A sample of 1,1-dimethoxycyclohexane was prepared as described by McCoy *et al.*;[4] n_D^{20} 1.4395; purity, 99.8% (oximation).

The dioxane was purified by treatment with sodium borohydride to remove peroxides, followed by distillation which provided a material which contained negligible absorption over the range of 250 to 350 mμ. The distillate was then redistilled from lithium aluminum hydride to remove last traces of water. This solvent was not satisfactory for use in the infrared work because it showed some absorption in the carbonyl region (5.8 μ) which was not removed by either the sodium borohydride or lithium aluminum hydride treatment.

t-Butyl alcohol was purified by distillation and was found to be free of carbonyl absorption in both the infrared and ultraviolet region of the spectrum. This material contained less than 0.01% water (Karl Fischer).

Chemical analyses. The determinations of the equilibrium concentrations for the neat mixtures were made by the following methods from Siggia:[12] total carbonyl, as cyclohexanone and 1,1-dimethoxycyclohexane, by the hydroxylamine method (1 hr. reaction time in a steam bath); cyclohexanone by the hydroxylamine-pyridine method (1 hr. reaction time at 27° ±5°); methanol by the phthalic anhydride–pyridine method (5 min. reaction time in a steam bath) and water by the Karl Fischer reagent.

To check the validity of these methods, a synthetic mixture of all components including the catalyst was made having near the equilibrium concentrations for a 2:1 mole ratio mixture (set up for $K_x = 0.172$). The value of K_x based on the analyses of the mixture was 0.157 which compares very well with the values shown in Table I-A. A further check of the methods is furnished by the results shown in Table I-A. In all three cases the total analysis is essentially 100% and the moles of ketal per 100 g. of mixture is essentially equal to the moles of water per 100 g. of mixture.

The values of K_x are considered to be only approximate inasmuch as the samples were not maintained at a constant temperature. In all cases, however, room temperature was 27° ±5°.

Spectral analyses. The ultraviolet measurements were made using a Carey Model 11 spectrophotometer. The solutions were run with either dioxane or *t*-butyl alcohol, as appropriate, in the comparison cell. Solutions of cyclohexanone in dioxane ($\lambda_{max} = 287$ mμ; $\epsilon = 15.77$) and *t*-butyl alcohol ($\lambda_{max} = 284$ mμ, $\epsilon = 15.74$) followed Beer's law over the concentrations checked in the ultraviolet.

The infrared measurements were made using a Perkin-Elmer Model 21 spectrophotometer. The samples were run in a 0.079 mm. sodium chloride cell and *t*-butyl alcohol was used as a blank. Because these solutions did not follow Beer's law, a curve was constructed for $\log \frac{I_0}{I}$ *versus* the concentration of cyclohexanone in *t*-butyl alcohol. The values used (for $\lambda_{max} = 5.83\ \mu$) were: $\log \frac{I_0}{I} = 0.071, 0.136, 0.230, 0.332$ for corresponding values of molarity of 0.0205, 0.0407, 0.0710, 0.104.

The solutions which were analyzed spectrally were made from the neat reaction mixtures of Table I-A with the appropriate solvent. The concentrations used are shown in Tables I-B, I-C, and I-D. The solutions were analyzed for cyclohexanone content and rechecked after about an hour—no variations were noted.

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(12) S. Siggia, *Quantitative Organic Analysis via Functional Groups*, 2nd ed., John Wiley and Sons, Inc., New York, 1957.

Cyanocarbon Chemistry. XVI.[1]
1,1,2,2-Tetracyanocyclopropane

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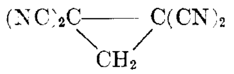
In the course of studies in the field of cyanocarbon chemistry, we have developed four independent syntheses of 1,1,2,2-tetracyanocyclopropane (I). Whereas 3-alkyl- and 3,3-dialkyl-1,1,2,2-tetracyanocyclopropanes have been prepared by earlier workers,[2,3] synthesis of the simplest member of the series has not been reported previously.

