A Ready and Novel Route to Vicinal Dichlorides and Chloro-olefins via the Action of Phosphorus Pentachloride on Epoxides in Benzene or Chloroform

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EXTENDED work on chloro-olefins,¹ the study of the kinetics and mechanism of methanolysis and ethanolysis of cis- and trans-ArCH=CCIMe with the corresponding alkoxides and the formation of the ether ArCH = C(OR)Me or the acetylene ArC=CMe according to whether Ar is 4-nitrophenyl or 2,4-dinitrophenyl respectively,² and in which the product depends on the structure of the chloro-olefin, led to the search for other chloroolefins of the 1,2-di- and 1,1,2-tri-aryl types. The epoxides of the dinitro- and trinitro-derivatives corresponding to these types [cf. (I)], easily obtained by insertion of carbanions into aldehydes,3 were investigated for reactivity with phosphorus pentachloride in chloroform or benzene, so as to open the epoxide ring with the formation of vicinal dichlorides, or to form directly the chloro-olefins. Vicinal dichlorides were the only products formed in quantitative yields.

Wurtz⁴ prepared ethylene dichloride from ethylene oxide, and Reboul⁵ prepared 1,2,3trichloropropane from 3-chloro-1,2-epoxypropane. The reverse route, the formation of the epoxide from the vicinal dichloride, is, however, the one usually required.

Treatment of (Ia) (cis or trans) with phosphorus pentachloride in refluxing chloroform gave quantitatively the dichloride (IIa) obtained by other routes.⁶ When (IIa) was heated with pyridine in a sealed tube a chloro-olefin (IIIa) was obtained, identical (mixed m.p. and i.r.) with that reported earlier.⁶



(a)
$$R^1 = R^3 = 4 - NO_2 \cdot C_6 H_4$$
; $R^2 = H$

(b)
$$R^1 = R^2 = 4 - NO_2 \cdot C_6 H_4$$
; $R^3 = Ph$

(c)
$$R^1 = R^2 + R^3 = 4 - NO_2 \cdot C_6 H_4$$

The dichloride (IIa) can theoretically exist in the *meso-* or the racemic form. Similarly, (IIIa)

should exist as the *cis*- or the *trans*-isomer. Careful recrystallisation of the product (m.p. 144°, previously reported as one product⁶) showed that it is a mixture of two compounds, one, m.p. 144—150°, and the other, m.p. 172°. The latter seems to be the one recently prepared by Zimmer⁷ by a totally different method. Whether this mixture of chloro-olefins results from an original mixture of dichlorides or from isomerisation during the process of elimination is still under investigation.

Similar treatment of (Ib) and (Ic) with phosphorus pentachloride in chloroform or benzene gave the corresponding dichlorides (IIb) and (IIc), which were readily converted to the chloroolefins (IIIb) and (IIIc) respectively when heated with pyridine. The epoxides [(Ib), m.p. 163—164°, and (Ic), m.p. 185—186°], the vicinal dichlorides [(IIb), m.p. 160°, and (IIc), m.p. 244°], and the chloroolefins [(IIIb), m.p. 163°, and (IIIc), m.p. 202°] are all new compounds and gave the required elemental analyses. Spectral data are consistent with structures. For the chloroolefins (IIIa), (IIIb), and (IIIc), $\lambda_{max} = 335$, 315, and 308, and $\epsilon_{max} = 24,000$, 15,500, and 24,500, respectively.

On the assumption that PCl_5 exists in solution⁸ in equilibrium with the ions PCl_4^+ and PCl_6^- , the following scheme is suggested for the action of PCl_5 on epoxides:



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The steps (2) and (3) may be through carboniumion intermediates or by $S_N 2$ attack of chloride ions from PCl6-, as shown. The non-formation of chloro-olefins directly from this reaction suggests that no free carbonium ions are formed, either in step (2) when $R^2 = H$, or in step (3), when both R^1 and R^2 are nitrophenyls.

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From the experimental point of view this seems a new and convenient route from readily available epoxides to vicinal dichlorides, and thus to chloroolefins, compared to previous methods.1,6,9

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