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OXYPHOSPHIRANE INTERMEDIATES IN BASE-INDUCED REARRANGEMENTS OF α-HALOPHOSPHINATES[1]

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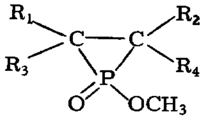
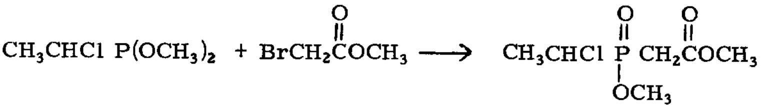
The synthesis and reactivity of heterocyclic three membered rings containing sulfur and nitrogen has been reported. However, there are few examples in the literature of three-membered ring compounds containing phosphorus. Compounds with trivalent phosphorus in a three-membered ring have been prepared[3,4],and an intermediate has been proposed for the addition of benzenephosphorus dichloride to cyclooctatetraenyl cation[5]. We report here evidence for the intermediacy of three membered rings containing pentavalent phosphorus, oxyphosphiranes (I), in two rearrangement reaction of α-halophosphinates.

(I)

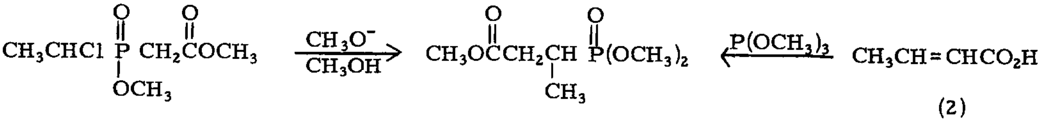


The first rearrangement was observed with the α-halophosphinate (III) synthesized[6] by eq. 1[7] Reaction of III with CH_3ONa in CH_3OH gave the rearranged phosphonate (IV) in 75% yield (eq. 2). The structure of IV was proved by comparison with a sample prepared from crotonic acid and trimethyl phosphite[10] (eq. 2).



$$CH_3CHCl\ P(OCH_3)_2 + BrCH_2\overset{O}{\overset{\|}{C}}OCH_3 \longrightarrow CH_3CHCl\ \underset{\underset{OCH_3}{|}}{\overset{\overset{O}{\|}}{P}}\ CH_2\overset{O}{\overset{\|}{C}}OCH_3 \qquad (1)$$

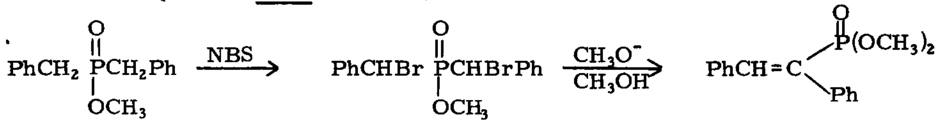
(II) (III)



$$CH_3CHCl\ \underset{\underset{OCH_3}{|}}{\overset{\overset{O}{\|}}{P}}\ CH_2\overset{O}{\overset{\|}{C}}OCH_3 \xrightarrow[CH_3OH]{CH_3O^-} CH_3O\overset{O}{\overset{\|}{C}}CH_2\underset{\underset{CH_3}{|}}{CH}\ \overset{\overset{O}{\|}}{P}(OCH_3)_2 \xleftarrow{P(OCH_3)_3} CH_3CH{=}CHCO_2H \qquad (2)$$

(II) (IV)

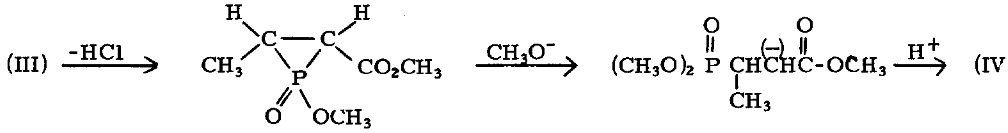
The second rearrangement was observed with the α,α'-dibromophosphinate (VI) synthesized[11] by bromination of V with N-bromosuccinimide (eq. 3). When a mixture of the isomers of (IV) was reacted with CH_3ONa in CH_3OH, a mixture (approximately 7:3) of cis- and trans- stilbenephosphonates (V) was obtained (eq. 3). The same ratio of isomers of (V) was obtained when the purified meso form of (IV) was reacted with sodium methoxide.



