[CONTRIBUTION FROM THE CHEMICAL RESEARCH LABORATORY OF POLAROID CORPORATION]

1-Phenyl-1,2-difluoro-2-chloroethylene and Phenyltrichloroethylene[1]

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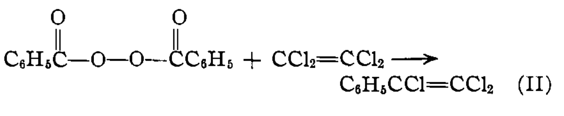
In extension of our work on phenyl per-fluorochloroethylenes,[1a] we have prepared 1-phenyl-1,2-difluoro-2-chloroethylene, $C_6H_5CF{=}CFCl$, by the following series of reactions.

$$C_6H_5COCH_3 \longrightarrow C_6H_5COCCl_3 \longrightarrow C_6H_5COCCl_2F$$
$$C_6H_5CCl_2CCl_2F \longrightarrow C_6H_5CClFCCl_2F \longrightarrow C_6H_5CF{=}CFCl \quad \text{(I)}$$

Trichloroacetophenone was prepared directly from acetophenone, the third atom of chlorine being introduced in the presence of sodium acetate.[2] Fluorination of trichloroacetophenone was effected by argentic fluoride in hydrogen fluoride[3]; cobaltic fluoride was ineffective under comparable conditions. Treatment of dichlorofluoroacetophenone with excess phosphorus pentachloride led to 1,1,2,2-tetrachloro-2-fluoroethylbenzene, advantage being taken of consumption of excess phosphorus pentachloride with acetone.[1] Conversion of this to 1,1,2-trichloro-1,2-difluoroethylbenzene and dechlorination of the latter to form I were carried out by standard procedures. In the course of this work, we have observed that the dechlorination by zinc of $C_6H_5CCl_2CF_2Cl$, $C_6H_5CCl_2CFCl_2$ and $C_6H_5CCl_2CCl_3$ proceeds readily in ether, while the dechlorination of $C_6H_5CClFCF_2Cl$ and $C_6H_5CClFCFCl_2$, in which the alpha carbon atoms bear one chlorine and one fluorine atom, does not proceed in ether and may be carried out in ethanol.

In the course of this work we found it of interest to prepare phenyl trichloroethylene, II, as a possible starting material for the preparation of the phenyl-fluoroethylenes. This was prepared both by the dechlorination of pentachloroethylbenzene and by the decomposition of benzoyl peroxide in tetrachloroethylene.

$$C_6H_5COCCl_3 \longrightarrow C_6H_5CCl_2CCl_3 \longrightarrow C_6H_5CCl{=}CCl_2 \quad \text{(II)}$$



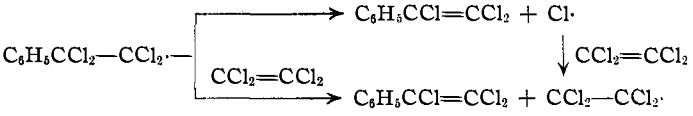
$$C_6H_5\overset{\overset{O}{\|}}{C}{-}O{-}O{-}\overset{\overset{O}{\|}}{C}C_6H_5 + CCl_2{=}CCl_2 \longrightarrow C_6H_5CCl{=}CCl_2 \quad \text{(II)}$$

The latter reaction had been carried out previously by Reijnhart[4] who decomposed one-half mole of benzoyl peroxide in 200 cc. of tetrachloroethylene at 110–115° and obtained chlorobenzene, 0.36 mole, 36%, hexachloroethane, 0.64%, and phenyltrichloroethylene, 19%. In carrying out this decomposition at the same temperature but at greater dilution we were able to detect no chlorobenzene but isolated benzoic acid, 19%, hexachloroethane, 11%, and phenyl-trichloroethylene, 28% yield. As had Reijnhart, we also found higher boiling unidentified product.

It seems likely that this reaction proceeds in large part by addition of the phenyl radicals to tetrachloroethylene.

$$C_6H_5\cdot + CCl_2{=}CCl_2 \longrightarrow C_6H_5CCl_2{-}CCl_2\cdot$$

The phenyl tetrachloroethyl radical may add to tetrachloroethylene to lead to the resinous residue, but to a considerable extent it apparently either loses a chlorine atom or donates one directly to a solvent molecule forming phenyl-trichloroethylene and the pentachloroethyl radical.



The pentachloroethyl radical either adds to tetrachloroethylene or is converted in part to hexachloroethane. No pentachloroethylbenzene was found.

Benzoic acid was obtained, whether the reaction product was distilled directly or whether it was first extracted with bicarbonate. It may be formed by extraction of hydrogen from phenyl groups by benzoate radicals and need not arise solely by hydrolysis of such possible precursors as the products of addition of the benzoate radical to tetrachloroethylene, or benzoyl chloride, which might arise from oxidation of phenyl trichloroethylene by benzoyl peroxide.

