

BASE PROMOTED DECOMPOSITION OF 2- AND 3-PHOSPHOLENIUM BROMIDES.

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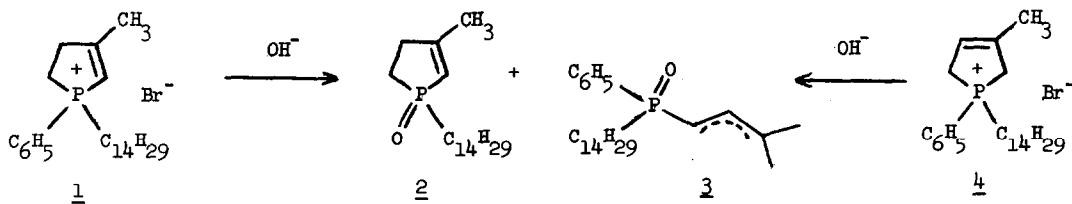
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(Received in USA 21 May 1971; received in UK for publication 25 May 1971)

Nucleophilic displacement on tetravalent phosphorus in saturated four and five membered rings occurs with retention¹ as well as inversion² of configuration. These and ring cleavage reactions of cyclic phosphonium salts^{1b,3} and esters⁴ may be interpreted readily by considering relative energies of isomeric phosphorane intermediates connected by one or more pseudorotations.⁵ We wish to report that 2- and 3-phospholenium bromides hydrolyze by divergent reaction pathways. Product composition may be understood within the framework of pseudorotation theory.

Some time ago a series of surface-active alkyl phospholene oxides were synthesized⁶ and incorrectly assigned a 3-phospholene structure.⁷ A typical example is 3-methyl-1-tetradecyl-2-phospholene oxide (2). Hydrolysis of 3-methyl-1-phenyl-1-tetradecyl-2-phospholenium bromide (1)⁸ with 5N sodium hydroxide in aqueous DMSO or DMF (1:4) provides compound 2 in 98% yield. Both chemical shift and coupling of the vinyl proton ($\tau(\text{CDCl}_3/\text{TMS})$ 4.14(1H, $J_{\text{PH}} = 25.0$ Hz)) are in accord with the 2-phospholene structure.⁹



A dramatic realignment of product ratio is observed as the basicity of the medium is decreased (Table 1). For example in aqueous hydroxide (5N NaOH) phospholenium bromide 1 decomposes to a 2:3 mixture of oxide 2 and ring cleavage products.¹⁰ Fragmentation to compound 2 is almost completely suppressed in preference to ring opening when salt 1 is treated with alcoholic KOH (1.7N). Under all of the tabulated conditions, isomeric salt 4⁸ provides the same products consistently rich in

ring opened materials, but at a qualitatively greater rate.

Product 3 is largely (nmr) a 2:1 mixture of the two 3-methylbutenyl isomers. Hydrogenation and fractional crystallization yields phenyltetradecyl-(3-methylbutyl) phosphine oxide (3a), mp 52-53.5°. The structure of oxide 3a has been confirmed by independent synthesis¹⁰ from diphenylchlorophosphine and (3-methyl)-butylmagnesium iodide. The resulting phosphine upon quaternization with tetradecyl bromide and subsequent treatment with alcoholic KOH gives oxide 3a. A mixture of double bond isomers 3 has been prepared likewise from the Grignard of 1-chloro-3-methylbutene-2 and $(C_6H_5)_3PCl_2$.⁶

Table 1. Product Distribution in Basic Media (%3/%2).^a

	<u>bromide 1</u>	<u>bromide 2</u>
NaOH/H ₂ O/DMSO:	2/98	75/25
NaOH/H ₂ O:	60/40	90/10
Na ₂ CO ₃ /H ₂ O(100°):	90/10	90/10
EtOH/KOH:	95/5	95/5

