Alcoholysis.—When refluxed with 5 ml. of absolute ethanol, I (0.215 g.) gave 0.270 g. (100%) of pale yellow oil after distilling the alcohol under reduced pressure. The oil was decolorized with charcoal in dichloromethane, evaporated, and degassed to give 2,2-dinitro-3-hydroxypropyl ethyl carbonate (IV).

Reaction with Pyridine.—I was destroyed when it was refluxed for 15 min. with dry pyridine. When purified I (0.192 g., 0.001 mole) in 10 ml. of dichloromethane was stirred for 18 hr. with pyridine (0.079 g., 0.001 mole) at 25°, a pale yellow precipitate was formed. It was filtered with suction, washed with dichloromethane, and dried; m.p. (with darkening) 180°, incomplete melting at 250°; yield, 0.10 g. (75%).

Anal. Calcd. for $(C_3H_5N_2O_4)_n$: C, 27.07; H, 3.79; N, 21.05. Found: C, 27.27; H, 3.72; N, 20.20.

Evaporation of the filtrates and washings gave 0.08 g. of yellow oil containing pyridine plus traces of the same solid. The new compound was insoluble in most organic solvents, but dissolved in concentrated hydrochloric acid. The salt-like character of the compound was further confirmed by its infrared absorption spectrum in potassium bromide with λ_{NO_2} 6.37 and 7.45, and $\lambda_{\bar{C}(NO_2)_2}$ 6.76, 8.09, and 8.71 μ.

Nitrolysis.—Heating I (0.19 g., 0.001 mole) with 1 ml. of 100% nitric acid at 93° for 0.5 hr. gave 0.11 g. (43%) of 2,2-dinitro-1,3-propanediol dinitrate, n^{25}_{D} 1.4780.

Acylation.—The carbonate I was unchanged by boiling acetyl chloride, ethyl chlorocarbonate, or heating with acetic anhydride at 90°. Refluxing with acetic anhydride for 0.5 hr. gave 2,2-dinitro-1,3-propanediol diacetate as the only product. The same diacetate was formed in 76% yield when I (0.050 g., 0.00026 mole) was refluxed in dichloromethane with 2 molar equivalents of acetyl chloride and pyridine for 2 hr.

2,2-Dinitro-1,3-propanediol Polycarbonate.—The polymeric carbonate was insoluble in dichloromethane and water. When heated with 100% nitric acid at 93° for 0.5 hr. it was recovered unchanged in 91% yield. [Under the same conditions, bis(2,2-dinitropropyl) carbonate was recovered in 95% yield.]

2,2-Dinitrotrimethylene Sulfite.—This compound was insoluble in cold water and remained undissolved in boiling water. After heating for 1 hr., it was recovered unchanged. Stirring with 8 ml. of 100% nitric acid at 80° for 0.5 hr. converted the sulfite (0.40 g.) to 2,2-dinitro-1,3-propanediol dinitrate in 20% yield.

2,2-Dinitro-1,3-propanediol Dinitrate.—Direct nitration of 2,2-dinitro-1,3-propanediol with 100% nitric acid was carried out by stirring at constant temperature for 35 min. and pouring on ice.[15] The nitrate was extracted with dichloromethane, the extracts washed with water, dried over sodium sulfate, and evaporated under reduced pressure. The yield at 10° (58%) was greater than those at higher temperatures. The crude nitrate melted at 12° and had d^{25}_{25} 1.640 and λ^{MeCN}_{max} 265 mμ (ϵ 85.5). It could be distilled[14] and boiled at 45° (0.005 mm.), but the distillate contained small amounts of impurities which depressed the melting point to 8°. On prolonged standing, it decomposed to the parent diol.

2-Methyl-2-nitrotrimethylene Carbonate.—The condensation reaction of 2-methyl-2-nitro-1,3-propanediol with phosgene and pyridine gave a 78% yield of carbonate, m.p. 138–145°. Sublimation at 90–115° (0.05 mm.) yielded 40% of pure cyclic carbonate, m.p. 112–114°; $\lambda_{C=O}$ 5.68, λ_{NO_2} 6.42, 7.39, λ_{C-O} 8.45, 9.00 μ in potassium bromide.

