The Thermal Decomposition of n-Alkyltriarylphosphonium Alkoxides

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Tri-p-deuteriophenylpropylphosphonium bromide and sodium methoxide at 260° give p-deuterioanisole free from other isomers and di-p-deuteriophenylpropylphosphine. Similarly, tri-m-chlorophenylpropylphosphonium bromide gives pure m-chloroanisole.

We previously showed ¹ that when n-alkyltriphenylphosphonium halides are heated with sodium alkoxides at $\sim 260^{\circ}$ the corresponding n-alkyldiphenylphosphine and alkyl phenyl ether are produced.

 $Ph_{3}RP^{+} - OR' \longrightarrow Ph_{2}PR + PhOR'$

However, we did not investigate whether the alkoxygroup of the ether occupied the position on the aromatic ring originally attached to phosphorus. Several of the mechanisms which can be suggested for the reaction predict otherwise, and this possibility has now been explored.

When any of the propyltritolylphosphonium bromides was heated at 260° with sodium methoxide or ethoxide, none of the corresponding alkyl tolyl ether could be detected. Tri-p-deuteriophenylphosphine was therefore prepared from *p*-deuteriophenylmagnesium bromide and phosphorus trichloride and converted into the propylphosphonium bromide. This with sodium methoxide gave p-deuterioanisole and di-p-deuteriophenylpropylphosphine identified as an oxide, an authentic sample of which was prepared by alkaline hydrolysis of the original salt. The p-deuterioanisole was shown to be free from ortho- and meta-isomers by comparison of the i.r. and n.m.r. spectra with those of authentic samples of the three isomers. In particular, the i.r. spectra of the isomers are very different. Subsequently tri-mchlorophenylpropylphosphonium bromide and sodium methoxide at 260° were found to give m-chloroanisole free from other isomers.

These results eliminate mechanisms for the reactions which involve attack of alkoxide anion *ortho* to the phosphorus, or which involve benzyne formation. Together with previous evidence ¹ they suggest collapse of a quinquevalent intermediate (I) in which negative charge accumulates on the migrating aryl group in the transition state.

EXPERIMENTAL

Tri-p-deuteriophenylpropylphosphonium Bromide.—Phosphorus trichloride $(9\cdot 0 \text{ g.})$ in ether (50 ml.) was added slowly to a stirred Grignard reagent prepared from magnesium $(8\cdot 0 \text{ g.})$ and p-deuteriobromobenzene (52 g.) in ether (200 ml.) cooled in ice, and the resulting suspension stirred at room temperature for 1 hr. 2N-Hydrochloric acid

 \dagger Analytical methods in which water is estimated coulometrically do not differentiate between deuterium and hydrogen, and the result is calculated assuming that all water produced on combustion is H₂O. (400 ml.) was slowly added and the ethereal solution washed with water, dried, and evaporated. The residue was kept at 80°/0·3 mm. for $\frac{1}{2}$ hr. and crystallised from ethanol to give tri-p-deuteriophenylphosphine (69%), m. p. 80—81°, $\nu_{\rm max.}$ 855vs cm.⁻¹. The phosphine (10 g.) was refluxed with 1-bromopropane

The phosphine (10 g.) was refluxed with 1-bromopropane (50 ml.) for 6 hr. to give the *phosphonium bromide* (89%), m. p. 240—241° (from chloroform-ethyl acetate), triplet (3H) at τ 8.76, multiplets (2 × 2H) centred on 6.24 and 8.2 and a multiplet (12H) at 2.2 (Found: C, 64.8; H, 5.5. C₂₁H₁₉BrD₃P requires C, 64.95; H, 5.65% †). Alkaline hydrolysis gave *di*-p-*deuteriophenylpropylphosphine oxide*, m. p. 100—101° (from ethyl acetate-light petroleum), v_{max} . 1180 cm.⁻¹ (Found: C, 73.0; H, 7.0. C₁₅H₁₅D₂OP requires C, 73.2; H, 6.9%). The aliphatic protons from τ 7.4 to 9.1 and the aromatic protons from 2.0 to 2.7 were in the ratio 7: 8.

Deuterioanisoles.—These were prepared by the addition of deuterium oxide to cooled solutions of anisylmagnesium bromides in ether. *p*-Deuterioanisole, b. p. 150—152°, v_{max} 1300s, 845s, 782w, 755m, 720w, and 690w cm.⁻¹, singlet (3H) at τ 6.55 and an AB-system (4H) centred on 2.95. *m*-Deuterioanisole, b. p. 36°/1 mm., v_{max} 1290s, 880m, 790m, 760s, and 680s cm.⁻¹, singlet (3H) at τ 6.56 and a multiplet (4H) centred on 3. *o*-Deuterioanisole, b. p. 149—150°, v_{max} 1310s, 1285s, 1125m, 780m, 760s, and 690w cm.⁻¹, singlet (3H) at τ 6.55 and a multiplet (4H) centred on 3.1. All the deuterioanisoles showed strong absorption around 1250 and 1150 cm.⁻¹.

The Reaction of Tri-p-deuteriophenylpropylphosphonium Bromide with Sodium Methoxide.—A mixture of the phosphonium salt ($23 \cdot 5$ g.) and sodium methoxide (from $2 \cdot 3$ g. of sodium) was kept at 260° for 2 hr. The distillate was redistilled to give *p*-deuterioanisole (1.0 g.), b. p. $30-32^{\circ}/$ 0.5 mm., having i.r. and n.m.r. spectra identical with those of an authentic sample. Distillation of the residue gave di-*p*-deuteriophenylpropylphosphine (10.0 g.), b. p. 120— $125^{\circ}/0.2$ mm., characterised as the oxide, m. p. 100—101°, having i.r. and n.m.r. spectra identical with those of an authentic sample.

The Reaction of Tri-m-chlorophenylpropylphosphonium Bromide with Sodium Methoxide.—Tri-m-chlorophenylphosphine (7.3 g.) and 1-bromopropane (50 ml.) were heated under reflux for 6 hr. and filtered, to give the phosphonium bromide, m. p. 236—237° (from chloroform-ethyl acetate) (Found: C, 51.7; H, 4.0; Cl, 21.9. $C_{21}H_{19}BrCl_3P$ requires C, 51.6; H, 3.9; Cl, 21.8%). A mixture of the salt (12 g.) and sodium methoxide (from 2.3 g. of sodium) was kept at 260° for 2 hr. Distillation then gave m-chloroanisole (0.8 g.), b. p. 38°/0.2 mm., having i.r. and n.m.r. spectra identical with those of an authentic sample.

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¹ C. T. Eyles and S. Trippett, J. Chem. Soc. (C), 1966, 67.