractive index $n^{25}D$ of 1.456, a characteristic infrared absorption at 2240 cm^{-1} (CCl$_4$), and nmr (CCl$_4$) bands at τ 7.47, 7.40, 7.36 (total area 2), 7.34, 7.23, 7.17, 7.21 (total area 2), and 3.32, 3.30, and 3.29 (total area 1); our material also analyzed properly for C_5H_5N.

Anal. Calcd for C_5H_5N: C, 75.92; H, 6.37; N, 17.71. Found: C, 75.38; H, 6.42; N, 17.38.

B. By Dehydrochlorination of 2-Chlorocyclobutanecarbonitrile.[5]—A round-bottomed flask (three-necked and thermometer well) was fitted with a pressure-equalizing dropping funnel, powerful motor-driven stirrer, thermometer, and a gas exit connected *via* rubber tubing (sufficient in length to be clamped by a hemostat), to a series of traps (Dry Ice and liquid N$_2$) containing a trace of hydroquinone. The gas exit (frequently called "nitrogen inlet tube") and traps were washed with concentrated HCl and with acetone and thoroughly dried before use; the rubber connecting tubing was washed with 3 *N* HCl and acetone and dried. The system was dried under vacuum and charged with 6.0 g (0.11 mol) of 85% KOH pellets and 50 ml of diphenyl ether (nitrogen atmosphere). The dropping funnel was charged with 5.8 g (0.05 mol) of the chloronitriles (99% cis, 1% trans), and the system was evacuated to 20 mm. The pot was heated with stirring to 115° to "liquefy" the KOH and the chloronitrile was added dropwise at 110–115° over 30 min. Judicious application of heat from a mantel and cooling from a water bath, as well as occasional application of the hemostat clamp, were necessary to moderate the reaction and prevent flooding over into the product collection traps. When the addition was complete, the pressure was slowly reduced to 0.3 mm (occasional clamping required) to strip off the product. The pot temperature dropped but was maintained at 50° with a hot-water bath for 1 hr. The contents of the Dry Ice trap were distilled (at 0.3 mm) into an acid-washed trap (containing hydroquinone). Compound I (2.3 g, 58%) thus obtained as shown to be gc pure and had an infrared spectrum identical with that of an authentic sample. The *trans*-2-chloronitrile reacted similarly to give I in 60–70% yields.

Ritter Reaction of I with *tert*-Butyl Alcohol.—A 10.1-g sample of 98% H$_2$SO$_4$ was added over 10 min to 7.9 g (0.1 mol) of I (97% pure), 7.4 g (0.1 mol) of dry *tert*-butyl alcohol, and 50 ml of glacial acetic acid at 25–30° with stirring. About 5 min after the addition, the temperature rose to 42° and an H$_2$O bath was used to keep the temperature below 40° for 45 min. The reaction mixture was poured onto 200 g of ice and the white precipitate which formed was collected on a filter, washed with H$_2$O and pentane, and air dried, mp 125°. The nmr spectrum showed C(CH$_3$)$_3$ at τ 8.68, –CH$_2$CH$_2$– and an A$_2$B$_2$ pattern at 7.4 and 7.6, NH at 7.14, and –CH═CCO at 3.5 (triplet, *J* = 0.6 Hz) required by unsaturated amide structure. Ir showed NH stretch at 3300 cm^{-1} and no C≡N; yield 7.0 g (46%). Uv showed λ_{max}^{EtOH} 215 mμ (ε 1090).

Anal. Calcd for $C_9H_{15}NO$ (153.22): N, 9.15. Found: N, 8.85.

Reaction of I with *tert*-Butyl Mercaptan.—A solution of 7.9 g of CCB, 1.0 g of "Vazo" (azobisisobutyronitrile), and 20 ml of *tert*-butyl mercaptan were refluxed for 3 hr, let stand overnight, and distilled through a spinning band column, giving 7.3 g (43%) of thioether, bp 58–80° (0.6 mm). Nmr showed –C(CH$_3$)$_3$ absorption at τ 8.8, –CH$_2$CH$_2$ at 7.7, and two >CH– protons at 6.3. Ir showed CH at 3.39, 3.42, and 3.50 μ, C≡N at 4.49 μ, and –ClCH$_3$ at 7.20 and 7.34 μ. Raman showed bands at 600 (C–S) and 2400 cm^{-1} (C≡N). The mass spectrum showed a parent at *m/e* 169 and a base peak at *m/e* 57 for –C(CH$_3$)$_3$.

Anal. Calcd for $C_9H_{15}SN$ (169.29): C, 63.85; H, 8.93; N, 8.28; S, 18.94. Found: C, 63.77; H, 8.91; N, 8.46; S, 19.22.