Anal. Calcd. for $C_5H_7NO_5$: C, 37.27; H, 4.38; N, 8.69. Found: C, 37.16; H, 4.97; N, 8.73.

When the phosgene was added very slowly to the diol–pyridine solution, the methanol-insoluble polymeric carbonate was formed as main product (56% yield). It was purified by adding methanol to the dichloromethane solution, melted at 218°, and had $\lambda_{C=O}$ 5.66, λ_{NO_2} 6.43, 7.40, and λ_{C-O} 7.95 μ in potassium bromide.

Anal. Calcd. for $(C_5H_7NO_5)_n$: C, 37.27; H, 4.38; N, 8.69. Found: C, 37.28; H, 4.79; N, 9.13.

2-Ethyl-2-nitrotrimethylene Carbonate.—The crude reaction product from 2-ethyl-2-nitro-1,3-propanediol and phosgene (89% yield) was crystallized from dichloromethane–petroleum ether. It melted at 72–74° and had $\lambda_{C=O}$ 5.68, λ_{NO_2} 6.45, 7.36, and λ_{C-O} 8.47, 9.02 μ in potassium bromide.

Anal. Calcd. for $C_6H_9NO_5$: C, 41.16; H, 5.18; N, 8.00. Found: C, 41.08; H, 5.57; N, 7.83.

The cyclic carbonate was unchanged by refluxing with excess acetyl chloride. When heated with 3% aluminum chloride at 120° it was converted to polycarbonate. The product was taken up in acetone and precipitated with water. The colorless solid had the following absorption bands in potassium bromide: $\lambda_{C=O}$ 5.65, λ_{NO_2} 6.43, 7.40, λ_{C-O} 8.02 μ.

Calcd. for $(C_6H_9NO_5)_n$: C, 41.16; H, 5.18; N, 8.00. Found: C, 41.09; H, 5.67; N, 7.62.

Partial isomerization occurred also when the cyclic carbonate was heated with excess sulfuryl chloride 0.5 hr. at 75°.

2-Methyl-2-nitrotrimethylene Sulfite.—The known sulfite[16] was obtained in 83% yield. It melted, resolidified, and remelted at 110°, boiled without change at 234° (cor.), (575 mm.), and had λ_{NO_2} 6.41, 7.41, $\lambda_{S=O}$ 8.48, λ_{other} 9.76, 10.15, 10.85, and 11.83 μ (in potassium bromide). The crystalline sulfite (0.09 g.) could be dissolved in 4 ml. of boiling water (92°, 570 mm.) and crystallized unchanged on cooling.

Anal. Calcd. for $C_4H_7NO_5S$: C, 26.52; H, 3.89; N, 7.73. Found: C, 26.85; H, 4.29; N, 7.07.

It was similarly unaffected by refluxing with sodium iodide in acetone and was stable toward potassium permanganate in acetone.

2-Methyl-2-nitrotrimethylene sulfite (0.10 g.) was dissolved in 100% nitric acid (2 ml.), heated at 93° for 0.5 hr., poured on ice, and extracted with dichloromethane. The dried extracts furnished 0.11 g. (87%) of 2-methyl-2-nitro-1,3-propanediol dinitrate,[17] n^{25}_{D} 1.4710; λ_{NO_2} 6.40, 7.42, λ_{NO_3} 6.02, 7.81, 11.95 μ in a liquid film. Authentic dinitrate, prepared by direct nitration of the diol, had n^{25}_{D} 1.4711, d^{25}_{25} 1.485, and an identical infrared spectrum.

1,3-Dichloro-2-methyl-2-nitropropane.—The reaction of 2-methyl-2-nitro-1,3-propanediol with sulfuryl chloride and pyridine gave 68% of crude product which on fractionation yielded about 30% of colorless liquid, b.p. 50–52° (1.5 mm.), with n^{25}_{D} 1.4730 and λ_{NO_2} 6.41, 7.41 μ in a liquid film.

Anal. Calcd. for $C_4H_7Cl_2NO_2$: C, 27.93; H, 4.10; Cl, 41.23. Found: C, 27.78; H, 4.11; Cl, 40.90.

