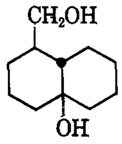
n^{24}_{D} 1.4957 (lit.[18] for 4, n^{24}_{D} 1.4982); λ_{max}^{neat} 5.88 and 10.2 μ; no indication of *cis* isomer at 14.2 μ. Capillary v.p.c. on a 150-ft. Ucon Polar column at 169° showed 97% of a single component with retention time the same as authentic[8] 4 (20.8 min.), and 3% of a minor component (21.2 min.).

10α-Hydroxy-*trans*-decalin-1β-carboxylic Acid (6).—To a solution of 2.00 g. (10.2 mmoles) of epoxide 5,[11] m.p. 132.5–133.5°, in 50 ml. of ether was added 0.589 g. (15.5 mmoles) of lithium aluminum hydride. Work-up, after stirring for 3 hr. at room temperature, gave 1.42 g. (70%) of crude acid 6, m.p. 119–125°, and 0.546 g. of neutral material. An analytical sample of 6 was obtained from the crude acid after four recrystallizations from chloroform, m.p. 133–134.5°.

Anal. Calcd. for $C_{11}H_{18}O_3$: C, 66.67; H, 9.09. Found: C, 66.96; H, 9.39.

Crystallization on a larger scale presented a problem as no satisfactory solvent was found. A single stage, high-yield purification to material of m.p. 127–130° could be effected with ether as solvent but the melting point could not be raised by further crystallization.



7

The neutral fraction yielded analytically pure diol 7, m.p. 114–115°, on crystallization from ether.

Anal. Calcd. for $C_{11}H_{20}O_2$: C, 71.74; H, 10.87. Found: C, 71.92; H, 11.06.

Electrolysis of 6.—To a 300-ml. beaker fitted with a cold-finger spiral condenser and two platinum electrodes separated by 2–3 mm., each 5 cm.^{2}, was added a solution of 4.76 g. of crude[19] 6, m.p. 119–125°, in 150 ml. of boiled methanol. A nitrogen atmosphere was maintained over the solution throughout the electrolysis. Sufficient sodium hydride was added to produce a current of *ca.* 0.5 amp. at constant applied voltage, 41 v. The current was stopped after the passage of 2.2 times the theoretical amount,[20] the methanol evaporated, and the residue worked up normally. Recovered crystalline 6 amounted to 0.37 g. (7%); the remainder was a neutral oil, 3.37 g. (92%, based on loss of carbon dioxide), which was subjected to short-path distillation. The yield of clear colorless liquid was 2.70 g. (80%); bath temperature, 85–110° (0.3 mm.); λ_{max}^{neat} 5.88 and 10.2 μ (no absorption at 14.2 μ). V.p.c. of the distilled product (168° on a 150-ft. capillary column with a Ucon Polar coating) showed the presence of the following components[21] (retention time in minutes, area): 1.8, 6%; 18.0, 7%; 22.3, 55%; 25.1, 7%; 39.5, 4%; 54.7, 4%. Treatment of 81 mg. of the distillate with a solution of 65 mg. of semicarbazide hydrochloride and 90 mg. of sodium acetate in 0.8 of ml. water, 20 min. at 70° and 48 hr. at room temperature, gave white crystals of the semicarbazone which were filtered from the solution and dried, 63 mg. (56%), m.p. 176–178°. Recrystallization from acetonitrile raised the m.p. to 182–183° (authentic[8] m.p. 183–184°, m.m.p. 182–183°); ultraviolet spectrum superimposable on that of authentic semicarbazone, $\lambda_{max}^{95\%\ EtOH}$ 232 mμ (ϵ 11,000).

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[18] E. M. Kosower, W. D. Closson, H. L. Goering, and J. C. Gross, *J. Am. Chem. Soc.*, **83**, 2013 (1961).

[19] Similar results were obtained using purified **6** on a smaller scale.

[20] The approximate quantity of electricity required to give high conversion without overelectrolysing was determined in trial runs.

