difficulty by the fact that the compounds gave elongated spots and had similar migrations ($R_{Galactose}$-values: methyl β galactoside: 1.74, I ~ 2.0 and II ~ 1.6). After two fractionations on thick filter paper I and II were obtained *ca.* 80 % pure (most of the impurity being the unreacted methyl galactoside). The bulk of the two fractions was reduced, but further fractionation of aliquots of I and II on thick filter paper gave amorphous but chromatographically pure products. From these fractionations the total yield of I and II could be estimated as *ca.* 0.9 % and 0.7 %, respectively.

Characterisation of the oxo-galactosides. The oxo-galactosides gave strong reducing reactions with silver nitrate-sodium ethoxide reagent, characteristic orange-brown colourations with anisidine hydrogen chloride and orange-grey colourations with resorcinol-hydrochloric acid reagent.

The oxo-galactosides dissolved in 70 % aqueous ethanol were reduced by refluxing for 5 h with excess of Raney-nickel [5]. The product was hydrolysed with 0.5 N sulphuric acid for 17 h and the sugars obtained fractionated by chromatography on thick filter papers (solvent C). Talose and galactose only were obtained from I, and gulose and galactose from II, together with small amounts of glucose.

Part of the isolated gulose was reduced with sodium borohydride at pH 9.5. The product obtained, after deionisation, was chromatographically indistinguishable from D-gulitol. The acetylated (acetic anhydride/pyridine) product, after recrystallisation from aqueous ethanol, had the same R_F-value as authentic D-gulitol hexacetate on chromatographing on dimethylsulphoxide impregnated paper using *iso*propyl ether-light petroleum (1:1) as irrigant [6], and m.p. and mixed m.p. 98–99°.

Talose was characterised by paper chromatographic data (*e.g.*, $R_{Galactose}$-values in solvent C: talose: 1.52, gulose: 1.29 and glucose 1.15), and as its methylphenylhydrazone, m.p. 147–149° after recrystallisation from aqueous methanol (literature value [7], 154°).

The authors indebted are to Dr. H. G. Fletcher, Jr., Bethesda, U.S.A., for specimens of D-gulose and D-talose and to Mr. A. Assarsson for skilful assistance.

1. Theander, O. *Acta Chem. Scand.* **11** (1957) 1557.
2. Assarsson, A. and Theander, O. *Acta Chem. Scand.* **12** (1958) 1507.
3. Brimacombe, E., Brimacombe, J. S. and Lindberg, B. *Acta Chem. Scand.* **14** (1960) 2236.
4. Theander, O. *Acta Chem. Scand.* **11** (1957) 717.
5. Karabinos, J. V. and Ballun, A. T. *J. Am. Chem. Soc.* **75** (1953) 4501.
6. Wickberg, B. *Acta Chem. Scand.* **12** (1958) 615.
7. Levene, P. A. and Tipson, R. S. *J. Biol. Chem.* **95** (1931) 631.

Received February 1, 1961.

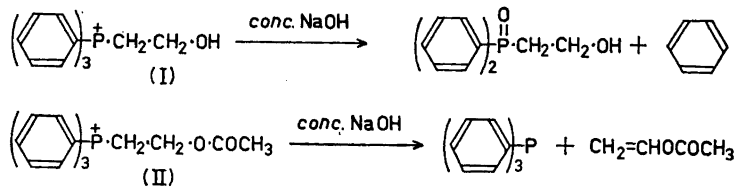
Alkaline Decomposition of Some Quaternary Phosphonium Compounds Containing Oxygen

GUNNAR AKSNES

Chemical Institute, University of Bergen, Bergen, Norway

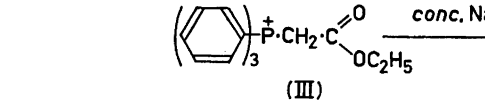
The alkaline decomposition of aliphatic and aromatic quaternary phosphonium compounds with hydroxides and alkoxides results in the formation of hydrocarbons, ethers and phosphine oxides [1-3]. The alkaline decomposition of some oxygen-containing phosphonium compounds is reported in this paper.