2-Methoxycyclobutanecarbonitriles. A. From I with Sodium Methoxide.—A solution of 3.95 g (0.05 mol) of I in 7 ml of methanol was added to a stirred solution of 5.4 g (0.1 mol) of sodium methoxide in 25 ml of dry methanol over 0.5 hr. The reaction mixture was stirred overnight at room temperature, cooled in an ice bath, and diluted with 100 ml of H$_2$O; ether extraction followed by washing (H$_2$O) and drying of the ether extracts led on evaporation to an 8:1 trans to cis mixture of methoxynitriles. Spinning-band distillation afforded 2.9 g (51%) of purified product, bp 44–49° (3 mm). The stereochemical assignments were made by direct comparison with the cis isomer from the catalytic hydrogenation of 2-methoxycyclobutenecarbonitrile (see below). Nmr showed –CHO at τ 5.9, –CHCN at 7.0, –OCH$_3$ at 6.64, and –Cl$_2$Cl$_2$ at 7.9 for the trans isomer. The ir spectrum showed CH at 3.33, 3.40, 3.47, and 3.53 μ, $C\equiv N$ at 4.47 μ, and CO– at 8.84 μ.

Anal. Calcd for C_6H_9ON (111.14): C, 64.84; H, 8.16; N, 12.61. Found: C, 64.37; H, 8.07; N, 12.62.

B. **By Hydrogenation of 2-Methoxycyclobutenecarbonitrile.**—Four Carius types were each loaded with 0.4 g of phenothiazine, 37.5 ml of acrylonitrile, and 25 ml of ket deneimethyl acetal. The tubes were heated to 150° for 24 hr. The contents of the tubes were combined and distilled into a Dry Ice–acetone cooled trap at full vacuum using a heat gun. The volatiles were distilled through a 15-in. spinning-band column to give 58 g of 2,2-dimethoxycyclobutanecarbonitrile,[8] bp 68° (2.5 mm). The liquid could be induced to crystallize by scratching, mp 31–32°, ir 3.50, 4.45, 8–10 μ.

Anal. Calcd for $C_7H_{11}O_2N$: C, 59.55; H, 7.85; N, 9.92. Found: C, 59.63; H, 7.72; N, 10.31.

A 13.3-g sample of 2,2-dimethoxycyclobutanecarbonitrile was heated in the pot of a spinning band column with *ca.* 1 g of *p*-toluenesulfonic acid (not hydrate; dried over weekend at 300 mm and 80°) under vacuum (0.5 mm). Two fractions (40 and 70–100°) were collected as well as two traps (ice, Dry Ice). The low-boiling fraction and the traps were combined and redistilled to give 4.5 g (44%) of 2-methoxycyclobutenecarbonitrile (>99% pure),[8] bp 32–40° (0.3 mm). The nmr spectrum ($CDCl_3$) showed $-OCH_3$ absorption at τ 6.00 and an A_2B_2 pattern from the ring methylenes centered at 7.5. The ir spectrum showed a –CN band at 2225 and enol ether double bond at 1645 cm^{-1}. The uv spectrum showed $\lambda_{max}^{CH_3CN}$ 232 mμ (ϵ 10,000). The mass spectrum showed a base peak for the parent at *m/e* 109.

Anal. Calcd for C_6H_7NO (109.13): C, 66.03; H, 6.46; N, 12.84. Found: C, 65.33; H, 6.62; N, 12.60.

The same reaction could be accomplished by heating a mixture of 58 g of cyano ketal and 58 g of phosphorus pentoxide under full vacuum (*ca.* 0.3 mm) in a short-path still. The volatiles were distilled through a spinning-band column to give 17.8 g (40%) of product and 13.1 g (22%) of recovered starting material.

A 3.6-g sample of the cyclobutane (prepared by the P_2O_5 route), 0.5 g of 5% $Pd/CaCO_3$, and 50 ml of methanol were hydrogenated in a Parr apparatus until H_2 uptake was 105% of theory. Distillation of the crude product, obtained by removing catalyst and concentration, gave 3.8 g (quantitative) of *cis*-2-methoxycyclobutanecarbonitrile, bp 52–60° (1.25–1.5 mm). The nmr spectrum ($CDCl_3$) showed $-OCH_3$ at τ 6.67, >CHCN at 6.6, $>CHOCH_3$ at 6.1, and ring CH_2 at 7.8. The infrared spectrum showed strong $-C\equiv N$ at 2250 and $-OCH_3$ at 2850 cm^{-1}. The mass spectrum showed a base peak at *m/e* 58, $CH_2{=}CH(OCH_3)^+$, and a large fragment at *m/e* 83 P − (C_2H_4).

Anal. Calcd for C_6H_9NO (111.14): C, 64.84; H, 8.16; N, 12.61. Found: C, 64.29; H, 8.29; N, 12.23.

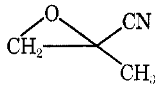
Reaction of I with Diazomethane.—*Caution!* A 7.9-g (0.1 mol) solution of I in ether was treated with excess dilute ethereal diazomethane. The disappearance of I was followed by gc. Very little I remained after about 8 hr. The ether solution was dried over $MgSO_4$ and the ether was evaporated. The oil obtained (10.7 g) had a nitrile band in the ir at 2250 cm^{-1}. The nmr spectrum showed an AB doublet of doublets at τ 5.16 and 5.25 (J = 14 Hz), the high-field proton split further (J = 1.5 Hz) by the methine proton ($\tau \approx 7.0$). Additional absorption (area 4) was found at τ 6.5–9.0 for the ethylene bridge. *The oil detonated on attempted distillation*, suggesting the azo structure.