This compound is presumably identical with the one described in the literature.[18]

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[15] H. Plaut, U. S. Patent 2,978,484; *Chem. Abstr.*, **55**, 15934 (1961).

[16] S. P. Lingo, U. S. Patent 2,471,274; *Chem. Abstr.*, **43**, 6222 (1949).

[17] J. A. Wyler, U. S. Patent 2,195,551; *Chem. Abstr.*, **34**, 5283 (1940); W. de C. Crater, U. S. Patent 2,112,749; *Chem. Abstr.*, **32**, 3964 (1938).

[18] R. Preussmann, *Arzneimittel-Forsch.*, **8**, 638 (1958).

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sym-Difluorotetrachloroacetone as a Source of Chlorofluorocarbene

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Hine, Ketley, and Tanabe[1] suggested that chlorofluorocarbene was an intermediate in the reaction of dichlorofluoromethane with strong nucleophiles. Attempts by Parham and Twelves[2] at preparing 1-chloro-1-fluoro bicyclo[4.1.0]heptane using dichlorofluoromethane as the carbene precursor and cyclohexene as the acceptor were only moderately successful in that very low yields of an impure product were isolated. Consequently, an efficient chlorofluorocarbene precursor and therefore, a direct route to 1-chloro-1-fluorocyclopropanes is not available.

We wish to report a convenient method for the preparation of chlorofluorcarbene in good yields by the reaction of *sym*-difluorotetrachloroacetone[3] with potas-

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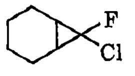
[1] J. Hine, A. D. Ketley, and K. Tanabe, *J. Am. Chem. Soc.*, **82**, 1398 (1960).

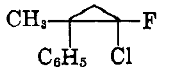
[2] W. E. Parham and R. R. Twelves, *J. Org. Chem.*, **23**, 730 (1958).

[3] Allied Chemical Corporation, General Chemical Division, Morris Township, N. J.

sium t-butoxide[4] in nonprotonic media. Pure 7-chloro-7-fluorobicyclo[4.1.0]heptane (I) and 1-chloro-1-fluoro-2-phenyl-2-methylcyclopropane (II) were readily isolated by the introduction of cyclohexene and α-methylstyrene as carbene acceptors.

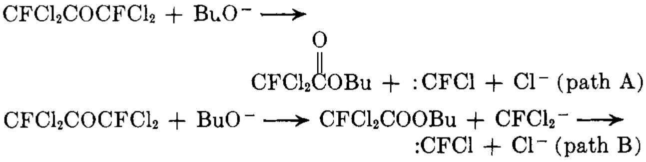


I



II

Our observations parallel those reported by Kadaba and Edwards[5] and by Cassie and Grant[6] for the alkaline decomposition of hexachloroacetone. The degradation of *sym*-difluorotetrachloroacetone may differ from that of hexachloroacetone in that chlorofluorocarbene could be produced through a concerted elimination of chloride and fluorodichloroacetate (path A) rather than through the occurrence of a fluorodichloromethyl anion[7] (path B).



$$CFCl_2COCFCl_2 + BuO^- \longrightarrow CFCl_2\overset{O}{\overset{\|}{C}}OBu + :CFCl + Cl^- \text{ (path A)}$$

$$CFCl_2COCFCl_2 + BuO^- \longrightarrow CFCl_2COOBu + CFCl_2^- \longrightarrow :CFCl + Cl^- \text{ (path B)}$$

The infrared spectra (λ_{max} μ) of the chlorofluorocyclopropanes prepared were consistent with their structures: I, 3.48 (cyclopropane CH),[8] 8.98, 9.15 (CF), 10.15 (cyclopropane ring), 6.90, 9.52, 10.24 (cyclohexane ring), and 12.58 (CCl); II, 3.42 (cyclopropane CH), 8.60, 8.75, 8.90 (CF), 10.48 (cyclopropane ring) and 11.98 (CCl). The observed shift of the CCl stretching band from the 13.5–14.5-μ region to shorter wave lengths is due to interaction with fluorine in I and with both flourine and the aromatic ring in II.[9]

Experimental

7-Chloro-7-fluorobicyclo[4.1.0]heptane.—A suspension of 112 g. (1.0 mole) potassium *tert*-butoxide in 500 ml. of cyclohexene was cooled to 0° and treated in 1 hr. with 116 g. (0.5 mole) of *sym*-difluorotetrachloroacetone. The reaction mixture was stirred for 3 hr. at 0–5°, filtered and the filtrate fractionated to give 27 g. (36%) 7-chloro-7-fluorobicyclo[4.1.0]heptane, b.p. 72–73° (38 mm.).