[21] Numerous minor peaks, each less than 3%, constituted the remaining 17%.

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cis- and *trans*-1,2,3-Tricyanocyclopropanes

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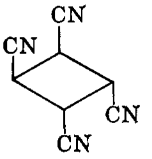
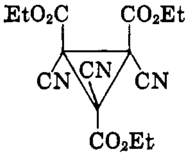
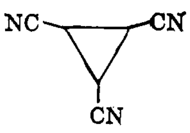
In 1958, Sadeh and Berger[1] reportedly obtained tetracyanocyclobutane (I) while attempting to synthesize ethyl cyanoacetoxyacetate from ethyl bromocyanoacetate and potassium acetate. The properties of their product were in no way similar to those of the solid state photodimer of fumaronitrile which we have shown has structure I.[2] However, it did not appear unreasonable that Sadeh and Berger's product might actually be the "all-*trans*" isomer of I in view of the possibility for thermodynamic equilibration under the reaction conditions. A structure proof was, therefore, undertaken.



I



II



IIIa, *cis*
b, *trans*

An initial literature survey revealed that, in 1900, Errera and Perciabosco[3] had obtained *trans*-1,2,3-tricyano-1,2,3-tricarbethoxycyclopropane (II)[4] on treating the anion of ethyl cyanoacetate with bromine. Subsequent hydrolysis of II with cold, dilute barium hydroxide afforded small amounts of a substance whose elemental analysis was consistent with that expected for a 1,2,3-tricyanocyclopropane (III). In view of the similarity of the reaction conditions and reagents employed by the two groups, it seemed reasonable that Sadeh and Berger's product, in reality, might be either *cis*- or *trans*-1,2,3-tricyanocyclopropane.

Preliminary investigations on a sample of Sadeh and Berger's nitrile[5] indicated that indeed it was a 1,2,3-tricyanocyclopropane and not a tetracyanocyclobutane. The infrared spectrum of the nitrile has a strong absorption band at 3063 cm.$^{-1}$ which may be attributed to the cyclopropyl C–H stretching[6] as well as a doublet at 2261 and 2278 cm.$^{-1}$ in the characteristic region for nitriles.[6] Hydrolysis with aqueous sodium hydroxide and subsequent esterification with diazomethane provided a material whose infrared and n.m.r. spectra are identical to those of an authentic sample of *trans*-1,2,3-tricarbomethoxycyclopropane.[7] The stereochemistry of the original nitrile, of course, cannot be inferred from these results.

It is noteworthy, that in our attempts to reproduce Sadeh and Berger's experiments, we obtained not one but two products (in a 1.2:1 ratio) which could be separated by chromatography on neutral alumina. Although infrared spectra of the two compounds possessed features in common, they were not identical. The major product (m.p. 201°) was identical in all respects with Sadeh and Berger's nitrile. The elemental analyses and ebullioscopic molecular weight determina-

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[1] T. Sadeh and A. Berger, *Bull. Res. Council Israel*, **7A**, 98 (1958).

[2] G. W. Griffin, J. E. Basinski, and L. I. Peterson, *J. Am. Chem. Soc.*, **84**, 1012 (1962).

[3] G. Errera and F. Perciabosco, *Chem. Ber.*, **33**, 2976 (1900).

[4] The infrared and n.m.r. spectra of II confirm Errera and Perciabosco's structural assignment. The stereochemistry was clearly established as *trans* from the n.m.r. spectrum which shows two equivalent and one nonequivalent ethyl groups.

[5] We wish to thank Dr. T. Sadeh for samples of his nitrile (*cis*-1,2,3-tricyanocyclopropane) and *trans*-1,2,3-tricarbethoxy-1,2,3-tricyanocyclopropane for purposes of comparison.

[6] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1958.

