Metathesis of sodium 1,1-dicyano-2,2,2-triethoxyethanide with cupric acetate produced the stable cupric salt.

### Experimental

**Potassium 1,1-Dicyano-2,2,2-trimethoxyethanide from Tetracyanoethylene and Potassium Cyanide in Methanol.**—To a solution of potassium cyanide (1.24 g., 19.1 mmoles) in methanol (60 ml.) at −80° under nitrogen was added a solution of tetracyanoethylene (2.50 g., 19.6 mmoles) in methanol (50 ml.) over the course of 3 hr. The solution was then warmed to −20° and held at this temperature for 2 hr. On addition of 300 ml. of diethyl ether, 2.4 g. of white, crystalline potassium 1,1-dicyano-2,2,2-trimethoxyethanide precipitated (2.4 g., 61% yield). Its infrared spectrum had nitrile bands at 2180 and 2130 cm.$^{-1}$, indicative of a substituted malononitrile anion, as well as strong absorption in the 1100- to 1000-cm.$^{-1}$ range due to the ortho ester group. An analytical sample was recrystallized three times from acetonitrile.

*Anal.* Calcd. for $C_7H_9KN_2O_3$: C, 40.4; H, 4.3; N, 14.5. Found: C, 40.5; H, 4.3; N, 13.8.

**Potassium 1,1-Dicyano-2,2,2-trimethoxyethanide from Tetracyanoethylene and Potassium Methoxide.**—To a solution of potassium hydroxide (22 g., 0.39 mole) in methanol (300 ml.) at −80° under nitrogen was added tetracyanoethylene (17 g., 0.133 mole) in tetrahydrofuran (100 ml.) over a 2-hr. period. The solution was allowed to warm to room temperature and then evaporated to dryness. The residue was extracted with a solution of 500 ml. of acetonitrile and 75 ml. of methanol. The extract was concentrated to give potassium 1,1-dicyano-2,2,2-trimethoxyethanide (18 g., 66% yield), identified by its infrared spectrum.

The sodium salt was prepared in a similar manner from a solution of sodium methoxide in methanol. (The sodium methoxide was prepared by dissolving sodium metal in methanol.)

**Potassium 1,1-Dicyano-2,2,2-trimethoxyethanide from Dicyanoketene Dimethyl Acetal and Potassium Methoxide.**—Potassium metal (1.0 g., 26 g.-atoms) was added to absolute methanol (100 ml.) at −80°. The potassium dissolved vigorously in a few minutes to form a solution of potassium methoxide. To this cold solution was added dicyanoketene dimethyl acetal (3.77 g., 27 mmoles). The solution was stirred while warming to room temperature over a period of 1 hr. The methanol was then evaporated, and the residue was recrystallized from a mixture of acetonitrile and methanol to give potassium 1,1-dicyano-2,2,2-trimethoxyethanide (3.9 g., 72% yield) identified by its infrared spectrum.

**Sodium 1,1-Dicyano-2,2,2-triethoxyethanide.**—To a solution of sodium metal (1.32 g., 57.4 g.-atoms) in absolute ethanol (100 ml.) at −20° under nitrogen was added dicyanoketene diethyl acetal[3] (8.62 g., 51.9 mmoles) in small portions over 15 min. The solution was rapidly filtered under dry nitrogen into 500 ml. of absolute ether. The white precipitate was collected on a filter and dried *in vacuo*. It totaled 11.05 g. (94%). An analytical sample recrystallized from acetonitrile had >250° dec. The infrared spectrum showed strong absorption at 4.58 and 4.62 $\mu$, characteristic of the $C(CN)_2^-$ group.

*Anal.* Calcd. for $C_{10}H_{15}N_2NaO_3$: C, 57.3; H, 6.45; N, 12.0. Found: C, 57.4; H, 6.61; N, 12.2.

**Sodium 1,1-Dicyano-2-ethoxy-2,2-ethylenedioxyethanide from Dicyanoketene Ethylene Acetal and Sodium Ethoxide.**—The above procedure was repeated with dicyanoketene ethylene acetal.[3] Sodium 1,1-dicyano-2-ethoxy-2,2-ethylenedioxyethanide was obtained in 87% yield and recrystallized from acetonitrile showing >250° dec.

*Anal.* Calcd. for $C_8H_9N_2NaO_3$: C, 47.1; H, 4.45; N, 13.7. Found: C, 47.5; H, 4.15; N, 14.2.