1,1,3,3-Tetracyanopropane[4] was brominated by *N*-bromosuccinimide in acetonitrile to give an 89–93% yield of an unstable dibromo derivative, probably 1,3-dibromo-1,1,3,3-tetracyanopropane (II). Addition of a solution of this compound in acetone to aqueous potassium iodide gave a 78% yield of the cyclopropane I. A smaller yield (28%) of I was obtained by reaction of an ethyl acetate solution of the dibromo compound with aqueous potassium cyanide. Proof of the structure of I is based on elemental analysis, molecular weight measurements, and infrared and proton-magnetic resonance spectral analyses.



I

$BrC(CN)_2CH_2C(CN)_2Br$

II

Addition of ethereal diazomethane to a solution of tetracyanoethylene[5] in tetrahydrofuran was accompanied by a vigorous evolution of nitrogen and precipitation of I, isolated in 38% yield after recrystallization. It is of interest that treatment of ethyl diazoacetate with tetracyanoethylene gave neither a cyclopropane nor a pyrazoline. Instead there was obtained an unstable compound, $C_{10}H_6N_6O_2$, that spectral evidence indicated may have been a 4-ethoxycarbonyl-5-tricyanovinyl-1,2,3-tri-

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(1) Paper XV, C. L. Dickenson, *J. Am. Chem. Soc.*, in press.

(2) S. Wideqvist (*Arkiv Kemi, Mineral. Geol.*, **B20**, No. **4**, 8 pp. (1945); *Chem. Abstr.*, **41**, 1621 (1947) reports the preparation of 3-alkyl- and 3,3-dialkyl-1,1,2,2-tetracyanocyclopropanes by the reaction of bromomalononitrile and potassium iodide with aldehydes or ketones. The method was unsuccessful when applied to the synthesis of I from formaldehyde. Cf. also S. Wideqvist, *Arkiv Kemi, Mineral. Geol.*, **14B**, No. **37**, 13 pp. (1941); *Chem. Abstr.*, **36**, 79 (1942).

(3) R. P. Mariella and A. J. Roth, III [*J. Org. Chem.*, **22**, 1130 (1957)] report the syntheses of 3-allyl-1,1,2,2-tetracyanocyclopropanes by the action of bromine on alkylidene bis(malononitriles).

(4) O. Diels and B. Conn, *Ber.*, **56**, 2076 (1923).

(5) T. L. Cairns, R. A. Carboni, D. D. Coffman, V. A. Engelhardt, R. E. Heckert, E. L. Little, E. G. McGeer, B. C. McKusick, W. J. Middleton, R. M. Scribner, C. W. Theobald, and H. E. Winberg, *J. Am. Chem. Soc.*, **80**, 2775 (1958).

azole,[6] formed by addition of the diazoacetic ester to a carbonitrile group of the tetracyanoethylene.

The third synthesis of I was carried out by modification of a published procedure[2] for the preparation of 3-alkyl-1,1,2,2-tetracyanocyclopropanes by the action of bromomalononitrile and potassium iodide on aldehydes. Use of aqueous formaldehyde in this reaction gave a 68% yield of I.

The most convenient preparation of I (in 85% yield) consisted of adding bromine water to an aqueous solution of malononitrile and formaldehyde in the presence of a trace of β-alanine.

Evidence for the delocalization of the electrons of cyclopropane ring systems[7] made it of interest to determine whether the hydrogen atoms of I were activated by the carbonitrile groups to such a degree that they would undergo reaction commonly associated with "active methylene" compounds. However, I was recovered unchanged after treatment with bromine in carbon tetrachloride, *N*-bromosuccinimide in boiling acetonitrile, selenium dioxide in boiling dioxane, hot sulfuryl chloride (with and without benzoyl peroxide added), and diazotized *m*-chloroaniline. Like the 3-alkyl- and 3,3-dialkyl-1,1,2,2-tetracyanocyclopropanes reported by Wideqvist,[2] I was soluble in 1*M* sodium hydroxide, presumably by saponification of one or more of its carbonitrile groups.

