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HYDROLYTIC CLEAVAGE OF QUATERNIZED METHYLENEBIS(DIPHENYLPHOSPHINE)

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We wish to report the facile, quantitative hydrolytic carbon to phosphorus bond cleavage of methylenebis(N-phenyldiphenylphosphine imide)(I) under acidic conditions and methylenebis(benzyldiphenylphosphonium)dibromide (IV) under basic conditions (10% aqueous sodium hydroxide at 50° for 15 minutes)(Eq. 1).

$$\underset{(I)}{[Ph_2P(NPh)]_2CH_2} + 2H_2O \xrightarrow{H^+} \underset{(II)}{Ph_2P(O)NHPh} + \underset{(III)}{Ph_2P(O)CH_3} + PhNH_2$$

$$[(Ph_2PCH_2Ph)_2CH_2]^{++}2Br^- + 2OH^- \xrightarrow[H_2O]{} \underset{(V)}{Ph_2P(O)CH_2Ph} + PhCH_3 + Ph_2P(O)CH_3$$

Equation 1.

Methylenebis(diphenylphosphine)dioxide (VI), the product expected from both of these reactions,[1,2] is completely unchanged after being subjected to the conditions employed in these hydrolyses.

Isolation of I was accomplished by cooling an ether solution of phenylazide and methylenebis(diphenylphosphine)(VII) from which traces of acid were rigorously excluded(Eq. 2).

$$\underset{(VII)}{(Ph_2P)_2CH_2} + 2\ PhN_3 \longrightarrow \underset{(I)}{[Ph_2P(NPh)]_2CH_2} + 2N_2$$

Equation 2.

When these precautions were not taken, diphenylphosphanilide (II) precipitated.[3]

Diphosphonium salt (IV) was prepared by reaction of (VII) with refluxing benzyl bromide as the solvent. (Eq. 3).

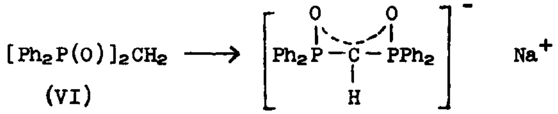
$$(Ph_2P)_2CH_2 + 2PhCH_2Br \longrightarrow [(Ph_2PCH_2Ph)_2CH_2]^{++}2Br^-$$

Equation 3.

Anal. Calcd. for $C_{37}H_{32}P_2N_2$: C, 78.5; H, 5.66; P, 10.92; N, 4.95; Found: C, 78.49; H, 5.73; P, 11.07; N, 4.87.
Anal. Calcd. for $C_{39}H_{36}P_2Br_2$: C, 64.46; H, 4.95; P, 8.53; Br, 22.04. Found: C, 64.63; H, 5.05; P, 8.47; Br, 22.16.
Compounds I and IV display the usual bands at 1440 and 1100 cm^{-1}, indicative of a partially positive phosphorus atom bonded to phenyl groups.[4] Bands in the 1485 and 1325 cm^{-1} region for I show that it is a phosphine imide.[4] The absence of any large bands in the 1175 cm^{-1} region demonstrates that a phosphoryl group is not present in either I or IV.[4]

Proton nuclear magnetic resonance spectra of deuteriochloroform solutions of I taken at 60Mc, using tetramethylsilane as a standard, show a sharp triplet centered at τ 6.3 ppm ($J_{P\text{-}CH}$ = 14 cps) and a series of complex peaks extending from τ 3.5 to τ 2.2 ppm. Integration of the areas show the ratio to be about 1:15 (triplet : complex). Assignment of the triplet to the methylene protons and the complex to the phenyl protons was made on the basis of analogy with the spectrum of methylenebis(diphenylphosphine)dioxide (VI)[(triplet at τ 6.43 ppm ($J_{P\text{-}CH} = 15$ cps)][3], area ratio and deuterium oxide exchange experiments. The methylene protons of I are more labile to isotopic exchange than those of the corresponding dioxide VI, as shown by the complete disappearance of the triplet in the nmr spectrum of a deuteriochloroform solution of I when deuterium oxide is added to the solution. The complex of peaks due to the phenyl protons is not altered in any way by this treatment, indicating that the compound is essentially unchanged in structure. Prolonged standing of the D_2O-$CDCl_3$ mixture does lead to changes in the phenyl hydrogen complex and only diphenylphosphanilide, II, can be recovered when the solvents are removed. Apparently, the D_2O-$CDCl_3$ mixture slowly produces enough acid to hydrolytically cleave I. Identical treatment of a $CDCl_3$ solution of VI leads to no change in the proton nmr spectrum.