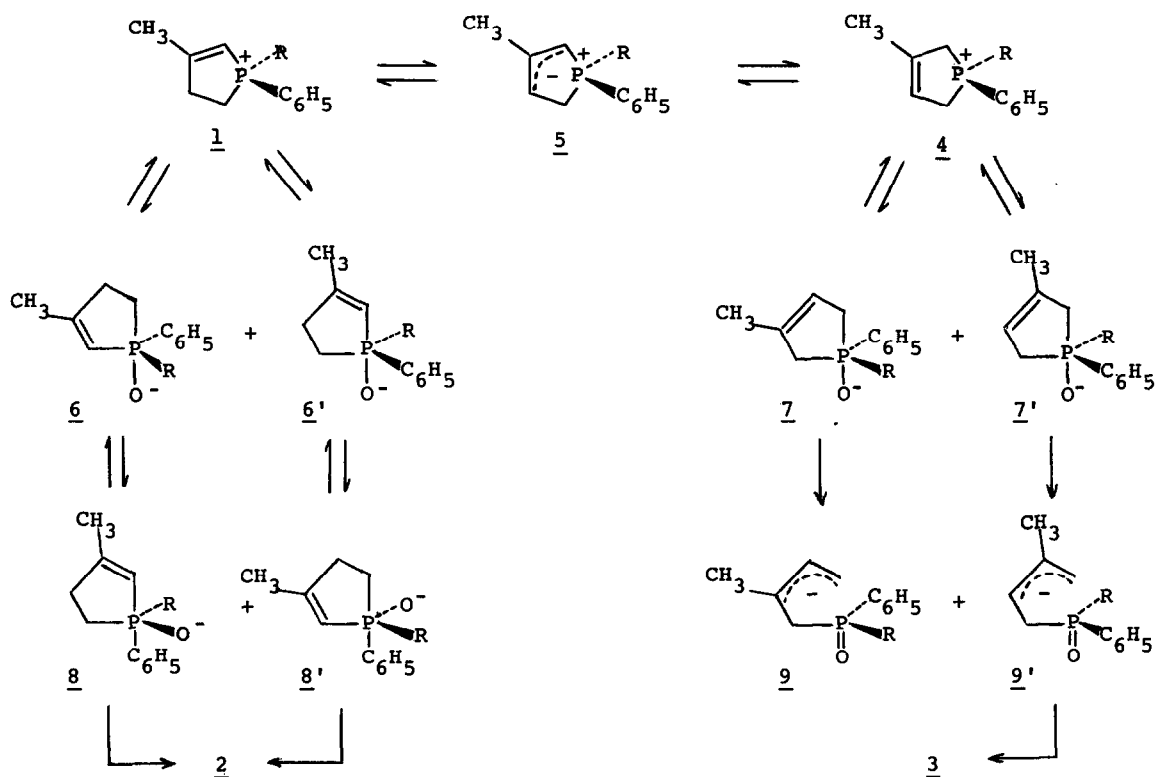
a. Yields by glpc.

A mechanism which encompasses the diverse behavior of phospholenium prototropic isomers (R = C₁₄H₂₉) is pictured below. Apical nucleophilic attack^{11,12} by hydroxide on salts 1 and 4 in a kinetically controlled reaction can lead to phosphorane pairs 6/6' and 7/7' respectively. Assuming ea rings⁵ and axial orientation by electronegative groups,¹¹ phosphoranones 7/7' probably decompose under all conditions rapidly without prior pseudorotation to allyl anions 9/9'. If hydroxide attack is sufficiently reversible relative to ligand departure,¹³ the transition state preceding anion 9' is expected to provide the lower energy pathway to ring-opened products in accord with our observations. Phosphorane pair 6/6', on the other hand, undoubtedly has a longer lifetime than 7/7' because of the relatively high pKa's of the anions available for elimination. Pseudorotation results in isomers 8/8' permitting apical departure of the phenyl anion.^{11,12} Loss of C₆H₅⁻ in preference to ring cleavage is consistent with the pKa order:¹⁴ C₆H₆ < CH₂=CH₂ < CH₃-CH₃.

Ylide formation (5) can compete with phosphorane generation, particularly in a medium where anions experience stabilization by solvation and reduced reactivity (dilute aqueous base, EtOH/KOH).

Product oxides 2 and 3 may thus be derived from either of the isomeric phospholenium bromides. Thermodynamic control accounts for the conversion of both salts in these circumstances predominately to acyclic products (3) through the relatively low energy anions 9/9'. Ylides have been implicated in the base decomposition of phosphonium salts, but only as "blind-alley" intermediates.¹⁵

3,4-Dimethyl-1-phenyl-1-tetradecyl-3-phospholenium bromide and isomeric phosphonium salts derived from butadiene in combination with a variety of alkyl chains on phosphorus behave in a similar manner. Differential behavior of 2- and 3-phospholenium halides in response to the action of hydroxide thus appears to be general. The mechanistic details of the reaction are under investigation.



ACKNOWLEDGEMENT. We are grateful to the National Science Foundation (Grant No. GP 9031) for partial support of the work and to Professor K. Mislow for helpful comments.

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