EXPERIMENTAL

1,3-Dibromo-1,1,3,3-tetracyanopropane II). A solution of 10.0 g. (0.07 mole) of 1,1,3,3-tetracyanopropane[4] (m.p. 133–135°) in 140 ml. of acetonitrile was stirred under an atmosphere of nitrogen while 24.8 g. (0.14 mole) of *N*-bromosuccinimide was added in small portions over a period of 15 min. The orange solution was stirred overnight at room temperature and solvent was removed under reduced pressure (25°) to give a white solid. After trituration with successive portions of water and drying at reduced pressure, the solid weighed 19.1 g. (91% yield) and melted at 124–129° dec. This compound was sensitive toward heat and efforts to purify it caused decomposition.

Anal. Calcd. for $C_7H_2Br_2N_4$: Br, 52.94. Found: Br, 51.45.

1,1,2,2-Tetracyanocyclopropane (I). *Method A.* A solution of 3.0 g. (0.01 mole) of 1,3-dibromo-1,1,2,2-tetracyanopropane (II) in 10 ml. of ethyl acetate was added dropwise with vigorous stirring over a period of 35 min. to a solution of 1.37 g. (0.21 mole) of potassium cyanide in 4 ml. of water maintained at −12° to −20°. The solution was stirred for an additional 40 min. while the temperature gradually rose to 15°. The organic layer was separated and washed with water, dried over magnesium sulfate, and evaporated to dryness under reduced pressure. Sublimation of the dark brown residue at 150° (0.03 mm.) gave 0.40 g. (28% yield) of white solid, m.p. 224° dec.[8] The infrared spectrum of this compound in potassium bromide showed the following bands: 3.23, 3.32 (C—H), 4.43 (C≡N), 6.90, 7.01, 8.25, 9.07, 9.88 (cyclopropane?), 13.69 and 14.06 μ. The proton magnetic resonance spectrum of a sample dissolved in deuterated acetone showed a single peak at −108 c.p.s.[9]

Anal. Calcd. for $C_7H_2N_4$: C, 59.16; H, 1.42; N, 39.42; mol. wt., 142. Found: C, 59.39; H, 1.54; N, 39.38; mol. wt. (ebullioscopic in acetone) 138, 136.

A solution of 14.2 g. (0.086 mole) of potassium iodide in 35 ml. of water was added with stirring to a solution of 3.0 g. (0.01 mole) of 1,3-dibromo-1,1,3,3-tetracyanopropane (II) in 15 ml. of acetone. The solution was allowed to stand for 15 min. and then filtered to give, after washing and drying, 1.1 g. (78%) of 1,1,2,2-tetracyanocyclopropane, m.p. 223°.[8] The infrared spectrum of this sample was identical with that of I obtained above.

Method B. A dry solution of 2.8 g. (0.067 mole) of diazomethane in 200 ml. of ether was added in portions (15 min.) with stirring to a solution of 8.5 g. (0.067 mole) of tetracyanoethylene[5] in 100 ml. of dry tetrahydrofuran. After evolution of gas had ceased, the yellow solution was stoppered loosely and allowed to stand for 2 days at room temperature, by which time it had turned bright red in color and had deposited a white solid. Removal of the solid by filtration and recrystallization from benzene-ethanol gave 3.6 g. (38%) of white crystals, m.p. 223–225° dec.[8] The infrared spectrum of this compound was identical with that of I obtained by Method A.

Anal. Found: N, 38.95.

Evaporation of the red ethereal solution remaining after removal of I left 6.5 g. of a dark red solid, m.p. 85–110°, that showed signs of extensive decomposition on standing for several days at room temperature. Attempts to recrystallize this substance and to eliminate nitrogen by boiling in benzene gave no isolable compounds.

Method C. To a solution of 5.2 g. (0.04 mole) of bromomalononitrile in 20 ml. of tetrahydrofuran diluted with 1 ml. of water was added 1.6 g. (0.02 mole) of 37% formalin followed by 6.6 g. (0.04 mole) of potassium iodide in 8 ml. of water. When the exothermic reaction had subsided, the mixture was diluted with a little water and filtered. The precipitate so obtained was washed with dilute potassium iodide solution and then with water, giving 2.2 g. of crude I (68% yield). Recrystallization from methanol (0.7 g./35 ml.) gave needles having an infrared absorption spectrum identical with that of I obtained by Method A.

