[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

The Action of Phosphorus Pentachloride with Ethers

BY FRANK C. WHITMORE AND D. P. LANGLOIS[1]

Because of the failure to convert neopentyl alcohol to a neopentyl halide without rearrangement[2] other methods were sought. The ordinary methods of preparing alkyl halides involve the use of acids or the formation of acids during the process. Since some believe that acids cause rearrangement (Meerwein) a method was sought which would involve no acid at any stage in the reaction. Such a process seemed to be presented by the action of phosphorus pentachloride with an ether. This reaction might be expected to give only alkyl halides and phosphorus oxychloride. Preliminary experiments raised doubts as to the accuracy of this conception.[3] A study of the literature revealed a surprisingly small amount of work on the action of ethers with phosphorus pentachloride. Dichlorodiethyl ether gave a small amount of ethyl chloride and 1,1,1-trichloroethane.[4] The treatment of diphenyl ether and diphenylene oxide with phosphorus pentachloride gave no recognizable products.[5] Mixed aryl alkyl ethers gave mainly chlorination products of the aryl part of the ether without splitting the ether linkage.[6]

In the present work several ethers and acetals were treated with phosphorus pentachloride. In no case was a practical yield of organic chloride obtained. Moreover, there was always a chlorinating action with the formation of hydrogen chloride. This destroyed the hope that an alkyl chloride could be formed in the absence of acid by the use of phosphorus pentachloride and an ether.

The neopentyl acetal of formaldehyde reacted with phosphorus pentachloride to give very little alkyl chloride. This was mainly if not entirely tertiary amyl chloride, a product of rearrangement.

Experimental

Preparation of Ethers and Acetals.—The following benzyl ethers were made with the indicated yields by the method of Lowe[7] using petroleum ether (60–90°) and vigorous stirring: dibenzyl ether, b. p. 198–200° (55 mm.), 46%; *n*-butyl benzyl ether, b. p. 217–219° (737 mm.), 34%; *n*-amyl benzyl ether, b. p. 237–240° (733 mm.), 51%; *sec*-amyl benzyl ether, b. p. 223–226° (735 mm.), 29%.

Neopentyl formal, $[(CH_3)_3CCH_2]_2CH_2$, b. p. 176–177.5° (737 mm.) was obtained in 65% yield.[8]

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[1] Submitted in partial fulfilment of the requirements for the Ph.D. degree.

[2] Whitmore and Rothrock, THIS JOURNAL, **54**, 3433 (1932).

[3] Since this was written, the study on the reaction of diethyl ether with phosphorus pentachloride by Guthmann [*ibid.*, **54**, 2938 (1932)] has appeared. This definitely proves the complexity of the reaction.

[4] Lieben, *Ann.*, **146**, 213, 218 (1868); Abeljanz, *ibid.*, **164**, 203 (1872).

[5] Hoffmeister, *Ber.*, **3**, 748 (1870); *Ann.*, **159**, 200, 212 (1871).

[6] Autenrieth and Muehlinghaus, *Ber.*, **39**, 4098 (1906).

[7] Lowe, *Ann.*, **241**, 374 (1887).

[8] *Cf.* Conant, Webb and Mendum, THIS JOURNAL, **51**, 1246 (1929).

Anal. Calcd. for $C_{11}H_{24}O_2$: C, 70.2. Found: C, 70.1 and 70.6.

Di-*n*-butyl formal, b. p. 177–178° (734 mm.), was made in 74% yield.

The phosphorus pentachloride was heated under reduced pressure to remove any free hydrogen chloride.

Action of Phosphorus Pentachloride with the Ethers and Acetals

Diisoamyl Ether.—Commercial diamyl ether[9] was fractionated. The 172–178° fraction was dried over sodium in the cold for two days, filtered and distilled. The boiling point of the material finally used was 174–176° (735 mm.). A mixture of 52 g. (1 mol) of phosphorus pentachloride and 39.5 g. (1 mol) of diisoamyl ether was heated on a water-bath under a reflux condenser. Much hydrogen chloride was evolved and the solid dissolved completely. After six hours the mixture was cooled. A loss in weight of 17 g. indicated the evolution of about 0.5 mole of hydrogen chloride. The mixture was decomposed with ice, separated and the oil was washed with water, with sodium carbonate solution, again with water and then dried two days over anhydrous sodium sulfate and fractionated carefully through a 27 × 0.8 cm. packed column,[10] using a reflux ratio of 20:1. A total of 27.5 g. distilled from 50 to 168° without any constant fraction even after several redistillations. The entire experiment was repeated several times with the same result. No evidence of the formation of isoamyl chloride was obtained.

Diisopropyl Ether.—The 65–69° fraction from the commercial ether[11] was dried for two days over sodium, filtered and redistilled, b. p. 67–68° (735 mm.). When the ether was refluxed for six hours with phosphorus pentachloride, it was recovered unchanged.

A sealed tube containing 10 g. (1 mol) of diisopropyl ether and 20 g. (2 mols) of phosphorus pentachloride was heated at 110° for six hours. Much hydrogen chloride escaped when the tube was cooled in ice and opened. The mixture was decomposed on ice and worked up in the usual way. Two careful fractionations gave 2 g. (24% yield) of isopropyl chloride (b. p. 35–36°, 43.2% Cl). The rest boiled from 36 to 130° without any constant fraction.

