THE ALKALINE DEGRADATION OF PHOSPHINIC ACIDS*

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Horner has observed that fusion of tertiary phosphine oxides with alkali at 200–300°C affords excellent yields of phosphinic acids with loss, as a hydrocarbon, of that group which is most stable as an anion. No mention was made of subsequent decomposition of the phosphinic acids. Two instances have been reported of thermal dephosphonation (240°C) of arylphosphonic acids to the corresponding hydrocarbon and inorganic phosphate in reasonable yields. The corresponding degradation of phosphinic acids does not seem to have been reported. Recently, we had occasion to determine the structures of a number of phosphinic acids and we have found that heating with dry sodium hydroxide to c. 300°C for 30 min results in the complete decomposition of the acid in a very clean reaction. The easily isolated products were of great assistance in determining the structures, and we report these results since the method may prove useful in structure determination of organophosphorus compounds.

Chlorodiphenylmethylphenylphosphinic chloride (I) decomposes smoothly to give benzophenone, benzhydrylphenylphosphinic acid, phenylphosphinic acid, and phenylphosphonic acid.

\[
\text{Ph}_2\text{C-Ph} \rightarrow \text{Ph}_2\text{CO} + \text{Ph}_2\text{CHPO(O)} + \text{PhP(O)} + \text{PhPO(OH)}_2
\]

Presumably this reaction proceeds via the hydroxy acid (VI), which subsequently decomposes in a manner analogous to the decomposition of α-hydroxy phosphonium salts.5

\[
\text{HO}^{-} + \text{H}^{-} + \text{PhC}_2 \rightarrow \text{Ph}^{-} \rightarrow \text{H}_2\text{O} + \text{Ph}_2\text{CO} + \text{PhP}^{-} + \text{O}^{-}
\]

Attack at phosphorus or carbon seems less likely on steric grounds. The anion (VII) is the dianion of phenylphosphonous acid which is a known reducing agent.

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agent in, for example, the thermally induced redox decomposition of monosubstituted phosphinic acids:⁶

\[ 3RP(O)H \rightarrow RPH_2 + 2RPO(OH)_2 \]

This dianion presumably reduces the hydroxy acid to (III). The structure of (III) follows from its analytical and spectral data and its identity with an authentic sample obtained as follows:

\[ \text{PhP(OMe)_2} + \text{Ph}_2\text{CHBr} \rightarrow \text{Ph}_2\text{CHP(O)OMe} + \text{H}^+ \]

The crude reaction product smelled strongly of phenylphosphine, further supporting the proposed pathway. A sample of the \( \alpha \)-hydroxy acid (VI) prepared by hydrolysis of the \( \alpha \)-chloro-acid chloride (I) decomposed in the same way.

A more complex example was the decomposition of the biphosphinic acid (VIII), but in this case the products were even more straightforward. Thus, degradation afforded diphenylmethane and \((p\text{-benzylphenyl})\text{phenylphosphinic acid (IX), which has been identified by oxidation to the benzoyl acid and comparison of this with a synthetic sample.}

\[ \text{PhP(O)-(p-C_6H_4)-CH-P(O)Ph} \rightarrow \text{Ph}_2\text{CH}_2 + \text{PhCH}_2-(p\text{-C}_6\text{H}_4-P(O)Ph} \]

The presence of alkali-sensitive groups leads to much more complex products. Thus, \( \alpha \)-hydroxy-o-chlorobenzylphenylphosphinic acid gave chlorobenzene, o-chlorotoluene, o-chlorobenzyl alcohol, salicylic acid, and phenylphosphonic acid. This complexity is understandable in terms of secondary reactions arising from initially liberated o-chlorobenzaldehyde, but is of little assistance in structure determination.

**Experimental**

*General Procedure*

The acid or derivative (1 mole) was mixed with powdered NaOH (3 mole) and placed in a long-necked bulb, made for the purpose from soda glass tubing. The temperature was raised slowly by heating in a Wood's metal or silicone oil-bath until fusion occurred, which usually happened about the melting point of the acid. When any reaction had subsided the temperature was further raised to 300° and held there for 30 min. The cooled melt was dissolved in water and extracted with benzene which was dried and evaporated to afford the neutral products. Acids were isolated by acidification of the aqueous layer.

**Chlorodiphenylmethylphenylphosphinic Chloride (I; 3.0 g)**

This afforded benzophenone (0.86 g), identified by its infrared spectrum and the m.p. and mixed m.p. of its 2,4-dinitrophenylhydrazone. Acidification of the aqueous layer gave

benzhydrylphenylphosphinic acid (III), m.p. 244-246° from aqueous ethanol (0.99 g), identified by m.p. and mixed m.p. and infrared spectral comparison with an authentic sample (see below).

Concentration of the aqueous mother liquors afforded phenylphosphinic acid (0.21 g). The mother liquors were taken to dryness and extracted with hot ethyl acetate to give traces of phenylphosphonic acid, m.p. 149-152°. These acids were identified by mixed m.p.

Benzhydrylphenylphosphinic Acid (III)

Dimethyl phenylphosphonite (2.3 g) was slowly added to stirred benzhydryl bromide (m.p. 39-40°; 2.6 g; 0.8 mole) at 100° during 0.5 hr and the mixture further heated (2.5 hr). The crude product was hydrolysed by boiling under reflux with aqueous ethanolic 0.5~KOH (12 hr). The cooled hydrolysate was extracted with benzene and the aqueous layer acidified to give benzhydrylphenylphosphinic acid, m.p. 244-246° from aqueous ethanol; 1.7 g (47%) (Found: C, 74.1; H, 5.8; P, 9.9; equiv. wt., 310. Calc. for C₁₉H₁₇O₂P: C, 74.0; H, 5.6; P, 10.05%; equiv. wt., 308). The n.m.r. of the sodium salt in D₂O showed 15 aromatic protons (δ 7.55-7.85) and one benzylic (δ 4.85; J_PCH 18 Hz) proton.

Concentration of the mother liquors afforded the expected by-product, methylphenylphosphinic acid, m.p. 127-128° (0.7 g; 41%), undepressed by an authentic sample.

(p-Phenylphosphonyldiphenylmethylphenylphosphinic Acid (IX)

This bis-acid (0.37 g) gave a neutral product identified as diphenylmethane (0.048 g; 34%) by infrared and gas chromatographic comparison with authentic samples. Purity by the latter technique was at least 95%. The acid fraction yielded (p-benzy1phenyl)phenylphosphinic acid (0.15 g; 59%), m.p. 155-156° from aqueous methanol (Found: C, 73.8; H, 5.7; P, 10.1; equiv. wt., 314. Calc. for C₁₉H₁₇O₂P: C, 74.0; H, 5.6; P, 10.05%; equiv. wt., 308); δ (CDCl₃): 3.9 (-CH₂-; 2H); 13.1 (POH; 1H); 7.05-7.85 (ArH; 14H).

α-Hydroxy-o-chlorobenzylphenylphosphinic Acid

The neutral products (see text) were identified by comparative gas chromatography. The acids were converted to their methyl esters with diazomethane and similarly identified. Phenylphosphonic acid (m.p. 152-154°) was isolated. A high-boiling neutral product was unidentified.