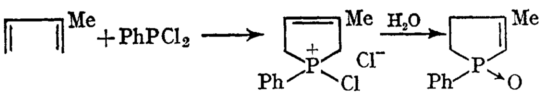
Structure of Isoprene–Phenylphosphonous Dihalide Cyclo-adducts

By LOUIS D. QUIN* and THOMAS P. BARKET
(*Department of Chemistry, Duke University, Durham, North Carolina* 27706)

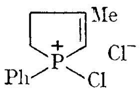
THE cyclo-adduct of isoprene and phenylphosphonous dichloride, originally thought to provide 3-methyl-1-phenyl-3-phospholene oxide on hydrolysis,[1] has recently given the isomeric 2-phospholene oxide.[2] It was assumed that the adduct possessed the 3-phospholene ring and that rearrangement occurred during hydrolysis.



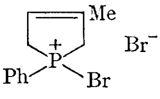
We have examined the adduct, as well as the derived oxide, and have concluded that *both* compounds possess the 2-phospholene system. Obtaining a rearranged product in a cycloaddition synthesis is a unique event, and of importance here, for the adduct is a highly reactive substance useful as a precursor to other derivatives of the same phospholene ring system. The rearrangement is dependent on the substituents of the phosphonous dihalide; it has been established that methylphosphonous dichloride[3] provides the expected 3-phospholene system, and here it will be shown that phenylphosphonous dibromide behaves similarly.

The presence of double bond isomerism in the phenylphosphonous dichloride adduct (I) and the dibromide adduct (II) is clearly seen in the 60 Mc./sec. ^{1}H n.m.r. spectra of the adducts in $CDCl_3$. Adduct (I) has a vinyl proton doublet (J_{PCH} = 32·2 c./sec.) at δ 7·0, while adduct (II) has this signal at δ 5·80 (J_{PCCH} = 37·5 c./sec.). The larger downfield shift of the vinyl proton of (I) is attributed to its position α to phosphorus. The adducts in $CDCl_3$ solution have tetracovalent (positive) phosphorus, rather than pentacovalent phosphorus, as seen by the low-field position of their ^{31}P signals (measured at 19·3 Mc./sec. by tube interchange with P_4O_6; (I) −99 p.p.m. from H_3PO_4; (II) −89 p.p.m.). This is in accord with observations recently made on related halides.[4] It is then reasonable to expect similar ^{1}H n.m.r. differences in quaternary phosphonium salts of the 2- and 3-phospholenes. In fact, the benzyl bromide salt of 3-methyl-1-phenyl-2-phospholene has the vinyl proton doublet at δ 6·60 ($J_{\text{PCH}} = 30$ c./sec.), that of 3-methyl-1-phenyl-3-phospholene at δ 5·43 ($J_{\text{PCCH}} = 31{\cdot}5$ c./sec.). Adducts (I) and (II) also differ in the methylene region. For (I), with each methylene in a different environment, a complex multiplet at δ 3·1—3·9 is observed. For (II), with both methylenes similarly deshielded by the double bond and phosphorus, a symmetrical but broad and unresolved peak occurs at the more downfield position of δ 4·15. A similar situation prevails for the corresponding benzyl bromide salts.

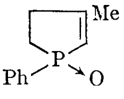
Adducts (I) and (II) on hydrolysis provide, respectively, the isomeric phospholene oxides (III) (low melting solid, b.p. 150° at 0·15 mm.) and (IV) (b.p. 133—134° at 0·24 mm.), and on reduction with magnesium in tetrahydrofuran[5] the isomeric phospholenes (V† and VI, respectively). The new oxide (IV) gave the correct analysis; the phospholenes were analyzed as the benzyl bromide salts [from (V), m.p. 178—180°; from (IV), m.p. 184—185°; mixed m.p. 166—176°]. The ^{1}H n.m.r. spectra fully support the assigned structures and will be described elsewhere.



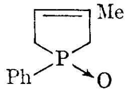
(I)



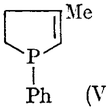
(II)



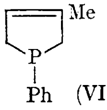
(III)



(IV)



(V)



(VI)

Preliminary experiments with *trans*-piperylene lead to the same conclusions: the phenylphosphonus dichloride adduct clearly contains the 2-phospholene ring (one vinyl H), while the phenylphosphonous dibromide adduct is the 3-isomer (two vinyl H). Isomeric oxides are formed on hydrolysis. However, the structure of an adduct is not determined by the phosphonous dihalide alone; the diene may also be involved. It has been shown[5] that the 2,3-dimethylbutadiene–phenylphosphonous dichloride adduct gives the 3-phospholene on magnesium reduction. This may be attributed to the stabilizing effect of the two methyl groups on the double bond when in the 3,4-position. A similar observation has been made for diene–phosphorus trichloride adducts;‡ 2-phospholene derivatives were commonly obtained on hydrolysis except with the adduct of 2,3-dimethylbutadiene.[2]

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† The reduction of the isoprene–phenylphosphonous dichloride adduct had been performed earlier (ref. 5), but the product was believed to be the 3-phospholene.

‡ These adducts have been claimed (ref. 2) to be 3-phospholene derivatives from their ^{1}H n.m.r. spectra, but no supporting data have been published.

[1] W. B. McCormack, U.S. Pat. 2,663,736, 1953 and 2,663,737 1953; See also W. B. McCormack, *Org. Syn.*, 1963, **43**, 73.

[2] K. Hunger, U. Hasserodt, and F. Korte, *Tetrahedron*, 1964, **20**, 1593.

[3] L. D. Quin, J. A. Peters, C. E. Griffin, and M. Gordon, *Tetrahedron Letters*, 1964, 3689.

[4] G. A. Wiley and W. R. Stine, *Tetrahedron Letters*, 1967, 2321.

[5] L. D. Quin and D. A. Mathewes, *J. Org. Chem.*, 1964, **29**, 836.