Non-stereospecificity in the Alkaline Hydrolysis of a Bisphosphonium Salt

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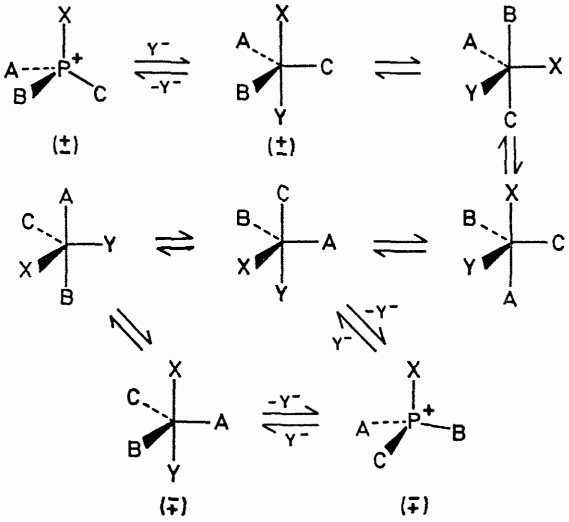
Summary Aqueous alkali converts either *cis*- or *trans*-1,4-dibenzyl-1,4-diphenyl-1,4-diphosphoniocyclohexane dibromide into a mixture of both *cis*- and *trans*-1,4-diphenyl-1,4-diphosphacyclohexane *PP'*-dioxides.

THE currently accepted mechanism for the reaction of phosphonium salts with aqueous alkali involves the intermediacy of phosphoranes:[1,2]

$$R_4P^+ + OH^- \rightleftharpoons \underset{(\mathbf{1})}{R_4POH} \rightleftharpoons \underset{(\mathbf{2})}{R_4PO^-} \rightarrow R_3PO + RH$$

Ligand reorganization (pseudo-rotation) in such quinquecovalent intermediates[2] can lead to racemization in a three- or five-step process depending on whether the formation of the phosphorane is reversible or not (see Scheme). Mislow and his collaborators have recently observed that racemization of phosphine oxides by lithium aluminium hydride proceeds faster than reduction to phosphines[3] and Cremer *et al.* have described the alkali-catalysed inversion of configuration in a phosphonium salt;[4] both reactions have been accounted for in terms of ligand reorganization in a quinquecovalent intermediate. We now describe the first non-stereospecific alkaline hydrolysis of a phosphonium salt which provides strong evidence for the involvement of a phosphorane in the reaction.

The preparation[5] of the bis-salt (**3**) affords a mixture of stereoisomers which may be readily separated by making use of their differing solubilities in warm acetic acid. Subsequent recrystallization affords a pure sample of each isomer (microanalysis, ^{1}H n.m.r., and t.l.c.). The two isomers have the same m.p. (>360°, decomp.) but distinct ^{1}H n.m.r. and i.r. spectra and R_F values (t.l.c.).†



SCHEME

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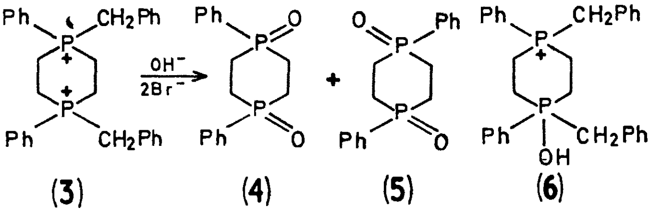
† The least soluble isomer has been tentatively assigned the *cis*-configuration and an *X*-ray study has been started. Our argument here depends only on stereochemical purity.

When the least soluble isomer reacts with a large excess of sodium hydroxide in aqueous solution the product consists of a mixture of two compounds, separated by chromatography and assigned the structures of *cis* (**4**; 39%) and *trans* (**5**; 22%) dioxides, m.p. 222—225 and 325° respectively.‡ The identity of these compounds rests on spectral (mass, ^{1}H n.m.r., and i.r.) and microanalytical data. No other products were detected (t.l.c.).

Since phosphine oxides are configurationally stable in aqueous alkali[6] inversion at phosphorus must have occurred at an intermediate stage, presumably by ligand reorganization in an intermediate phosphorane. As alkaline hydrolysis of phosphonium salts is normally stereospecific,[1,2] non-stereospecificity in this instance suggests that the phosphorane in this reaction is much more long-lived than usual; this may be accounted for by assuming that inversion occurs in the monophosphorane (**6**) whose formation should be essentially irreversible due to the relief of electrostatic repulsion between the two positively-charged centres which accompanies its formation.



Similar behaviour is observed for the more soluble of the isomeric bis-salts (t.l.c.).

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‡ Stereochemical assignments are tentative and based on m.p. (ref. 2) and i.r. spectra: the *cis*-isomer shows two phosphoryl bands (1195 and 1145 cm^{-1}) whereas the *trans* shows only one (1160 cm^{-1}).

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