

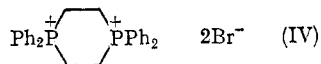
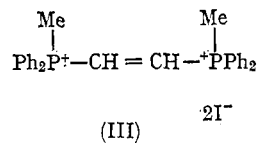
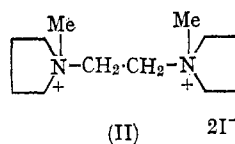
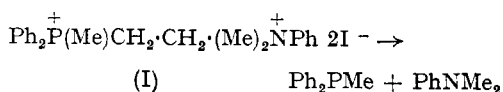
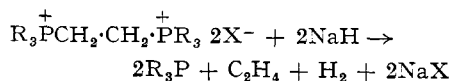
## The Cleavage of Bisphosphonium Salts by Sodium Hydride

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SODIUM HYDRIDE is extensively used as a base in organic chemistry but a study of other reactions of the potentially interesting hydride ion is largely precluded by its insolubility without decomposition in all the usual solvents. We have observed a reaction which apparently involves nucleophilic attack by hydride ion under exceptionally mild conditions.

When a suspension of a bisphosphonium salt of the type  $R_3\overset{+}{P}CH_2\cdot CH_2\cdot\overset{+}{P}R_3$   $2X^-$  ( $R$  = alkyl or aryl;  $X$  = halogen) is stirred with a suspension of sodium hydride (2 mol.) in tetrahydrofuran at room temperature for 9 hr., complete decomposition occurs with the formation of the phosphine  $R_3P$  (2 mol.), ethylene, and hydrogen (identified by mass spectrometry). No ethane could be detected. The reaction appears to be general and occurs even when one or more of the substituents,  $R$ , is benzyl, in marked contrast to the reaction of such salts with lithium aluminium hydride.<sup>1</sup> The mixed phosphonium-ammonium salt (I) is similarly decomposed but the bisammonium salt (II) is recovered unchanged under these conditions.



Even more remarkably, ethylene-1,2-bis(methyl-diphenylphosphonium) di-iodide [(III); stereochemistry believed *trans*] is decomposed in this way but the rate is very much slower.

In this case the presence of acetylene has only been shown qualitatively. Trimethylene 1,3-bis(diphenylphosphonium) dibromide is largely unaffected (90% recovery after 9 hr.) but some triphenylphosphine oxide was isolated on work-up, possibly arising from phosphorane formation.

Only two mechanisms seem feasible: (a) nucleophilic attack by hydride ion with synchronous formation of  $R_3\overset{+}{P}H$ , ethylene, and  $R_3P$ ; (b) formation of a quinquivalent intermediate by attack of hydride ion at phosphorus followed by attack of hydride on this intermediate to give hydrogen,  $R_3P$ , and ethylene. We favour (b) in view of its analogy with the accepted<sup>2</sup> mechanism for hydrolysis of phosphonium salts and because of the failure of the bisammonium salt (II) to react.

It seems probable that the driving force for the reaction stems from the very strong conformational preference for the *trans*-rotamer which must be present in view of the extensive nonbonded and electrostatic repulsions between the two  $\text{PR}_3$  groups. The two groups are thus held in the most favourable orientation (*trans*-coplanar) for an elimination. In support of this we find that the cyclic bis-salt (IV), in which the two groups must be at an angle of about  $60^\circ$  to one another, decomposes by a more complex pathway giving only

a low yield of ethylene-1,2-bis(diphenylphosphine) together with other as yet unidentified products. The same stereochemical factors may also explain the complete absence of eliminations of the type  $\rightarrow \text{R}_3\text{P} + \text{R}_3\overset{+}{\text{P}}\text{CH} = \text{CH}_2 \quad \text{X}^-$  under the conditions used by us.

Other nucleophiles behave in a similar fashion with ethylenebisphosphonium salts and these will be reported later.

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<sup>1</sup> R. C. Hinton and F. G. Mann, *J. Chem. Soc.*, 1959, 2835.

<sup>2</sup> W. E. McEwen, "Topics in Phosphorus Chemistry", vol. 2. Wiley, New York, 1965, p. 5.