(V) (VI) (VII) (3)

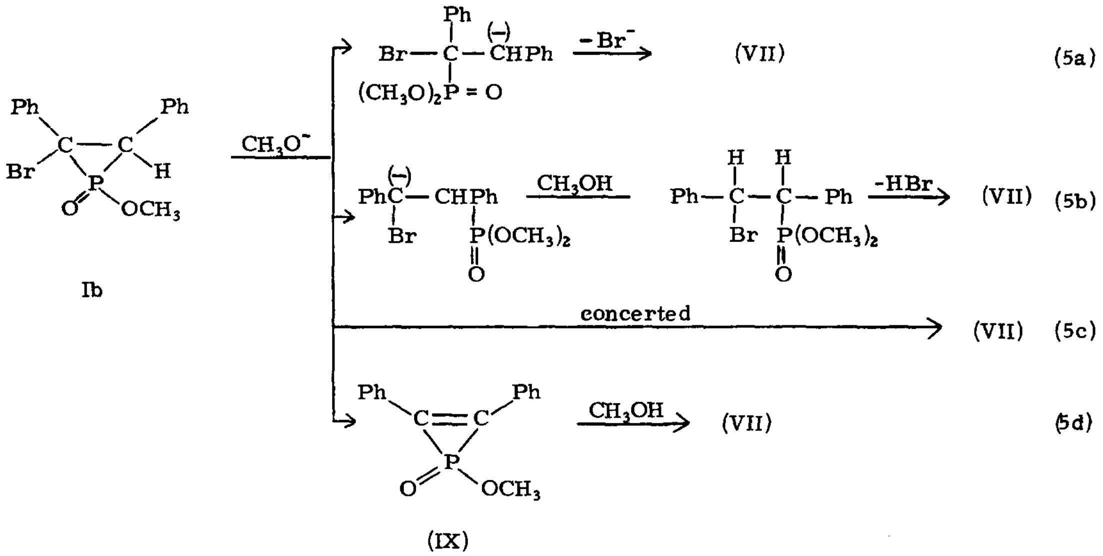
The reactions in equations 2 and 3 can only be explained by three-membered ring intermediates (I), which are formed from (III) and (VI) by elimination of HCl and HBr respectively.

The simplest mechanism for the ring opening of the cyclic intermediate (Ia) generated from (III) involves nucleophilic attack on phosphorus by methoxide anion and generation of the enolate anion (VIII) which would yield (IV) on protonation:



(Ia) VIII (4)

Several mechanisms are possible for the rearrangement observed in the dehydrohalogenation of (VI). However, all of them require as a first step an oxyphosphirane intermediate (Ib). Attack of methoxide on the phosphorus atom in (Ib) could generate two different carbanions which can lead to the formation of the stilbenes (VII) by different pathways (eqs. 5a, b). A concerted mechanism of nucleophilic attack of CH_3O^- on phosphorus and elimination of Br^- is not excluded because it is possible to write three isomers of (Ib), two of them leading to the cis stilbene and the other to the trans, and this could account for the ratio of isomeric stilbenes (VII) found in the reactions of (IV) (eq. 5c). Formation of the stilbenes (VII), could also arise from ring opening of an oxyphosphirene intermediate (IX), formed by elimination of HBr from (Ib)[12] (eq. 5d). We plan further research to resolve the mechanistic problems in this reaction.



The high reactivity of these three-membered ring intermediates may be due to the tendency of phosphorus to react through pentacoordinate species which should have less strain in the ring, so that strain is relieved in the transition state.[13]

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6. Compound II was prepared by methanolysis of the corresponding dichloride which has been obtained following the procedure described by Uhing[8] and Kabachnik[9] for the preparation of chloromethylphosphorus dichloride.
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