The phosphorus analogs of choline(I) and choline acetate (II) were found to decompose in the following ways:



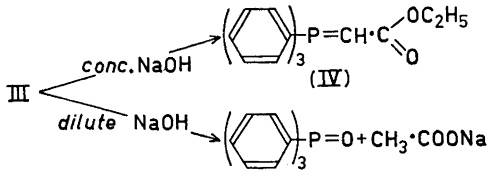
The reason for the different behaviour of (I) and (II) must be due to an easier ionization of the hydrogen in the hydroxyl group of (I) as compared with the hydrogen of the methylene group adjacent to the hydroxyl. A negative charge on the oxygen will thus prevent the attack of hydroxyl ion on the methylene hydrogen and the compound will therefore decompose according to the usual scheme for quaternary phosphonium compounds [1]. In the phosphonocholine acetate (II) the attack of the hydroxyl ion must be easier on the methylene hydrogen than on the carbonyl carbon or phosphorus.

Michaelis and Gimborn [4] and Worrall [5] have claimed that the betaine analogs of phosphorus can be obtained by treatment of the corresponding esters with strong alkali:

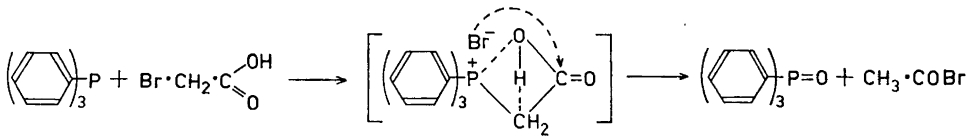


(III)

We have found that the compound isolated by Michaelis and Gimborn [4] does not correspond to the above formula. Its physical and chemical data show that the compound is a phosphorane and its formation is analogous to the formation of phosphoranes described by Ramirez and Dershowitz [6]:



Treatment of (III) with dilute alkali or moist silver oxide in water gives phosphine oxide and acetic acid as already described by Michaelis and Gimborn [4]. The same authors have reported that chloroacetic acid does not react with triphenylphosphine. We have observed that bromoacetic acid reacts with triphenylphosphine but that the reaction does not give the expected betaine hydrobromide. Phosphine oxide and acetyl bromide are formed in nearly quantitative yields:



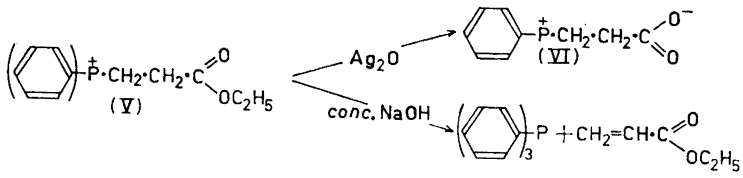
The phosphorus analogs of "propionbetaine" could be prepared from the corresponding ester by the use of moist silver oxide or dilute alkali. Treatment of the ester with concentrated sodium hydroxide gave on the other hand chiefly phosphine and the ester of acrylic acid. The "phosphonopropionbetaine" thus corresponds in its behaviour with the "propionbetaine"[7]. See p. 440.

Experimental. Phosphonocholine chloride (I). 10 g triphenylphosphine was added to 10 ml β-chloroethanol. The mixture was boiled for 2 h. The phosphonocholine chloride (I) crystallized by cooling of the reaction mixture. The compound was recrystallized from absolute ethanol. Yield 10 g; m.p. 233°. (Found: Cl 10.2. Calc. for $C_{20}H_{20}POCl$: Cl 10.4.)

Decomposition of (I) with conc. sodium hydroxide. 6 g of (I) was dissolved in 4 ml water. To the solution was added 5 ml conc. sodium hydroxide. Upon distillation 1.3 g benzene was recovered from the distillate (87 % of theory). The benzene was characterized as *m*-dinitrobenzene, m.p. 89°. Mixed melting point with pure *m*-dinitrobenzene showed no depression.

Acetylphosphonocholine chloride (II). 10 g triphenylphosphine and 6 g β-chloroethylacetate was boiled under reflux for 4 h. Upon diluting the reaction mixture with 5 ml acetone the chloride crystallized. The compound recrystallized from acetone-alcohol gave small needles, m.p. 287°. (Found: C 68.5; H 5.7. Calc. for $C_{22}H_{22}PO_2Cl$: C 69.2; H 5.6.)