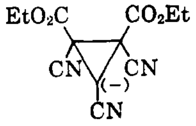
[7] Prepared according to the method of E. Buchner, *Chem. Ber.*, **21**, 2637 (1888).

tions for both nitriles are compatible with tricyanocyclopropane structures. The mass spectra of the two compounds exhibit a parent peak at *m/e* 117 as expected, and all of the major fragment peaks are easily interpreted assuming cyclopropyl structures.[8] The minor product (m.p. 191.5–192.5°) was shown to be the isomeric tricyanocyclopropane by basic hydrolysis and subsequent esterification to *trans*-1,2,3-tricarbomethoxycyclopropane. The n.m.r. spectrum of the minor product determined in acetonitrile exhibits resonance characteristic of an AB_2 multiplet, centered at τ 7.10. In contrast, the n.m.r. spectrum of Sadeh and Berger's compound (also determined in acetonitrile) shows only one peak at τ 7.28. The combined chemical and spectral data unequivocally identifies Sadeh and Berger's product as *cis*-1,2,3-tricyanocyclopropane (IIIa). The accompanying minor product must then possess the isomeric *trans*-1,2,3-tricyanocyclopropane structure IIIb.

A probable intermediate in the formation of the isomeric tricyanocyclopropanes from ethyl bromocyanoacetate is 1,2,3-tricarbethoxy-1,2,3-tricyanocyclopropane (II). Subsequent hydrolysis and decarboxylation would lead to the observed products. That this is indeed a plausible route was demonstrated by subjecting *trans*-1,2,3-tricarbethoxy-1,2,3-tricyanocyclopropane to the reaction conditions. The triester II smoothly underwent hydrolysis and decarboxylation in 95% ethanol solution containing potassium acetate. The products were exclusively *cis*- and *trans*-1,2,3-tricyanocyclopropane, formed in a 1.35:1 ratio, respectively.

The decarboxylation reaction is clearly kinetically controlled. Each of the isomeric trinitriles IIIa and IIIb was found to be stable under the reaction conditions; however, isomerization of *cis*-1,2,3-tricyanocyclopropane to the thermodynamically more stable *trans* isomer was achieved with potassium *t*-butoxide in *t*-butyl alcohol.

An attractive mechanism for the decarboxylation of II to afford predominately the *cis* nitrile IIIa involves the preferential attack of the proton donor from the less hindered side of the intermediate cyanoanion IV.[9]



IV

After initial loss of a molecule of carbon dioxide and subsequent acquisition of a proton, the side possessing the hydrogen atom becomes the less hindered side in the two ensuing decarboxylation steps.

This reaction offers a direct route to the *cis*-1,2,3-trisubstituted cyclopropane series.[10] The utility of 1,2,3-trisubstituted cyclopropanes as precursors for the unknown trimethylenecyclopropane is currently being investigated.

Experimental

Preparation of the *cis* and *trans* 1,2,3,-Tricyanocyclopropanes (IIIa and IIIb).—These compounds were prepared by essentially the same procedure employed by Sadeh and Berger.[1] Ethyl bromocyanoacetate [10.0 g., 0.052 mole, b.p. 135° (40 mm.)], prepared according to the method of Errera and Perciabosco,[3] was added dropwise to a stirred solution of 5.5 g. (0.056 mole) of potassium acetate in 50 ml. of 95% ethanol. The reaction temperature was maintained at 20° during the course of the addition and the resulting deep red reaction mixture was stirred overnight. The solvent was then removed under vacuum, and the product was separated from potassium acetate by extraction with 30 ml. of cold acetonitrile. Subsequent removal of the solvent under reduced pressure gave a mixture of the isomeric tricyanocyclopropanes whose n.m.r. spectrum, determined in acetonitrile, showed a *cis* to *trans* ratio of 2.1:1. The crude mixture was separated by chromatography on neutral alumina. Since the tricyanocyclopropanes are insoluble in nonpolar solvents, the solid mixture was intimately ground with an equal volume of alumina and placed in a narrow band on top of the prepacked column. The solvents used for elution were benzene, ethyl acetate, and methanol in the order of increasing polarity. *trans*-1,2,3-Tricyanocyclopropane (IIIb) (280 mg., m.p. 191.5–192.5°) was eluted in a benzene–ethyl acetate fraction. The *cis* isomer IIIa (360 mg., m.p. 199–200°) was obtained from an ethyl acetate–methanol fraction. The total yield of the tricyanocyclopropanes was 32%. Both compounds were recrystallized from aqueous ethanol.

