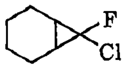
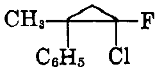
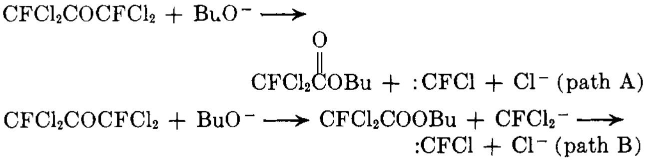
sium *t*-butoxide[4] in nonprotonic media. Pure 7-chloro-7-fluorobicyclo[4.1.0]heptane (I) and 1-chloro-1-fluoro-2-phenyl-2-methylcyclopropane (II) were readily isolated by the introduction of cyclohexene and α-methylstyrene as carbene acceptors.


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).



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

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

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.

Triphenylphosphine Oxide–Hydrogen Peroxide Adduct[1]

R. D. TEMPLE,[2] Y. TSUNO, AND J. E. LEFFLER

Department of Chemistry, Florida State University, Tallahassee, Florida

Received May 3, 1963

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.

---

(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).

(1) This investigation was supported in part under a contract with the Office of Naval Research.

(2) National Science Foundation Graduate Fellow.

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