The Hydrolysis of Bisphosphonium Salts

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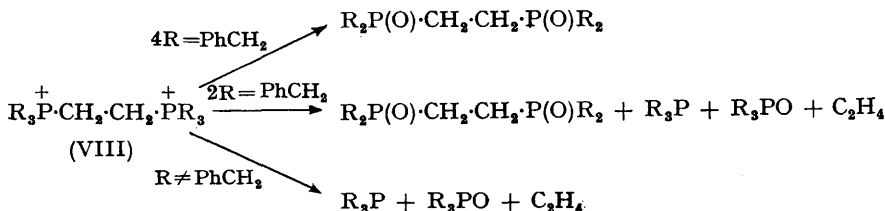
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AGUIAR has reported[1] that hydrolysis of both 1,1,4,4-tetraphenyl-1,4-diphosphoniacyclohexane dibromide (I) and 1,1,4,4-tetraphenyl-1,4-diphosphoniacyclohex-2-ene dibromide (II) gave 1,2-ethanebis(diphenylphosphine) P-oxide (III).

As part of a study of the action of nucleophiles on bisphosphonium salts, we confirmed these results and also observed that the slow addition of aqueous sodium hydroxide to an excess of an aqueous solution of the bis-salt (I) gave the phosphonium bromide (IV; 95% based on re-covered bis-salt). A small amount of (III) was also obtained. Reaction of (IV) with an excess of dilute aqueous sodium hydroxide gave the PP'-dioxide (V), confirming the expectation that (IV) is not an intermediate in the formation of (III).

Treatment of (II) under the same conditions used for (I) yielded the hydroxyethyl derivative (VI; 50%) as the major product (presumably via hydration of the initially formed vinyl salt). N.m.r. data confirmed the presence of a small amount of the alternative ring-opened product (VII).
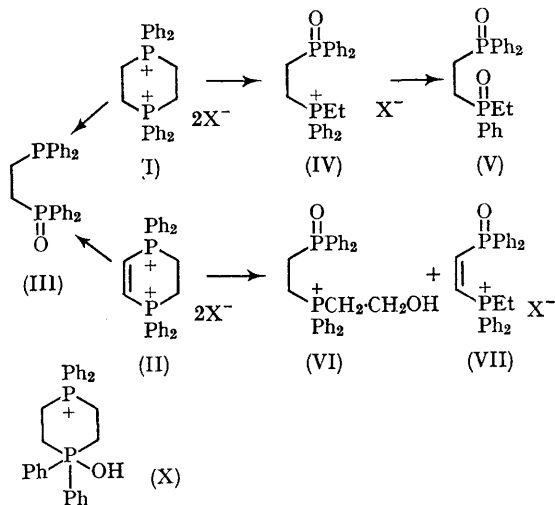
These results with the cyclic salts contrast sharply with our findings for the acyclic analogues (VIII) whose behaviour on hydrolysis is a function of the substituents on phosphorus. Where these are other than benzyl, exclusive loss of the ethylene bridge is observed. When one substituent on each phosphorus atom is benzyl, a competitive reaction occurs and where two substituents on each phosphorus atom are benzyl, no loss of ethylene takes place. These results are sum-marised in equation 1.

elimination could be obtained and the initial product postulated by Wittig,[2] $Ph_3\overset{+}{P}\cdot CH=CH_2$ X^-, has been shown to be rapidly converted into the hydrated salt, $Ph_3\overset{+}{P}\cdot CH_2\cdot CH_2OH$ X^-, which is known[3] to form 2-hydroxyethyldiphenylphosphine oxide with an excess of alkali.

The rates of reaction of both cyclic and acyclic bis-salts are substantially greater than for a representative mono-salt such as tribenzyl-p-chlorobenzylphosphonium bromide (IX).[4] The half-lives are as follows: mono-salt (IX), 1; acyclic bis-salt (VII; R = Ph), 50; cyclic bis-salt (I), 300. These results are only very approximate

$$4R=PhCH_2 \nearrow R_2P(O)\cdot CH_2\cdot CH_2\cdot P(O)R_2$$

$$\underset{(VIII)}{R_3\overset{+}{P}\cdot CH_2\cdot CH_2\cdot \overset{+}{P}R_3} \xrightarrow{\;2R=PhCH_2\;} R_2P(O)\cdot CH_2\cdot CH_2\cdot P(O)R_2 + R_3P + R_3PO + C_2H_4$$

$$R\neq PhCH_2 \searrow R_3P + R_3PO + C_2H_4$$

Loss of ethylene and benzyl groups occurs at competitive rates. For (VIII; R = Ph) the reaction follows second-order kinetics when carried out in the presence of a large excess of the bis-salt and the products are the same regardless of which reagent is present in excess. No evidence of

but show that the decomposition of the cyclic bis-salt is easier than for either the acyclic bis-salt or the mono-salt.

The increase in the rate of hydrolysis of (I) over (VIII) can be explained as follows: in the intermediate (X), the electrostatic repulsive forces

between the two phosphonium centres of the bis-salt has been relieved by neutralisation of charge on one of them. The driving force for ring opening, rather than the anticipated loss of the phenyl group, is presumably relief of steric strain (caused by the pentacovalent phosphorus) in the inter-mediate (X).

The increased rate for the acyclic bis-salt may be due to coplanarity of the P–CH₂–CH₂–P system as has been suggested in the related reaction of these salts with sodium hydride.[5] The loss of ethylene (or acetylene) when the cyclic bis-salts (I) and (II) react with an excess of alkali is presumably a synchronous process in which both phosphonium centres in the bis-salt have been neutralised. Models indicate that coplanarity of the P–C–C–P system is not possible in the saturated salt (irrespective of the configuration of the intermediate) though it is for the un-saturated salt, allowing the preferential expulsion of acetylene in this case.

The difference in reaction pathway for the cyclic bis-salts when they are present in excess is attributed to the fact that uptake of the first hydroxide ion is much more energetically favourable than the second since in the latter case, the driving force of relief of electrostatic repulsion is absent.

[1] (a) A. M. Aguiar, H. Aguiar, and D. Daigle, *J. Amer. Chem. Soc.*, 1965, **87**, 671; (b) A. M. Aguiar and H. Aguiar, *ibid.*, 1966, **88**, 4090.

[2] G. Wittig, H. Eggers, and P. Duffner, *Annalen*, 1958, **619**, 10.

[3] A. R. Hands and A. J. H. Mercer, *J. Chem. Soc.*, 1965, 6055.

[4] W. E. McEwan, G. Axelrad, M. Zanger, and C. A. Vander Werf, *J. Amer. Chem. Soc.*, 1965, **87**, 3948.

[5] J. J. Brophy and M. J. Gallagher, *Chem. Comm.*, 1966, 531.