Anal. (IIIa). Calcd. for $C_6H_3N_3$: C, 61.53; H, 2.58; N, 35.89; mol. wt., 117. Found: C, 61.79; H, 2.45; N, 35.71; mol. wt., 121 (ebullioscopic with 2-butanone as the solvent).

Anal. (IIIb). Calcd. for $C_6H_3N_3$: C, 61.53; H, 2.58; N, 35.89; mol. wt., 117. Found: C, 61.72; H, 2.56; N, 36.13; mol. wt., 120 (ebullioscopic with 2-butanone as the solvent).

Preparation of the *cis*- and *trans*-1,2,3-Tricyanocyclopropanes (IIIa and IIIb) from *trans*-1,2,3-Tricyano-1,2,3-tricarbethoxycyclopropane (II).—*trans*-1,2,3-Tricyano-1,2,3-tricarbethoxycyclopropane (6.1 g., 0.018 mole, m.p. 123–124°), prepared according to the method of Sadeh and Berger,[1] was dissolved with stirring in a solution of 2.65 g. (0.028 mole) of potassium acetate in 200 ml. of 95% ethanol. Stirring was continued overnight at 20°. After removal of all volatile solvents, the product was extracted from the residual potassium acetate with 30 ml. of cold acetonitrile. Evaporation of the acetonitrile gave 2.1 g. (99%) of a mixture of *cis*- and *trans*-1,2,3-tricyanocyclopropanes in a 1.35:1 ratio, respectively. The ratio was again determined from the n.m.r. spectrum of the mixture. The infrared spectrum of the crude reaction mixture showed absorption due only to the two isomeric trinitriles IIIa and IIIb. The pure compounds where isolated by alumina chromatography as in the preceding case.

Conversion of the Isomeric Tricyanocyclopropanes (IIIa and IIIb) to *trans*-1,2,3-Tricarbomethoxycyclopropane.—*cis*-1,2,3-Tricyanocyclopropane (IIIa) (0.075 g. 0.64 mmole, m.p. 199–200°) was added to a solution of 0.30 g. (7.5 mmoles) of sodium hydroxide in 25 ml. of water. The reaction mixture was heated under reflux overnight and subsequently acidified with hydrochloric acid. The volatile solvents were removed under vacuum and the resulting solid was esterified with diazomethane in benzene. After removal of the benzene under vacuum, the desired product was extracted from the residual sodium chloride with carbon tetrachloride. The n.m.r. and infrared spectra of the reaction product in carbon tetrachloride were identical in all respects with those for an authentic sample of *trans*-1,2,3-tricarbomethoxycyclopropane.[7] The melting point of the triester after recrystallization from aqueous methanol was 56–57° (lit.[7] m.p. 61°).

Similarly, the *trans* isomer IIIb (m.p. 191.5–192.5°) also was converted to *trans*-1,2,3-tricarbomethoxycyclopropane.

Acknowledgment.—We are indebted to the Army Research Office (Durham) for financial support of this work.

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(8) We are indebted to Dr. T. Aczel and the Mass Spectral Group of the Research and Development Division of the Humble Oil and Refining Company, Baytown Texas, for the mass spectral data.

(9) A similar explanation was advanced to explain the predominant formation of the more sterically crowded isomer on decarboxylation of either of the two half esters of *cis*-2,5-dimethylcyclopentane dicarboxylic acid: see M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 358.

(10) Recently Ettlinger has reported the synthesis of the first member of this series, *cis*-1,2,3-tricarboxycyclopropane and its corresponding methyl ester: see M. G. Ettlinger and J. Kagen, *Chem. Ind.* (London), 1574 (1962).