Corresponding behavior of the aminothiazoles has been reported,[8] although the compounds in this series were apparently less stable. Nitrosation of 2-aminothiazole and its directly methylated derivative resulted in the formation of highly colored products, while the isomeric N-methyl derivative prepared from dichloroethyl ether and methylthiourea yielded a yellowish white nitroso compound.

Experimental[9]

2-Nitrosoiminothiazolidine (II).—A solution of 10 g. of I[10] in 50 ml. of glacial acetic acid was cooled in an ice bath, 60 ml. of ice-cold aqueous sodium nitrite was added, and the mixture was allowed to stand at ice temperature. After *ca.* 5 min., a yellow solid began to precipitate. After standing overnight, the solid was collected on a filter, washed with a little water, and recrystallized from absolute ethanol: decomposed explosively at 154–155°; infrared spectrum ($CHCl_3$), 3.29 (NH), 6.30 (C=N), 7.25, 8.84 μ (N=O).

Anal. Calcd. for $C_3H_5N_3OS$: N, 32.04. Found: N, 32.11.

The compound gave a positive Liebermann's nitrosoamine test. When II was treated with concentrated HCl, nitrous acid was formed. Subsequent evaporation of the solution yielded the hydrochloride of I, m.p. 198–200° (lit.[7] m.p. 198–199°).

Potassium Δ²-Thiazoline-2-diazotate (III).—Several pieces of potassium hydroxide were dissolved in absolute ethanol and some II was added to a small amount of the solution. The solution was cooled and dry ether was added until a white precipitate formed. The latter was collected on a suction filter and washed with chloroform and ether. The compound was pale yellow: dec. pt. 244–246°; infrared spectrum (KBr), 6.33 (C=N), 7.65–8.26 μ (diazotate.)

Anal. Calcd. for $C_3H_4KN_3OS$: ash (sulfate), 51.4. Found: ash, 49.8.

When reprecipitated from ethanol with ether, the compound was white but darkened again after being exposed to air for several minutes. Acidification with cold glacial acetic acid regenerated II.

2-Imino-3-methylthiazolidine (IV).—A quantity of I was dissolved in dry ether, an equivalent amount of methyl iodide was added, and the mixture was warmed on the steam bath for several minutes. White crystals precipitated immediately. After standing overnight, the precipitate was collected on a filter; m.p. 157–158° (lit.[7] m.p. 159–160°).

The hydriodide was treated with 33% KOH. The oil which separated was extracted with benzene, the extract was dried and evaporated, and the oily residue was used directly in the following experiment.

2-Nitrosoimino-3-methylthiazolidine (V).—Compound IV was dissolved in cold glacial acetic acid and treated with excess cold 10% aqueous $NaNO_2$. The mixture was allowed to stand overnight at ice temperature. It was then extracted with ether. The bright orange extract was dried over anhydrous Na_2SO_4, and the solvent was evaporated. An orange residue remained which, on crystallization from benzene–hexane, decomposed at 124–125°; infrared spectrum ($CHCl_3$), 6.31 (C=N), 7.32, 9.17 μ (N=O).

Anal. Calcd. for $C_4H_7N_3OS$: N, 28.94. Found: N, 29.18.

The compound gave a positive Liebermann's test.

2-Methylimino-3-nitrosothiazolidine (VII).—A solution of 5 g. of VI[11] in 25 ml. of glacial acetic acid was cooled on ice and treated with excess cold 10% aqueous $NaNO_2$. A white precipitate formed after about 10 min. The mixture was allowed to stand at ice temperature for several hours, after which time 3.8 g. of a yellowish white solid was collected on a filter. Recrystallization from hexane gave crystals: m.p. 40–41°; infrared spectrum ($CHCl_3$), 6.19 (C=N), 7.41, 9.60 μ (N=O).

Anal. Calcd. for $C_4H_7N_3OS$: N, 28.94. Found: N, 29.32.

The compound gave a positive Liebermann's test and evolved nitrous acid when treated with concentrated HCl.

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(8) E. Näf, *Ann.*, **265**, 108 (1891).

(9) All melting points were taken on a Fisher-Johns block. Analyses are by H. Beck, J. Sorenson, and C. White.

(10) Prepared according to G. W. Raiziss and L. W. Clemmence, *J. Am. Chem. Soc.*, **63**, 3124 (1941).

(11) Prepared according to directions in ref. 7.

1,1-Dicyano-2,2,2-trialkoxyethane Salts

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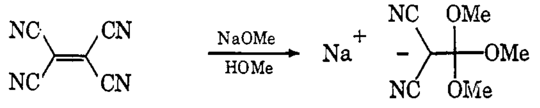
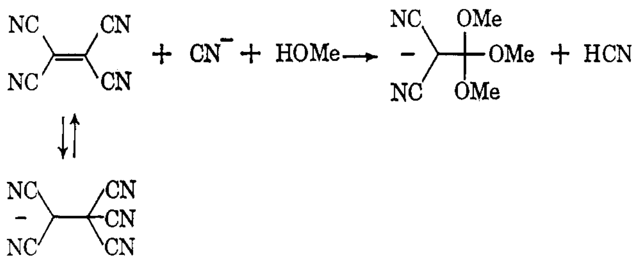
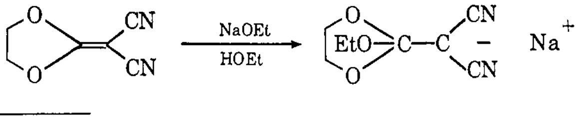
Tetracyanoethylene reacts with methanolic sodium methoxide to give sodium 1,1-dicyano-2,2,2-trimethoxyethanide, a stable white salt. The corresponding potassium salt is produced from methanolic potassium hydroxide and tetracyanoethylene. This result points out the presence of potassium methoxide in "methanolic potassium hydroxide" as well as a greater rate of reaction for the methoxide since tetracyanoethylene reacts with hydroxide ion to give mainly pentacyanopropenide.[1] Surprisingly, methanolic potassium cyanide and tetracyanoethylene also give the trimethoxy compound. In contrast, potassium cyanide, in acetonitrile, adds to tetracyanoethylene to form potassium pentacyanoethanide.[2] Possibly the pentacyanoethanide is formed to some extent in the methanol solution in equilibrium with TCNE and cyanide ion, but is removed by the irreversible formation of the trimethoxide.





The products can be accounted for by the stepwise addition of methoxide ion and elimination of cyanide ion.

The addition of potassium methoxide to dicyanoketene dimethyl acetal,[3] of sodium ethoxide to dicyanoketene diethyl acetal,[3] and of sodium ethoxide to dicyanoketene ethylene acetal[3] supports the last step of the proposed reaction sequence and confirms the structural assignments. In addition, the last example indicates that an equilibrium is not established in the final addition of alkoxide, for then the product would be sodium dicyanotriethoxyethanide.



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(1) W. J. Middleton, E. L. Little, D. D. Coffman, and V. A. Engelhardt, *J. Am. Chem. Soc.*, **80**, 2795 (1958).

(2) O. W. Webster, W. Mahler, and R. E. Benson, *ibid.*, **84**, 3678 (1962).

(3) W. J. Middleton and V. A. Engelhardt, *ibid.*, **80**, 2788 (1958).

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 μ, 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.

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).