Dibenzyl Ether.—The reagents (0.25 mole of each) were refluxed in an apparatus fitted to absorb the evolved gas. About 0.4 mole of hydrogen chloride was evolved (titration). The organic products obtained were 24 g., b. p. 82–86° (27 mm.), 28 g., b. p. 95–96° (25 mm.), and a semi-solid residue which was insoluble in water and ether. The first liquid was benzyl chloride as shown by its conversion to *p*-nitrobenzyl chloride, m. p. 70–71°. The second liquid was a mixture of benzal chloride and benzotrichloride. Boiling sodium hydroxide solution left an oily layer which gave the phenylhydrazone of benzaldehyde, m. p. 155–156°. The alkaline solution gave benzoic acid, m. p. 120–122°, which was converted to benzanilide, m. p. 160°. The solid product from the original reaction was refluxed three hours with normal sodium hydroxide solution. Part of it dissolved. Steam distillation gave a small amount of benzyl alcohol (3,5-dinitrobenzoate, m. p. 104–106°), and benzaldehyde. The products of the action of dibenzyl ether with phosphorus pentachloride are benzyl chloride, benzal chloride, benzotrichloride and probably a phosphate of benzyl alcohol.

***n*-Butyl Benzyl Ether.**—The products obtained from 33 g. of the ether and 2 mols of phosphorus pentachloride were 3.5 g., b. p. 77.5° (733 mm.) (38.7% Cl), 2 g., b. p. 98° (733 mm.) (47.2% Cl) and traces of benzyl chloride, benzal chloride and benzotrichloride. The first liquid fraction was *n*-butyl chloride in 19% yield and the second was probably impure butylidene chloride.

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(9) Supplied by the Sharples Solvents Corp., of Philadelphia.

(10) Whitmore and Lux, THIS JOURNAL, **54**, 3448 (1932).

(11) Supplied by the Carbide and Carbon Chemicals Corp., of N. Y.

***n*-Amyl Benzyl Ether.**—The products from 32 g. of the ether and 2 mols of phosphorus pentachloride were 3.5 g., b. p. 101–105° (716 mm.) (32.0% Cl); 6.5 g., b. p. 170–180° (716 mm.), 12.5 g., b. p. 185–187° (716 mm.) (44.6% Cl). The first was *n*-amyl chloride in 18% yield. The others were benzyl and benzal chlorides.

***Sec*-amyl Benzyl Ether.**—From 44.5 g. of the ether and 2 mols of phosphorus pentachloride were obtained 4 g., b. p. 93° (716 mm.) (32.8% Cl); 6.5 g., b. p. 95.5° (720 mm.) (31.7% Cl); 7.5 g., b. p. 80–90° (27 mm.), and a viscous residue of 23 g. The first two were impure 2-chloropentane in 39% yield. Hydrolysis of the other fraction gave benzaldehyde and benzoic acid.

Diphenylene Oxide.—The treatment of 84 g. of diphenylene oxide with 2 mols of phosphorus pentachloride gave an 80% yield of a monochlorodiphenylene oxide, m. p. 94–96°.

Anal. Calcd. for $C_{12}H_7OCl$: Cl, 17.0. Found: Cl, 16.4.

Di-*n*-butyl Acetal of Formaldehyde.—To 160 g. (1 mol) of the acetal in a flask fitted with a reflux condenser and an absorber for hydrogen chloride was added slowly 208 g. (1 mol.) of phosphorus pentachloride. The reaction was violent and hydrogen chloride was evolved. The mixture was heated until no more gas formed and was then decomposed on ice in the usual way. The product was carefully distilled through the 27 × 0.8 cm. column at 738 mm., twelve fractions being obtained. Formaldehyde was evolved during the heating. The most important fractions were No. 2, 43 g., b. p. 77–79° (37.5% Cl) identified as *n*-butyl chloride by formation of the 3,5-dinitrobenzoate, m. p. and mixed m. p. 63–64°, yield of *n*-butyl chloride, 23%; No. 4, 3 g., b. p. 103–110° (27.4% Cl), probably chloromethyl *n*-butyl ether; No. 6, 3 g., b. p. 160–165° (20.5% Cl), probably monochlorodibutyl ether; and No. 8, 26 g., b. p. 175–178°, unchanged acetal.

Di-neopentyl Acetal of Formaldehyde.—From 63 g. of the acetal and 2 mols of phosphorus pentachloride were obtained six fractions at 738 mm. Only 6 g., b. p., 85–98°, was obtained in the amyl chloride range. Treatment of this with sodium hydroxide gave tertiary amyl alcohol, 3,5-dinitrobenzoate, m. p. 86–88°, mixture with known 3,5-dinitrobenzoates, of tertiary amyl alcohol, m. p. 86–88°, mixed m. p. 86–88°; of neopentyl alcohol, m. p. 92–93°, mixed m. p. 70–73°. The other fractions contained 15 to 21% Cl but were not identified although Fraction No. 5, 9 g., b. p. 171–173° (17.0% Cl), may have been the impure monochloroacetal.

The action of the di-neopentyl acetal of formaldehyde with phosphorus pentachloride gave small amounts of amyl chlorides. No evidence of neopentyl chloride was obtained.

Summary

1. The action of phosphorus pentachloride with several types of ethers and acetals (formals) has been studied.

2. The production of RCl from R_2O or from $(RO)_2CH_2$ and phosphorus pentachloride is small or entirely absent.

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