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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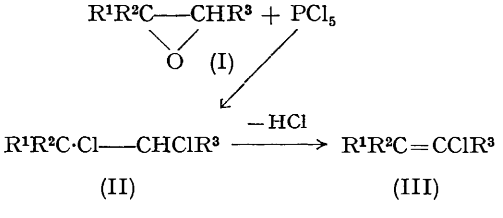
EXTENDED work on chloro-olefins,[1] the study of the kinetics and mechanism of methanolysis and ethanolysis of *cis-* and *trans-*ArCH=CClMe with the corresponding alkoxides and the formation of the ether ArCH=C(OR)Me or the acetylene ArC≡CMe according to whether Ar is 4-nitrophenyl or 2,4-dinitrophenyl respectively,[2] and in which the product depends on the structure of the chloro-olefin, led to the search for other chloro-olefins 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.

Wurtz[4] prepared ethylene dichloride from ethylene oxide, and Reboul[5] prepared 1,2,3-trichloropropane 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) $R^1 = R^3 = 4\text{-}NO_2{\cdot}C_6H_4$; $R^2 = H$

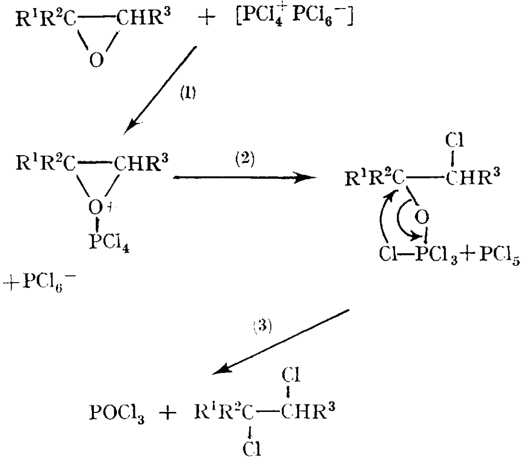
(b) $R^1 = R^2 = 4\text{-}NO_2{\cdot}C_6H_4$; $R^3 = Ph$

(c) $R^1 = R^2 + R^3 = 4\text{-}NO_2{\cdot}C_6H_4$

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 product[6]) 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 Zimmer[7] 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 chloro-olefins (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 chloro-olefins [(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 chloro-olefins (IIIa), (IIIb), and (IIIc), λ_{max} = 335, 315, and 308, and ϵ_{max} = 24,000, 15,500, and 24,500, respectively.

On the assumption that PCl_5 exists in solution[8] in equilibrium with the ions PCl_4^+ and PCl_6^-, the following scheme is suggested for the action of PCl_5 on epoxides:



The steps (2) and (3) may be through carbonium-ion intermediates or by S_N2 attack of chloride ions from PCl_6^-, 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.

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

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