Anal. Found: C, 59.26, 59.16; H, 1.58, 1.66; N, 39.57, 39.64.

Method D. A solution of 13.2 g. (0.2 mole) of malononitrile in 100 ml. of water was mixed with 8.1 g. (0.1 mole) of 37% formalin in a 2-l. flask equipped with a stirrer and a dropping funnel. Fifty milligrams of β-alanine was added to the solution and a solution of 5.15 ml. (0.1 mole) of bromine in 500 ml. of water was added during 5 min. The colorless solution was warmed to 45°, stirred for 1 hr., and cooled in ice. The white crystalline product removed by filtration weighed 12.0 g. (85%) and was nearly pure I.

Addition of ethyl diazoacetate to tetracyanoethylene. To 10.2 g. (0.15 mole) of tetracyanoethylene[5] dissolved in 125 ml. of dry tetrahydrofuran was added with stirring 20 g. (0.18 mole) of ethyl diazoacetate. After the solution had been allowed to stand for 5 hr. at room temperature, 600 ml. of cyclohexane was added. After 3 days the clear, orange solution was decanted from about 5 g. of black tar and evaporated under reduced pressure (40°). During the evaporation

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(6) Analogy for such a reaction is to be found in the reaction of diazomethane with methoxycarbonyl cyanide to give a 1,2,3-triazole [*cf.* Thesing and Witzel, *Angew. Chem.*, **68**, 425 (1956)]. Methoxycarbonyl cyanide, like tetracyanoethylene, has an electrophilic substituent adjacent to a carbonitrile group.

(7) *Cf.* for example E. N. Trachtenberg and C. Odian, *J. Am. Chem. Soc.*, **80**, 4018 (1958) and G. W. Cannon, A. A. Santilli, and P. Shenian, *J. Am. Chem. Soc.*, **81**, 4264 (1959).

(8) The melting point is strongly dependent on the rate of heating. Samples were placed on a hot stage preheated to 200°.

(9) Obtained by means of a Varian Model 4300 high-resolution spectrometer operating at an R_f field of 56.4 Mc. per second. Spectra were calibrated in terms of displacements in c.p.s. from the proton resonance of water.

process dark, gummy material precipitated until about two thirds of the original volume of liquid remained, at which time a yellow solid began to precipitate. At this point the clear solution was decanted again from the solid and evaporated to dryness under reduced pressure. Recrystallization of the yellow residue (20 g.) from 500 ml. of benzene-ethyl acetate (12:1) gave 16 g. of yellow amorphous solid, m.p. 120–123°. An analytical sample was prepared by two more crystallizations from benzene, carried out quickly in order to minimize decomposition. Samples stored at room temperature underwent considerable darkening after several days. The infrared spectrum (potassium bromide) showed bands at 2.95 μ (NH), 3.35 μ (CH), 4.45 μ and 4.55 μ (conjugated C≡N), 5.74 μ (ethoxycarbonyl), and 6.25 μ (conjugated C=C or C=N). The ultraviolet spectrum (ethanol) showed absorption peaks at 423 mμ ($\epsilon\lambda_{max}$ 2200), 273 mμ ($\epsilon\lambda_{max}$ 1840), 245 mμ ($\epsilon\lambda_{max}$ 4600) and 215 mμ ($\epsilon\lambda_{max}$ 5330).

Anal. Calcd. for $C_{10}H_6N_6O_2$: C, 49.59; H, 2.50; N, 34.70; mol. wt., 242. Found: C, 50.05; H, 2.66; N (Dumas) 33.56, 33.81; N (Kjeldahl) 24.02, 23.89; mol. wt. (ebullioscopic in acetone) 233, 259.

