

1, 1-Dichloroheptane¹

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The recent successes of halogen compounds, as insecticides, particularly D.D.T., have caused renewed activity in the synthesis of polyhalogen compounds. Because of the availability of carbonyl compounds one of the potentially most useful approaches is the reaction of phosphorus pentachloride with aldehydes and ketones (4). However, this reaction suffers the disadvantages that the acidic medium may cause polymerization (5) or that the dichloro compound may be unstable under the reaction conditions (1, 4), and give an unsaturated monochloro compound.

During the course of some investigations on products derived from castor oil (3), we prepared 1, 1-dichloroheptane from heptaldehyde. This preparation has been carried out by several investigators (6), using heptaldehyde with phosphorus pentachloride alone, heated or in the cold, or in benzene at 20°C.

It was found that using ether as a solvent, washing the reaction mixture with sodium bisulfite and keeping the reaction temperature between 20-30°C resulted in a 62 per cent yield from 100 gm. of heptaldehyde in contrast to lower yields previously reported (5) for similar size runs. The low solubility of phosphorus oxychloride in ether and the low temperature contact before complete removal of byproducts may explain the increased yield.

The use of ether as a solvent may aid in the preparation of other dichlorides from carbonyl compounds by phosphorus pentachloride.

EXPERIMENTAL

One hundred eighty grams (0.86 mole) of phosphorus pentachloride was placed in one-liter, three-necked round-bottomed flask fitted with a stirrer, dropping funnel and thermometer. The flask was set in a cooling mixture and 75 ml. of dry ether was added. With vigorous stirring, 100 gm. (0.88 mole) of heptaldehyde was slowly added over a period of one

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hour, the temperature being kept below 30°C. When addition was completed, the mixture was stirred for an additional fifteen minutes, poured into a one-liter flask and allowed to stand overnight. Most of the phosphorus pentachloride had reacted and the mixture was yellow in color.

The phosphorus oxychloride was then decomposed by pouring the mixture over ice water. The dichloroheptane was extracted with ether, and the ether layer was washed with sodium carbonate solution until neutral and then washed twice with water and dried over anhydrous sodium sulfate. During all of these washings and extractions the mixture was kept cold.

Removal of the ether and distillation of the residue at 16 mm. Hg pressure gave 98 gm. of product, b. p., 68-90°C. Redistillation at 73-75°C at 16 mm. yielded 91 gm. $n_d^{20}=1.4450$. Bachman and Hill (2) reported the boiling point as 82°C (20 mm.); $n_d^{20}=1.4440$.

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