Preparation, isolation, and use of the sodium or potassium salts of methylenebis(diphenylphosphine)dioxide(VI) establishes the fact that the methylene hydrogens in the dioxides are, as expected, fairly acidic[5](Eq. 4).



$$\underset{(VI)}{[Ph_2P(O)]_2CH_2} \longrightarrow \left[Ph_2\overset{O}{\overset{|}{P}}-\underset{H}{\underset{|}{C}}-\overset{O}{\overset{|}{P}}Ph_2 \right]^- \quad Na^+$$

Equation 4.

While, at room temperature, I "dissolves" in 5% HCl, it is not soluble in 10% KOH.

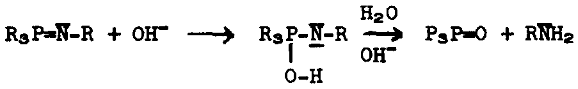
Deuteriochloroform solutions of compound IV in concentrations sufficiently high for nmr work could not be prepared but trifluoroacetic acid solutions showed two phenyl proton complexes at τ 2.3 ppm and at τ 3.00 ppm, along with what appears to be a triplet centered at τ 4.8 ppm (J_{P-CH}= 15 cps) and a doublet centered at τ 5.27 ppm (J_{P-CH} = 13 cps) assigned to the P-CH_2-P and P-CH_2-Ph methylene protons respectively. The ratio if 10:5:1:2.

Basic hydrolysis (as contrasted to acidic hydrolysis) of I leads, as is usual for phosphine imides, to the diphosphine dioxide,VI, and aniline (Eq. 5).

$$\underset{\text{(I)}}{[Ph_2P(NPh)]_2CH_2} + 2H_2O \longrightarrow \underset{\text{(VI)}}{[Ph_2P(O)]_2CH_2} + 2\ PhNH_2$$

Equation 5.

Basic hydrolysis of phosphine imides is presumed to occur by initial attack of hydroxide ion at the phosphorus atom followed by eventual elimination of amine and production of a phosphine oxide (Eq. 6).



$$R_3P{=}\overline{N}{-}R + OH^- \longrightarrow \underset{\displaystyle O{-}H}{R_3P}{-}\overline{N}^-{-}R \xrightarrow[OH^-]{H_2O} P_3P{=}O + R\overline{N}H_2$$

Equation 6.

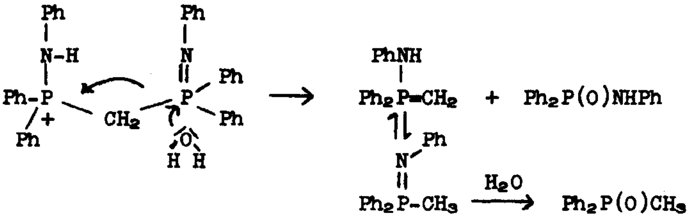
Acidic hydrolysis, on the other hand, would involve initial protonation at the nitrogen atom (Eq. 7).

$$R_3P{=}\overline{N}{-}R \ + \ H^+ \longrightarrow R_3\overset{+}{P}{-}NHR$$

Equation 7.

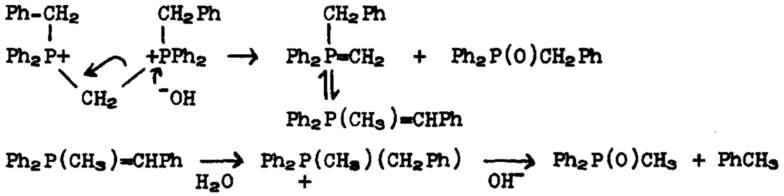
Further protonation, followed by attack of water again, leads to the amine and phosphine oxide.

In the acid catalized hydrolysis, the positive charge on the phosphorus atom is increased while in the basic medium, the reverse is true. Neutralization of this positive charge can occur by donation of an electron pair from an adjacent atom. This can occur in I by cleavage of the bond between the adjacent carbon and the other phosphorus atom. This would be facilitated by nucleophilic attack of water at the latter center (Eq. 8).



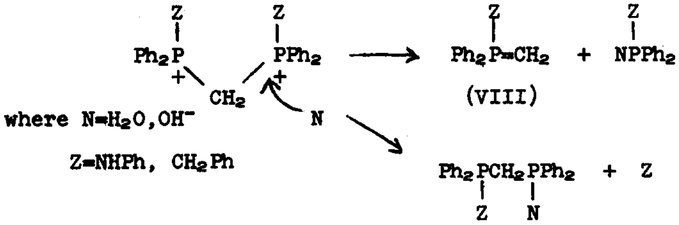
Equation 8.

Diphosphonium salt, IV, however, has positive charges almost completely localized on the phosphorus atoms so that nucleophilic attack of hydroxide ion is sufficient to cause the cleavage to occur (Eq. 9).



Equation 9.

It seems that 3d-2pπ resonance stabilized ylides of type VIII are more easily ejected than both anilide and benzyl anions (Eq. 10).



where N=H$_2$O, OH$^-$

Z=NHPh, CH$_2$Ph

Equation 10.

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