Anal. Calcd. for $C_7H_{10}ClF$: Cl, 24.9; F, 12.8. Found: Cl, 25.1; F, 12.6.

1-Chloro-1-fluoro-2-methyl-2-phenylcyclopropane.—A suspension of 112 g. (1.0 mole) of potassium *tert*-butoxide in 250 ml. of α-methylstyrene and 250 ml. of hexane was treated with 116 g. (0.5 mole) of difluorotetrachloroacetone. There was obtained 41 g. (44%) of 1-chloro-1-fluoro-2-methyl-2-phenylcyclopropane, b.p. 69–70° (5 mm.).

Anal. Calcd. for $C_{10}H_{10}ClF$: Cl, 19.2; F, 10.3. Found: Cl, 19.0; F, 10.3.

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(4) M.S.A. Chemical Corporation, Callery, Pa.

(5) P. K. Kadaba and J. O. Edwards, *J. Org. Chem.*, **25**, 1431 (1960).

(6) F. W. Grant and W. B. Cassie, *ibid.*, **25**, 1433 (1960).

(7) W. E. Parham and E. E. Schweizer, *ibid.*, **24**, 1733 (1959).

(8) W. R. Moore and H. R. Ward, *ibid.*, **25**, 2073 (1960).

(9) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., p. 331 (1959).

Triphenylphosphine Oxide–Hydrogen Per oxide Adduct[1]

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A recent publication by Oswald and Guertin[3] reports the preparation and isolation of several trialkylamine oxide–hydrogen peroxide adducts. This prompts us to report a similar type of compound which has been prepared and investigated in this laboratory.

When a solution of triphenylphosphine or triphenylphosphine oxide in dioxane is treated with an excess of 30% hydrogen peroxide at 0°, a crystalline complex $[(C_6H_5)_3PO]_2 \cdot H_2O_2$ is obtained in high yield.

Anal. Calcd. for $C_{36}H_{32}O_4P_2$: C, 73.21; H, 5.47; P, 10.49; equiv. wt., 304; mol. wt., 608. Found: C, 73.79; H, 5.62; P, 10.52; equiv. wt., 303 (iodometry), 282 (gas evolution); mol. wt., 523 ± 30 (cryoscopic in benzene).

The triphenylphosphine oxide–hydrogen peroxide adduct is very soluble in dioxane, chloroform, acetone, dimethylformamide, and methanol, sparingly soluble in benzene, ether, and chlorobenzene, and insoluble in water, cyclohexane, and pentane. It melts at 132–133° with vigorous gas evolution. The complex is stable for several months at room temperature but decomposes on heating with or without solvent to give oxygen and triphenylphosphine oxide. The infrared spectrum in chloroform or Nujol is very similar to that of triphenylphosphine oxide, but an additional band is present at 3.2 μ. This suggests a hydrogen-bonded complex, as found for the amine oxide adducts.[3]

Although the adduct appeared to be largely associated in solution, the oxygen-evolving species is probably free hydrogen peroxide. The rate of decomposition was not reproducible, apparently being subject to catalysis by the surface of the glass reaction vessels. The half-life of the adduct in chlorobenzene at 79.5° and at concentrations of 0.01 to 0.07 molar varied irregularly from 2000 to 3000 seconds. Copper turnings, precipitated silver, and manganese dioxide catalyze the decomposition.

The adduct in benzene is capable of oxidizing benzhydrol to benzophenone and anthracene to anthraquinone, even in the absence of light. Warming the adduct with styrene gave methanol-insoluble polymer and oxygen.

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[2] National Science Foundation Graduate Fellow.

[3] A. A. Oswald and D. L. Guertin, *J. Org. Chem.*, **28**, 651 (1963).