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Improved Preparation of Triphenylmethyl Perchlorate and Fluoroborate for Use in Hydride Ion Exchange Reactions[1]

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The synthesis of tropenium (cycloheptatrienylium) salts by hydride ion abstraction from cycloheptatriene by trityl (triphenylmethyl) carbonium ion[4] has been extended recently to the preparation of a series of substituted tropenium ions,[5] several π-tropenium ion-metal carbonyl complexes,[6,7a] perinaphthenium ion,[7a] triphenylcyclopropenium ion,[7b] and various substituted triphenylmethylcarbonium ions.[7b]

$$\mathrm{R{-}H} + (\mathrm{C_6H_5})_3\mathrm{C}^+,\mathrm{Y}^- \longrightarrow \mathrm{R}^+,\mathrm{Y}^- + (\mathrm{C_6H_5})_3\mathrm{CH}$$

In the course of these studies it was found that when trityl halides were used as the hydride ion abstracting reagents, reaction was slow (except in sulfur dioxide solvent) and halide salts formed frequently had undesirable properties, *e.g.*, tropenium chloride and bromide were quite hygroscopic,[5,8] some substituted tropenium ions reacted with halide ions at their substituent groups,[5] and perinaphthenium halides were found to be only transiently stable.[7a] For these reasons, use of other trityl salts, particularly those with anions of low nucleophilicity, was investigated. Trityl perchlorate and trityl fluoroborate were found to give rapid hydride ion exchange in a number of different solvents and aromatic carbonium ion salt products of unusual stability.[4–7] The consequent need for convenient routes to these trityl salts led to an examination of the known preparative methods, and has resulted in a simplified procedure for the preparation of trityl perchlorate and a convenient new synthesis of trityl fluoroborate.

Trityl perchlorate has been prepared by essentially three different methods: (i) from trityl chloride and silver perchlorate in nitrobenzene on precipitation by benzene addition[9]; (ii) from trityl chloride or triphenylcarbinol in nitrobenzene or ether and 71% perchloric acid, followed by removal of all water by evaporation in a desiccator[9,10]; and (iii) from triphenylcarbinol in acetic anhydride and 71% perchloric acid, the product separating partially from concentrated solution, or by evaporation of dilute solutions in a vacuum desiccator.[10] Method i suffers from the disadvantages of the need for prior preparation of trityl chloride and the use of explosive silver perchlorate, and method ii requires complete removal of water by slow, and potentially dangerous, evaporation. Method iii, on the other hand, employs a convenient starting material and removes the water by reaction with acetic anhydride, but possesses the disadvantage, even when run in concentrated solution, of furnishing conveniently and directly only moderate yields of pure product. However, because of the lower solubility of the salt product in acetic anhydride than in acetic acid, conduct of the reaction of triphenylcarbinol and 71% perchloric acid in an adequate excess of acetic anhydride leads to the direct separation of yellow crystals of trityl perchlorate in 76–92% yield. Circumvention of the evaporation step not only greatly simplifies the preparation but also avoids formation of a dark-colored product that is not satisfactory for most hydride ion exchange reactions; decomposition of substituted tropenium

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[4] H. J. Dauben, Jr., and D. L. Pearson, Abstracts, 126th Meeting, American Chemical Society, New York, N. Y., Sept. 13, 1954, p. 18-O.

[5] (a) H. J. Dauben, Jr., F. A. Gadecki, K. M. Harmon, and D. L. Pearson, *J. Am. Chem. Soc.*, **79**, 4557 (1957); (b) H. J. Dauben, Jr. and K. M. Harmon, Abstracts, 134th Meeting, American Chemical Society, Chicago, Ill., Sept. 9, 1958, p. 35-P; (c) K. M. Harmon, Ph.D. thesis, University of Washington, 1958.

[6] H. J. Dauben, Jr. and L. R. Honnen, *J. Am. Chem. Soc.*, **80**, 5570 (1958); Abstracts, 15th Southwest Regional Meeting, American Chemical Society, Baton Rouge, La., Dec. 3, 1959, p. 89.

[7] (a) L. R. Honnen, Ph.D. thesis, University of Washington, 1960; (b) L. L. McDonough, Ph.D. thesis, University of Washington, 1960.

[8] *Cf.* W. v. E. Doering and L. H. Knox, *J. Am. Chem. Soc.*, **76**, 3203 (1954).

[9] M. Gomberg and L. H. Cone, *Ann.*, **370**, 142 (1909).

[10] K. A. Hofmann and H. Kirmreuther, *Ber.*, **42**, 4856 (1909).