1130. *The Action of Bases on 2-Hydroxyethyltriphenylphosphonium Iodide*

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The action of alcoholic solutions of sodium alkoxides on 2-hydroxyethyltriphenylphosphonium iodide has been shown to give 2-alkoxyethyldiphenylphosphine oxides. The reaction of the iodide with sodium hydroxide has also been investigated.

It has been found that 2-hydroxyethyltriphenylphosphonium iodide, when heated with alcoholic sodium alkoxide, gives the 2-alkoxyethyldiphenylphosphine oxide (I; R = Me, Et, Bu^t, or $PhCH_2$) in 39—96% yield. The products showed $\nu_{max.}$ 1180 ± 10 cm.$^{-1}$,

$$Ph_3\overset{+}{P}\cdot CH_2\cdot CH_2\cdot OH\ RO^- \longrightarrow Ph_2P(O)\cdot CH_2\cdot CH_2\cdot OR\ (I) + PhH$$

indicative of the P=O group,[1] and all were oxidised to diphenylphosphinic acid. The methyl and ethyl compounds were monomeric in camphor. The ethyl compound was identical with 2-ethoxyethyldiphenylphosphine oxide.

These reactions may be interpreted as an initial loss of a proton from the 2-hydroxyethyltriphenylphosphonium ion to give (IIa) or (IIb), followed by further attack by an alkoxide anion to give the 2-alkoxyethyldiphenylphosphine oxide (III) and a phenyl anion, the latter attacking the solvent to form benzene and an alkoxide anion.

$$RO^- + Ph_3\overset{+}{P}\cdot CH_2\cdot CH_2\cdot OH \rightleftharpoons ROH + Ph_3\overset{+}{P}\cdot CH_2\cdot CH_2\cdot O^- \rightleftharpoons Ph_3P\!\!<\!\!\begin{matrix}CH_2\\ |\\ O\!-\!CH_2\end{matrix}$$

(IIa) (IIb)

$$Ph_2P(Ph)\!-\!CH_2\!-\!CH_2\!-\!O\!-\!OR \longrightarrow Ph_2P(O)\cdot CH_2\cdot CH_2\cdot OR\ (III) + Ph^-$$

$$Ph^- + ROH \longrightarrow PhH + RO^-$$

[1] L. W. Daasch and D. C. Smith, *Analyt. Chem.*, 1951, **23**, 853.

Experimental

Chromatographic Alumina.—Alumina (Spence, grade H) (2 kg.) was shaken with 10% aqueous acetic acid (100 ml.) for 20 min.

2-Hydroxyethyltriphenylphosphonium Iodide.—Triphenylphosphine (262 g.), 2-iodoethanol (172 g.), and benzene (2 l.) were refluxed together for 10 hr., cooled, and filtered, to give 2-hydroxyethyltriphenylphosphonium iodide (410 g., 95%), needles (from acetone), m. p. 187° (lit.,[2] 185—186°) (Found: C, 55·4; H, 4·8; I, 29·4; P, 7·1. Calc. for $C_{20}H_{20}IOP$: C, 55·3; H, 4·7; I, 29·3; P, 7·1%).

2-Methoxyethyldiphenylphosphine Oxide.—2-Hydroxyethyltriphenylphosphonium iodide (21·7 g.) was added to a solution of sodium (1·15 g.) in methanol (250 ml.). The mixture was refluxed for 15 min. and evaporated under reduced pressure at 25°, to give an oil, which was extracted with boiling ether (10 × 200 ml.). Evaporation of the extracts gave an oil which solidified, on standing *in vacuo* over phosphorus pentoxide, to waxy crystals of *2-methoxyethyldiphenylphosphine oxide* (11·8 g., 91%), m. p. 50—52° (Found: C, 69·6; H, 6·0; P, 11·4%; *M*, 262. $C_{15}H_{17}O_2P$ requires C, 69·3; H, 6·6; P, 11·9%; *M*, 260).