Our failure to obtain chlorobenzene may indicate that with increased dilution, the reactions which are likely to lead to this product become less probable. These may be the reactions of chlorine atoms or phenyltetrachloroethyl or pentachloroethyl type radicals with phenyl or benzoate radicals, or with benzoyl peroxide, or the reactions of phenyl or benzoate radicals with perchloroalkane type molecules.

Treatments of phenyl trichloroethylene with antimony trifluoride and with cobaltic fluoride failed to lead to replacement of fluorine by chlorine.

Experimental

Trichloroacetophenone.[5]—Acetophenone, 240 g., in 1 l. of acetic acid was treated with chlorine at 55–60° in a tared flask as described for the preparation of dichloroacetophenone.[6] Nitrogen was passed through for half an

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[1a] Cohen, Wolosinski and Scheuer, THIS JOURNAL, **71**, 3439 (1949).

[2] Aston, Newkirk, Dorsky and Jenkins, *ibid.*, **64**, 1413 (1942).

[3] Simons and Herman, *ibid.*, **65**, 2064 (1943).

[4] Reijnhart, *Rec. trav. chim.*, **46**, 72 (1927).

[5] Prepared by Mr. Claude Valle, Jr.

[6] Aston, Newkirk, Jenkins and Dorsky, "Organic Syntheses," **23**, 48 (1943).

hour removing all but about 21 g. of hydrogen chlorine. Fused sodium acetate, 300 g., was added, the temperature was raised to 95° and chlorine was passed in for two hours, the heat of reaction maintaining the temperature at 99° during much of this time. Excess chlorine was swept out with nitrogen, the mixture was cooled and poured into a solution of 24 g. of sodium sulfite in 3 l. of water. The product was extracted with ether, dried and distilled, 421 g., b. p. 99–102.5° (3.5 mm.), $n^{20}\mathrm{D}$ 1.5685. *Anal.* Calcd. for $C_8H_5OCl_3$: Cl, 47.7. Found, Cl, 47.0. A sample was warmed with aqueous alkali, leading to chloroform and a quantitative yield of benzoic acid.

Fluorodichloroacetophenone[3] was prepared by the interaction of trichloroacetophenone, 150 g., argentic fluoride, 180 g., and hydrogen fluoride, 300 g., with stirring under reflux in a stainless steel vessel at 3–9° for 2.5 hours, 75 g., b. p. 110–113° (24–25 mm.), $n^{20}\mathrm{D}$ 1.5288.

2-Fluoro-1,1,2,2-tetrachloroethylbenzene was prepared by the interaction of fluorodichloroacetophenone, 117 g., and phosphorus pentachloride, 177 g., at 170° for twenty-one hours. Excess phosphorus pentachloride was destroyed with acetone and the product was distilled, leading to 2-fluoro-1,1,2,2-tetrachloroethylbenzene, 100 g., and a mixture of this and the starting materials, 42 g. The latter material was treated with 62 g. of phosphorus pentachloride. The total yield of $C_6H_5CCl_2CCl_2F$ was 134 g., 89%, b. p. 111–114° (7 mm.), $n^{20}\mathrm{D}$ 1.5447. *Anal.* Calcd. for $C_3H_5Cl_4F$: Cl, 54.1. Found: Cl, 53.9.

1,2-Difluoro-1,2,2-trichloroethylbenzene was prepared by the interaction of 156 g. of $C_6H_5CCl_2CCl_2F$ with one-third mole of antimony trifluoride and 5 mole per cent. of bromine at 125–130° for 45 minutes. The product was taken up in ether, washed and distilled leading to materials boiling at (i) 74.2–76.6° (15 mm.), $n^{20}\mathrm{D}$ 1.4730, 14.4 g.; (ii) 100–104° (15 mm.), $n^{20}\mathrm{D}$ 1.516, 67.6 g., 46% yield; and (iii) 110° (8 mm.), $n^{20}\mathrm{D}$ 1.545, 14.0 g., as well as two fractions. Fractions i and iii were probably difluorination product and starting material, respectively. Fraction ii was apparently the desired $C_6H_5CClFCCl_2F$. A sample boiling at 102–103° (15 mm.), $n^{20}\mathrm{D}$ 1.5145 was analyzed. *Anal.* Calcd. for $C_8H_5Cl_3F_2$: Cl, 43.3. Found: Cl, 41.6.

1-Phenyl-1,2-difluoro-2-chloroethylene was prepared by the interaction of $C_6H_5CClFCCl_2F$, 66 g., 0.27 mole, and zinc, 18.5 g., 0.28 mole, in 85 cc. of absolute ethanol in the presence of a few crystals of zinc chloride under reflux for one hour. The product was taken up in ether, washed and distilled, leading to $C_6H_5CF{=}CFCl$, 48% yield, b. p. 89–92° (41 mm.), $n^{20}\mathrm{D}$ 1.5242. A sample boiling at 89–90° (41 mm.), $n^{20}\mathrm{D}$ 1.5242 was analyzed. *Anal.* Calcd. for $C_8H_5F_2Cl$: C, 55.0; H, 2.9; Cl, 20.3. Found: C, 55.4; H, 3.1; Cl, 20.0.

