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REDUCTION OF PERHALOCOMPOUNDS WITH TERTIARY PHOSPHINES AND PHOSPHOROUS TRIS (DI-N-ALKYL)AMIDES.

I. M. Downie and J. B. Lee.

Organic Chemistry Laboratories, The University, Loughborough, Leics..

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In connection with some other work, we wished to convert a trichloromethyl group to an aldehyde or dichloromethylene group. A number of routes were considered, all involving several stages. We considered the use of trivalent phosphorous derivatives, since these are known to give nucleophilic attack upon halide atoms (1) and selectivity might be possible as a result of the varying electrophilic character of the halo-compounds to be examined. Also, the nucleophilic character of the attacking phosphorus atom can be varied by choice of suitable compounds, which should facilitate control of the process.

The overall reaction envisaged can be summarised

$$R_3P + R'CX_3 + R''OH = R_3PO + R'CHX_2 + R''X$$

where R" = methyl or ethyl to facilitate removal from the reaction mixture as the volatile halide.

We therefore examined the reaction of triphenylphosphine (I), tributylphosphine (II), trioctylphosphine (III), phosphorous tris (di-N-ethyl) amide (IV), and phosphorous tris (di-N-methyl)amide (V), with some perhalo compounds. We find that reaction proceeds readily, and with increasing vigour as the nucleophilic character of the phosphorus compound increases, viz., $Ph_3P < Bu_3P \cong Oct_3P < (Et_2N)_3P \cong (Me_2N)_3P$. Thus for example, admixture of benzotrichloride with phosphorous tris (di-N-ethyl)amide in ether containing ethanol (1 mol.) at room temperature led to rapid, practically quantitative formation of benzylidene chloride. In contrast, the use of tributylphosphine or trioctylphosphine required several hours at 35°C. for a similar conversion.

Negligible reaction was noted using triphenylphosphine under these conditions. The reaction in this case proceded after several hours at higher temperature.

Some attack upon the dihalomethyl compound to give the monohalo compound is possible if more severe conditions are used. Thus compound IV reacted very slowly with benzylidene chloride in ether under reflux to give some benzyl chloride. As might be expected, bromo derivatives are more susceptible to attack than chloro, and milder conditions are needed for these.

The formation of aldehyde by hydrolysis of the dihalocompounds generally presents no difficulty, and the application of this method to the synthesis of some dichloromethyl analogues of *D.D.T.*, together with the corresponding aldehydes, is under investigation.

REFERENCES.

1. For a summary and references see R. F. Hudson,"Structure and Mechanism in Organophosphorus Chemistry", Academic Press Inc., London, 1965. Also chapters in "*Topics in Phosphorus Chemistry" Vol. 1 - 4; Interscience Publ., New York, 1964-7.*