Decomposition of (II) with conc. sodium hydroxide gave 95 % yield of triphenylphos-

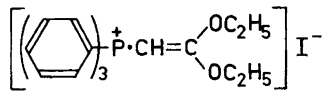


phine, m.p. 79–80°. Its infrared spectrum was identical with that of an authentic specimen.

Ethylester of phosphonobetaine bromide (III). 5 g bromoacetic acid ethylester was added to 10 g of triphenylphosphine. The mixture was heated to 80° and kept there for 5 min. The crystalline mass which separated upon cooling was recrystallized from alcohol-ether, m.p. 157°. (Found: Br 18.7. Calc. for $C_{22}H_{22}PO_2Br$: Br 18.7.)

Preparation of the phosphorane (IV). 4 g of (III) was dissolved in 4 ml water. Five ml cold conc. sodium hydroxide was added. The thick oil which immediately separated was extracted with ether. Upon evaporation of the ether the phosphorane (IV) solidified. It was crystallized from ether, m.p. 126–127° (Michaelis and Gimborn [4] 124–126°). (Found: C 75.7; H 6.06; P 9.15. Calc. for $C_{22}H_{21}PO_2$: C 76.2; H 6.05; P 8.79.)

Treatment of (IV) with HBr in ether solution gave a crystalline compound, m.p. 157° the infrared spectrum of which was identical with that of (III). Treatment of (IV) with excess ethyl iodide in alcohol gave a crystalline compound, m.p. 162° presumably:



(Found: I 25.0. Calc. for $C_{24}H_{26}PO_2I$: I 25.1.

Ethylester of "phosphonopropionbetaine bromide" (V). 7 g β-bromopropionic acid ethylester was added to 9 g triphenylphosphine. The mixture was heated to 100° for 5 min. The product was washed with ether and acetone and recrystallized from 50 % water-alcohol mixture; small needles, m.p. 126°. (Found: Br 18.0. Calc. for $C_{23}H_{24}PO_2Br$: Br 18.0.)

Treatment of (V) with conc. sodium hydroxide gave triphenylphosphine, m.p. 79–80°. Its infrared spectrum was identical with that of an authentic specimen.

"Phosphonopropionbetaine" (VI). 2 g of (V) was dissolved in 50 ml of water. The solution was shaken with 3 g moist silver oxide. The silver bromide was filtered off and the solution concentrated to 5 ml in a vacuum. A small amount of triphenylphosphine formed during the hydrolysis was removed by shaking with 10 ml of ether. The phosphonopropionbetaine (VI) crystallizes from a concentrated water solution in white plates. The compound was dried at 140° for 1 h, m.p. 186°. (Found: C 75.2; H 5.7; P 9.5. Calc. for $C_{21}H_{19}PO_2$: C 74.5; H 5.5; P 9.0.)

The betaine (VI) was also formed on hydrolysis of (V) with hydrobromic acid followed by treatment of the betaine hydrobromide with moist silver oxide.

The reaction between triphenylphosphine and bromoacetic acid. 2.5 g bromoacetic acid and 5 g triphenylphosphine (1 equiv.) was heated to approximately 80°. The reaction started with evolution of acetyl bromide (characterized as ethyl acetate). An almost quantitative amount of triphenylphosphine oxide, m.p. 152° was recovered from the residue. Its infrared spectrum was identical with that of an authentic specimen of triphenylphosphine oxide.

My sincere thanks are due to the *Norwegian Defence Research Establishment* for financial support and to Senior Research Chemist Arnljot Nærland at the same institute for recording of the infrared spectra.

1. Fenton, G. W. and Ingold, C. K. *J. Chem. Soc.* **1929** 2342.
2. Hey, L. and Ingold, C. K. *J. Chem. Soc.* **1933** 531.
3. Grayson, M. and Keough, P. T. *J. Am. Chem. Soc.* **82** (1960) 3919.
4. Michaelis, A. and Gimborn, H. V. *Ber.* **27** (1894) 272.
5. Worrall, D. E. *J. Am. Chem. Soc.* **52** (1930) 2933.
6. Ramirez, F. and Dershowitz, S. *J. Org. Chem.* **22** (1957) 41.
7. Aksnes, G. and Prue, J. E. *J. Chem. Soc.* **1959** 103.

Received January 23, 1961.