1-Cyanobutenecarbonitrile Epoxide.—A suspension of 20 g of 85% *m*-chloroperbenzoic acid 7.9 g (0.1 mol) of I, and 100 ml of methylene chloride was stirred at room temperature for 3 months. The solution was filtered and washed with 5% $NaHCO_3$ solution (until basic), dilute $NaHSO_3$ (until no peroxide present), and then with brine and H_2O, then dried over $MgSO_4$. Concentration and distillation (spinning band) at 58° (12 mm) led to 0.95 g (10%) of cyano epoxide. The ir spectrum had –CN at 2250, bands at 1245, 1145, and 850 cm^{-1} for –OC–, and was blank in the 6-μ region. The nmr spectrum showed 1 H at τ 5.62 (epoxide H) split further and a very complex A_2B_2 pattern centered at 8.0 for $-CH_2CH_2-$. The mass spectrum showed a peak at *m/e* 95 for the parent ion, and peaks at *m/e* 94 (M − H) and 67 (M − C_2H_4).

Anal. Calcd for C_5H_5ON (95.11): C, 63.1; H, 5.30; N, 14.73. Found: C, 62.69; H, 5.36; N, 14.74.

The above procedure was improved to 30% yield by refluxing the reagents for 24 hr (60% converted), concentrating the $CHCl_3$ filtrate, and collecting the volatile from this filtrate into a Dry Ice trap by pumping under reduced pressure. The volatiles were then distilled directly, avoiding a wet work-up.

Methacrylonitrile Epoxide.—A solution of 30 g of *m*-chloroperbenzoic acid (85%), 100 ml of ethanol-free $CHCl_3$, and 7 g of methacrylonitrile was heated at reflux for 47 hr (precipitate formed). The solution was cooled, most of the solid was removed by filtration, and the filtrate was concentrated. The volatiles were distilled into a Dry Ice trap and redistilled through a small spinning band column. Two cuts, bp 46–48° (12 mm), were obtained (3.4 g) contaminated by chlorobenzene (gc yield 2.2 g, 26%). A sample was purified by preparative gc and showed the following nmr spectrum: AB quartet at τ 6.87, 7.11 (J = 11 Hz split further) for



and a singlet (split further) at τ 8.4 for the methyl group. The mass spectrum was consistent with a monomeric structure.

Anal. Calcd for C_4H_5NO (83.10): C, 57.81; H, 6.06; N, 16.84. Found: C, 57.84; H, 6.20; N, 17.04.

1,2-Dibromo-1-cyclobutanecarbonitrile.—To a magnetically stirred solution of 7.9 g (0.1 mol) of I (97% pure) in 50 ml of CCl_4 at room temperature was added over 2 hr a solution of 16 g (0.1 mol) of Br_2 in 100 ml of CCl_4. An induction period was noted with only little discharge of Br_2 color during the first 0.5 hr. The Br_2 color could be discharged completely, however, during the remaining 1.5 hr of addition. Only 95% of the Br_2 was added; no more color discharged. The CCl_4 was removed under reduced pressure and the liquid residue was distilled through a small spinning band still. The bromide, 20.0 g (84%), boiled at 63° (0.4 mm). Ir analysis showed strong $C\equiv N$ absorption but no saturation. The nmr spectrum showed $-CH_2CH_2-$ at τ 6.6–7.6 and >CHBr at τ 5.15.

Anal. Calcd for $C_5H_5Br_2N$ (238.93): C, 25.14; H, 2.11; Br, 66.86; N, 5.86. Found: C, 25.74; H, 2.45; Br, 66.67; N, 5.72.

Registry No.—I, 23519-88-2; II, 3396-17-6; III, 5167-62-4; *cis*-2-chlorocyclobutanecarbonitrile, 36178-64-0; *trans*-2-chlorocyclobutanecarbonitrile, 36178-63-9; *tert*-butyl alcohol, 75-65-0; *tert*-butyl mercaptan, 75-66-1; sodium methoxide, 124-41-4; *cis*-2-methoxycyclobutanecarbonitrile, 37445-36-6; *trans*-2-methoxycyclobutanecarbonitrile, 37445-37-7; 2,2-dimethoxycyclobutanecarbonitrile, 37447-58-8; 2-methoxycyclobutenecarbonitrile, 37447-59-9; cyclobutene, 822-35-5; diazomethane, 334-88-3; 1-cyclobutenecarbonitrile epoxide, 37447-60-2; methacrylonitrile epoxide, 37447-61-3; 1,2-dibromo-1-cyclobutanecarbonitrile, 37447-62-4; *m*-chloroperbenzoic acid, 937-14-4.

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