Pentachloroethylbenzene[3] was prepared by treatment of trichloroacetophenone with phosphorus pentachloride. The product, boiling at 155° (15 mm.), was obtained in three fractions, 29 g., m. p. 18–33°, 143 g., m. p. 30–35°, 64 g., m. p. 33–36°, total 236 g., 75% yield.

Phenyl-trichloroethylene.—Pentachloroethylbenzene, 109 g., 0.48 mole, was treated with acid washed zinc dust, 31 g., 0.48 mole, in 250 cc. of anhydrous ether under reflux for 3.5 hours. The product was decanted from 12 g. of solid, washed with dilute hydrochloric acid and water, dried and distilled, leading to phenyl-trichloroethylene, 81% yield, b. p. 104° (8 mm.), $n^{26}\mathrm{D}$ 1.5803. *Anal.* Calcd. for $C_8H_5Cl_3$: C, 46.3; H, 2.4; Cl, 51.2. Found: C, 46.7; H, 2.5; Cl, 50.7.

Decomposition of Benzoyl Peroxide in Tetrachloroethylene.—Tetrachloroethylene, 100 cc., was heated to 120° under reflux with stirring in a stream of dry nitrogen. Benzoyl peroxide, 109 g., was added over a period of two hours in ten portions, each dissolved in 50 cc. of warm tetrachloroethylene; the temperature of the reaction solution was maintained at 120°. Most of the solvent was distilled, 646 g., b. p. 118–121°, $n^{20}\mathrm{D}$ 1.5058. The residue was extracted repeatedly with sodium bicarbonate solution, washed with water, dried and distilled, leading to a partially solid material (i) 34.6 g., boiling to 102° (10 mm.), liquids (ii) 54.5 g., boiling at 103–110° (10 mm.), $n^{20}\mathrm{D}$ 1.5759–1.5832, a partially solid fraction (iii) 27 g. boiling at 110–140° (5 mm.), $n^{20}\mathrm{D}$ 1.5808 and a liquid (iv) 5 g., b. p. 140–151° (5 mm.), $n^{20}\mathrm{D}$ 1.5860. Fraction (i) led to hexachloroethane, 10.4 g., m. p. 182–184°, mixed m. p. 185–186°, fractions i and ii led to phenyltrichloroethylene, 51 g., b. p. 85° (3 mm.), $n^{20}\mathrm{D}$ 1.5820, m. p. 12–14°. *Anal.* Calcd. for $C_8H_5Cl_3$: C, 46.3; H, 2.4; Cl, 51.2. Found: C, 46.8; H, 2.5; Cl, 51.1. Fraction iii led to 1.8 g. of benzoic acid, which when combined with that obtained from the bicarbonate extracts led to a total of 18.3 g. The liquid portion of fraction iii was redistilled leading to iiia, 7.2 g., b. p. 63–124° (4–5 mm.), $n^{20}\mathrm{D}$ 1.5722, and iiib, 7.5 g., b. p. 124–125° (4–5 mm.), $n^{20}\mathrm{D}$ 1.5805, d^{30}_{30} 1.6980. Product iiib was analyzed, C, 24.1; H, 0.8; Cl, 73.5; approximate empirical formula $(C_2HCl_2)_n$. The combined recovered solvents and lower boiling fractions were carefully redistilled but no evidence of chlorobenzene was found.

Treatment of phenyl-trichloroethylene (0.121 mole) with antimony trifluoride, 0.242 mole, and antimony pentachloride, 0.024 mole, for twenty hours at 170° under reflux, or at 220° for twenty-one hours in a pressure vessel led to recovery of unreacted starting material. Treatment of phenyl-trichloroethylene (0.08 mole) with cobaltic fluoride (0.17 mole) for two hours at 140–150° led to recovery of starting material only (67%).

Summary

1-Phenyl-1,2-difluoro-2-chloroethylene was prepared by the series of reactions: $C_6H_5COCH_3 \rightarrow C_6H_5COCCl_3 \rightarrow C_6H_5COCCl_2F \rightarrow C_6H_5CCl_2CCl_2F \rightarrow C_6H_5CClFCCl_2F \rightarrow C_6H_5CF{=}CFCl$. Phenyl-trichloroethylene was prepared both by dechlorination of pentachloroethylbenzene and by the decomposition of benzoyl peroxide in tetrachloroethylene. Hexachloroethane and benzoic acid were also formed in this reaction, while chlorobenzene and pentachloroethylbenzene were not found.

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