**Cupric 1,1-Dicyano-2,2,2-triethoxyethanide from Sodium 1,1-Dicyano-2,2,2-triethoxyethanide and Cupric Acetate.**—To sodium 1,1-dicyano-2,2,2-triethoxyethanide (2.0 g.) in warm water (50 ml.) was added cupric acetate monohydrate (2.0 g.) in hot water (50 ml.). The solution was refrigerated overnight. The cold reaction mixture was filtered to give intensely green, cubic crystals of cupric 1,1-dicyano-2,2,2-triethoxyethanide (1.71 g.), m.p. 230–233°.

*Anal.* Calcd. for $C_{20}H_{30}CuN_4O_6$: C, 49.4; H, 6.22. Found: C. 49.3; H, 6.01.

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# Symmetrical and Unsymmetrical Fluoroalkoxy- and Fluorophenoxy-s-triazines and Related Compounds

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In the course of preparing a series of symmetrical and unsymmetrical fluoroalkoxy-[1] and fluorophenoxy-*s*-triazines, methods of synthesis described in the literature proved unsatisfactory. The preparation of the unsymmetrical compounds required the stepwise replacement of chlorine from cyanuric chloride. Dudley's[2] method of preparing trialkoxy-*s*-triazine from cyanuric chloride and an excess of an alcohol gave yields below 40% when acetone was substituted for the excess alcohol. The procedure of Koopman and co-workers[3,4] for preparing 2-alkoxy-4,6-dichloro-*s*-triazines by treating cyanuric chloride with an alcohol in the presence of *s*-collidine in acetone and hydrolyzing the product gave unreproducible yields from 25 to 50%. Holt[5] and Maynard's method of converting the fluoro alcohol to the sodium salt with sodium hydride prior to condensation with cyanuric chloride was cumbersome and the yields were low.

It was found that both the partially and wholly substituted derivatives could be prepared conveniently in good yields by treating a mixture of the fluoro alcohol and cyanuric chloride dissolved in ether or toluene with the stoichiometric quantity of *s*-collidine, refluxing the mixture, filtering off the salts, and purifying the product by fractional distillation or recrystallization. The method was generally applicable to the synthesis of a systematic series of compounds which is reported elsewhere. The required degree of substitution could be obtained by proper adjustment of the stoichiometry provided sufficiently high reaction temperatures were employed. Diethyl ether was a satisfactory solvent when the first or second chlorine atom of cyanuric chloride was substituted, but the higher temperature of refluxing toluene was required for the substitution of the third chlorine atom by a fluoroalkoxy group. Because perfluorophenol is more acidic than the fluoro alcohols, the introduction of the perfluorophenoxy group as the third group could be accomplished in high yield in ether.

Another method was satisfactory for preparing certain completely substituted *s*-triazines. In this procedure, a two-phase solvent system, carbon tetrachloride–water, was employed with sodium hydroxide acting as the acid acceptor for the reaction between

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(1) The fluoro alcohols employed in this work were the commercially available telomer alcohols, $H(CF_2CF_2)_nCH_2OH$ (where *n* is 1, 2, 3, 4, and 5), $F(CF_2)_3CH_2OH$, and $F(CF_2)_7CH_2OH$. In this paper, these compounds are named 1,1,3-tri-H-perfluoropropanol, 1,1,5-tri-H-perfluoropentanol, 1,1,7-tri-H-perfluoroheptanol, 1,1,9-tri-H-perfluorononanol, 1,1,11-tri-H-perfluoroundecanol, 1,1-di-H-perfluorobutanol, and 1,1-di-H-perfluorooctanol, respectively.

(2) J. R. Dudley, J. T. Thurston, F. C. Schaefer, D. Holm-Hansen, C. J. Hull, and P. Adams, *J. Am. Chem. Soc.*, **73**, 2986 (1951).

(3) H. Koopman, J. H. Uhlenbroek, H. H. Haeck, J. Daams, and M. J. Koopmans, *Rec. trav. chim.*, **78**, 967 (1959).

(4) J. H. Uhlenbroek, H. Koopman, H. H. Haeck, J. Daams, and J. D. Bijloo, U. S. Patent 2,911,337 (Nov. 3, 1959).

(5) H. S. Holt and J. T. Maynard, U. S. Patent 2,741,606 (April 10, 1956).

cyanuric chloride and the fluoro alcohol. Yields of 65–80% were obtained when 1,1,5-tri-H-perfluoropentanol or 1,1,7-tri-H-perfluoroheptanol were used, but low yields were obtained from the other fluoro alcohols, probably because of solubility differences.