A similar reaction of the iodide (21·7 g.) with a solution of sodium (1·15 g.) in ethanol (250 ml.) gave 2-ethoxyethyldiphenylphosphine oxide (13·1 g., 96%), prisms (from ether), m. p. 69—70° (lit.,[3] 69—71°) (Found: C, 69·8; H, 6·8; P, 11·0; OEt, 16·4%; *M*, 253. Calc. for $C_{16}H_{19}O_2P$: C, 70·0; H, 7·0; P, 11·3; OEt, 16·4%; *M*, 274).

A similar reaction of the iodide (21·7 g.) with a solution of sodium (1·15 g.) in t-butyl alcohol (100 ml.) gave *2-t-butoxyethyldiphenylphosphine oxide* (10·9 g., 72%), needles (from ether), m. p. 90·5—92° (Found: C, 72·3; H, 7·5; P, 10·0. $C_{16}H_{23}O_2P$ requires C, 71·5; H, 7·7; P, 10·2%).

A similar reaction of the iodide (21·7 g.) with a solution of sodium (1·15 g.) in benzyl alcohol (125 ml.) gave *2-benzyloxyethyldiphenylphosphine oxide* (6·6 g., 39%), needles (from ether), m. p. 82·0—82·5° (Found: C, 75·0; H, 6·1; P, 9·2. $C_{21}H_{21}O_2P$ requires C, 75·0; H, 6·3; P, 9·2%).

Reaction of 2-Hydroxyethyltriphenylphosphonium Iodide with Aqueous Potassium Hydroxide Solution.—2-Hydroxyethyltriphenylphosphonium iodide (43·4 g.), water (100 ml.), and potassium hydroxide (5 g.) were slowly distilled together for 30 min. under a stream of nitrogen. The gas from the apparatus was passed through bromine water to absorb ethylene. The excess of bromine was destroyed with potassium carbonate, and the ethylene dibromide was removed with a pipette and converted into ethane-1,2-bis(isothiouronium) picrate (1·67 g., equivalent to 2·6% of ethylene). The upper layer of the distillate from the reaction was separated and dried ($MgSO_4$), to give benzene, n_D^{20} 1·5064 (6·5 g., 83·4%). The residue in the distillation flask was cooled, diluted with water (300 ml.), and extracted with chloroform (2 × 250 ml.). The extracts were dried ($MgSO_4$) and evaporated under reduced pressure at 40°, to give an oil (28·3 g.) which was chromatographed on alumina (900 g.). Elution with ether, evaporation of the eluate, and recrystallisation of the residue from ether gave triphenylphosphine oxide (2·1 g., 7·6%), m. p. 152—153°, mixed m. p. 152—154°. Further elution with methanol (4 l.) gave 2-hydroxyethyldiphenylphosphine oxide (20·65 g., 84%), plates (from ether), m. p. 94·5—95·5° (lit.,[4] 111—114°) (Found: C, 68·6; H, 6·3; P, 12·6. Calc. for $C_{14}H_{15}O_2P$: C, 68·3; H, 6·2; P, 12·6%).

Synthesis of 2-Ethoxyethyldiphenylphosphine Oxide.—2-Ethoxyethyldiphenylphosphine (prepared from sodiodiphenylphosphine and 2-bromoethyl ethyl ether [5]) was oxidised with alkaline hydrogen peroxide in aqueous acetone, to give 2-ethoxyethyldiphenylphosphine oxide, m. p. and mixed m. p. with material from 2-hydroxyethyltriphenylphosphonium iodide 66—68°.

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[2] A. Michaelis and H. von Gimborn, *Ber.*, 1894, **27**, 272.
[3] M. I. Kabachnik, T. Ya. Medved, Yu. M. Polikarpov, and K. S. Yudina, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1962, 1584.
[4] K. Issleib and H.-M. Möbius, *Chem. Ber.*, 1961, **94**, 102.
[5] W. Kuchen and H. Buchwald, *Chem. Ber.*, 1959, **92**, 227.