The toluene–collidine method could be successfully applied to the synthesis of the bridged compound 2,2,-3,3-tetrafluoro-1,4-bis[2,4-bis(1,1,5-tri-H-perfluoropentoxy)-*s*-triazine-6-oxy]butane from 2,2,3,3-tetrafluorobutane-1,4-diol and 2-chloro-4,6-bis(1,1,5-tri-H-perfluoropentoxy)-*s*-triazine in a moderate yield. The result was somewhat unexpected since cyanuric chloride and 1,4-butanediol are reported to give tetrahydrofuran in the presence of aqueous sodium hydroxide.[6] None of the fluorine-substituted tetrahydrofuran derivative could be isolated from the reaction mixture in this work.

Fully chlorinated derivatives could be prepared by the ultraviolet-catalyzed chlorination of the fluoroalkoxy-*s*-triazines in carbon tetrachloride. The chlorinated derivatives were less stable than the unchlorinated compounds and could not be distilled. Although antimony fluorides have been used to fluorinate fluorine-substituted α-chloro ethers, no reaction occurred when the chlorinated fluoroalkoxy-*s*-triazines were treated with $SbCl_3$ and $SbCl_3F_2$, either in the absence of a solvent or in a nonreactive solvent such as *n*-decane or benzotrifluoride. Other solvents such as dimethyl sulfoxide and dimethylacetamide decomposed the chlorinated fluoroalkoxy-*s*-triazines.

## Experimental

**2,4,6-Tris(1,1,7-tri-H-perfluoroheptoxy)-*s*-triazine.**—A stirred solution of 14.7 g. (0.080 mole) of cyanuric chloride in 100 ml. of toluene was treated sequentially with solutions of 83.6 g. (0.25 mole) of 1,1,7-tri-H-perfluoroheptanol in 130 ml. of toluene and 30.6 g. (0.25 mole) of *s*-collidine in 50 ml. of toluene. The time required for each addition was about 15 min. After the resulting mixture was refluxed for 2 hr., cooled, and filtered, 36.0 g. (calcd. 37.1 g.) of collidine hydrochloride was recovered by filtration. Evaporation of the solvent and distillation of the product through a 30-cm. vacuum-jacketed column gave 72.0 g. (84%) of 2,4,6-tris(1,1,7-H-perfluoroheptoxy)-*s*-triazine, b.p. 172–182° (0.04 mm.). After recrystallization from a 1:1 mixture of toluene and petroleum ether (b.p. 35–60°), 67.2 g. (78%) of the product, m.p. 54–55.5°, was obtained.

*Anal.* Calcd. for $C_{24}H_9F_{36}N_3O_3$: C, 26.90; H, 0.85; F, 63.85. Found: C, 26.59; H, 0.74; F, 63.63.

Diethyl ether was used as the solvent in one preparation of tris(1,1,7-tri-H-perfluoroheptoxy)-*s*-triazine; however, only 63% of the required collidine hydrochloride was isolated. Replacement of the ether with toluene and additional heating was required to precipitate the remaining collidine hydrochloride.

**2,4-Bis(perfluorophenoxy)-6-(1,1,7-tri-H-perfluoroheptoxy)-*s*-triazine.**—To a stirred solution of 48.0 g. (0.100 mole) of 2,4-dichloro-6-(1,1,7-tri-H-perfluoroheptoxy)-*s*-triazine in 100 ml. of ether was added a solution of 38.8 g. (0.210 mole) of pentafluorophenol in 80 ml. of diethyl ether, and the resulting mixture was treated with a solution of 25.4 g. (0.210 mole) of *s*-collidine in 60 ml. of ether. Each addition required about 15 min. The mixture was refluxed for 2 hr., cooled, and filtered to give 35.5 g. (calcd. 31.4 g.) of collidine hydrochloride. Evaporation of the ether and fractional distillation of the residue gave 69.0 g. (89%) of 2,4-bis(perfluorophenoxy)-6-(1,1,7-tri-H-perfluoroheptoxy)-*s*-triazine, b.p. 161–162° (0.07 mm.), $n^{30}D$ 1.4238.

*Anal.* Calcd. for $C_{22}H_3F_{22}N_3O_3$: C, 34.08; H, 0.39; F, 53.92. Found: C, 34.40; H, 0.57; F, 53.65.

**2,4-Dichloro-6-(1,1,3-tri-H-perfluoropropoxy)-*s*-triazine.**—A stirred solution of 184 g. (1.00 mole) of cyanuric chloride in 2250 ml. of diethyl ether was treated first with 131 g. (1.00 mole) of 1,1,3-tri-H-perfluoropropanol in 500 ml. of ether, and then with a solution of 121 g. (1.00 mole) of *s*-collidine in 200 ml. of ether. Both reagents were added in rapid drops. When the product was refluxed 2 hr., cooled, and filtered, 147 g. (calcd. 157 g.) of collidine hydrochloride was recovered. Evaporation of the solvent and distillation of the residue through a 30-cm. vacuum-jacketed column gave 195 g. (70%) of 2,4-dichloro-6-(1,1,3-tri-H-perfluoropropoxy)-*s*-triazine, b.p. 111–116° (5.6 mm.), $n^{25}D$ 1.4624. Redistillation gave 173 g. of the product boiling at 118° (9 mm.), $n^{27}D$ 1.4613.

*Anal.* Calcd. for $C_6H_3Cl_2F_4N_3O$: C, 25.73; H, 1.08; Cl, 25.32; F, 27.15. Found: C, 25.77; H, 1.35; Cl, 25.09; F, 27.09.

**2,4-Bis(1,1,7-tri-H-perfluoroheptyloxy)-6-(1,1,5-tri-H-perfluoropentoxy)-*s*-triazine.**—A solution of 38.0 g. (0.10 mole) of 2,4-dichloro-6-(1,1,5-tri-H-perfluoropentoxy)-*s*-triazine in 100 ml. of carbon tetrachloride was added to 66.4 g. (0.20 mole) of 1,1,7-tri-H-perfluoroheptanol dissolved in 100 ml. of 2 *N* sodium hydroxide solution and stirred and maintained at 0° for 2 hr. After the organic phase was separated and evaporated, the product distilled at 182–187° (0.3 mm.) and weighed 67.4 g. (69%), $n^{29}D$ 1.3595.

*Anal.* Calcd. for $C_{22}H_9F_{32}N_3O_3$: C, 27.20; H, 0.93; F, 62.60. Found: C, 27.51; H, 1.18; F, 62.88.

**2,2,3,3-Tetrafluoro-1,4-bis[2,4-bis(1,1,5-tri-H-perfluoropentoxy)-*s*-triazine-6-oxy]butane.**—A stirred mixture of 3.2 g. (0.02 mole) of 2,2,3,3-tetrafluorobutane-1,4-diol and 23.0 g. (0.04 mole) of 2-chloro-4,6-bis(1,1,5-tri-H-perfluoropentoxy)-*s*-triazine in 100 ml. of toluene was treated with a solution of 4.8 g. (0.04 mole) of *s*-collidine in 15 ml. of toluene, and the mixture was refluxed 2 hr. The product was cooled to 50–60° and filtered, and the solvent was evaporated from the filtrate. The residual oil crystallized on storage at 4°. Recrystallization from a 1:1 (v./v.) mixture of toluene and petroleum ether (b.p. 60–90°) gave 14.7 g. (59%) of the product melting at 99–103°. Two additional crystallizations gave 7.5 g. (30%) of the purified product, m.p. 105.5–106.5°.

*Anal.* Calcd. for $C_{30}H_{16}F_{36}N_6O_6$: C, 29.05; H, 1.30; F, 55.14. Found: C, 29.20; H, 1.18; F, 55.04.

**2,4,6-Tris(1,1,7-trichloroperfluoroheptoxy)-*s*-triazine.**—A solution of 21.4 g. (0.020 mole) of 2,4,6-tris(1,1,7-tri-H-perfluoroheptoxy)-*s*-triazine in 150 ml. of carbon tetrachloride at 50° was treated with chlorine under ultraviolet irradiation, the gas being introduced below the surface of the liquid at a rate of 2 bubbles/sec. for 72 hr. When the product was cooled to room temperature and filtered, 10.4 g. of crystals, m.p. 102.5–104.0°, was obtained. Additional cooling in an ice bath gave 13.8 g. of product, m.p. 107.5–108.5°, and evaporation of filtrate gave another 2.1 g. of crystals, m.p. 107–108.5°. The combined fractions (26.3 g.) represented a 96% yield. Recrystallization from carbon tetrachloride gave 24.3 g. (89%) of product, m.p. 105–106°. The n.m.r. spectrum indicated that the compound did not contain hydrogen.

*Anal.* Calcd. for $C_{24}Cl_9F_{36}N_3O_3$: C, 20.87; H, 0.00; Cl, 23.10; F, 49.52. Found: C, 20.80; H, 0.0; Cl, 23.24; F, 49.33.

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[6] A. J. Matuszko and M. S. Chang, *Chem. Ind.* (London), 882 (1963).

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# A Stable 1,4-Dihydronaphthalen-1,4-imine

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Previous attempts[1-3] to prepare 1,4-dihydronaphthalen-1,4-imines by the addition of benzyne to various

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[1] G. Wittig and W. Behnisch, *Ber.*, **91**, 2358 (1958).

[2] G. Wittig and B. Reichel, *ibid.*, **96**, 2851 (1963).

[3] E. Wolthuis, D. Vander Jagt, S. Mels, and A. De Boer, *J. Org. Chem.*, **30**, 190 (1965).