Reactions of Sodium Hydride with ω-Hydroxyalkyl-phosphonium, -arsonium and -ammonium Salts

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The reaction of sodium hydride with ω -hydroxyalkyltriphenylphosphonium salts $Ph_3P(CH_2)_nOH X^-$ (I) has been investigated. The salt (I: n = 1, X = I) gave triphenylphosphine and formaldehyde. The salt (I: n = 2, X = I) gave triphenylphosphine oxide and ethylene. The salts (I: n = 4 or 5, X = I or CI) could not be prepared. The salt (I: n = 6, X = I) gave mainly triphenylphosphine and hex-5-en-1-ol with some 6-hydroxyhexyldiphenylphosphine, 6-phenoxyhexyldiphenylphosphine, and 6-phenoxyhexyldiphenylphosphorae. The salt (I: n = 1, X = B) gave 11-phenoxyundecyldiphenylphosphine, 11-hydroxyundecyldiphenylphosphine, and 11-phenoxyundecyldiphenylphosphine, 31-hydroxypropyltriphenylphosphonium iodide gave triphenylphosphine oxide and allyl alcohol.

Similar reactions were carried out with ω -hydroxyalkyltriphenylarsonium salts. Ph₃As(CH₂)_nOH X⁻ (XIV). The salt (XIV; n = 6, X = I) gave triphenylarsine and hex-5-en-1-ol. The salt (XIV; n = 11 X = Br) gave mainly triphenylarsine and undec-10-en-1-ol.

Similar reactions were carried out with ω -hydroxyalkyldimethylphenylammonium salts, Ph(Me)₂N(CH₂)_nOH X⁻(XV). The salt (XV; n = 3, X = I) gave dimethylaniline and allyl alcohol. The salt (XV; n = 11, X = Br) gave 11-methoxyundecylmethylphenylamine.

Four cases of the action of bases on hydroxyalkylphosphonium salts have been reported; ¹⁻³ only one of these ³ dealt with the action of sodium hydride which with 3-hydroxypropyltriphenylphosphonium iodide gave 2,2,2-triphenyl-1,2-oxaphosph(v)olan. This paper deals with the action of sodium hydride on a series of ω -hydroxyalkyltriphenylphosphonium salts (I; n = 1, 2, 4, 5,6, 11).

$$\begin{array}{ccc} \operatorname{Ph}_{3}\overset{-}{\mathrm{P}}(\mathrm{CH}_{2})_{n}\mathrm{OH} \ \mathrm{X}^{-} & \operatorname{Ph}_{3}\overset{+}{\mathrm{P}}(\mathrm{CH}_{2})_{n}\mathrm{O}^{-} \\ (\mathrm{I}) & (\mathrm{III}) \end{array}$$

Hydroxymethyltriphenylphosphonium iodide (I; n = 1, X = I) reacted with sodium hydride to give triphenylphosphine and formaldehdye (identified as the dimedone derivative) via the betaine (II):

$$Ph_3 \stackrel{+}{P}CH_2O^- \longrightarrow Ph_3P + CH_2O$$
(II)

2-Hydroxyethyltriphenylphosphonium iodide (I; n = 2, X = I) reacted with sodium hydride to give triphenylphosphine oxide and ethylene [estimated as ethane-1,2bis(isothiouronium)picrate] via the betaine (III; n = 2) similar to that involved in the Wittig reaction.⁴ Attempts to prepare 4-hydroxybutyl- and 5-hydroxypentyl-triphenylphosphonium salts were unsuccessful. Reaction of triphenylphosphine with the chloro-alcohols gave tetrahydrofuran and tetrahydropyran respectively by internal nucleophilic substitution. Attempts to convert the chloro-alcohols into iodo-alcohols with sodium iodide in acetone gave $\alpha\omega$ -di-iodoparaffins.

Conversion of 6-chlorohexanol, using sodium iodide in acetone, to 6-iodohexanol yielded a product with 1,6-diiodohexane (ca. 6%) as an impurity, and thus the reaction with triphenylphosphine gave a mixture of 6-hydroxyhexyltriphenylphosphonium iodide (I; n = 6, X = I) with some hexane-1,6-bis(triphenylphosphonium)iodide. The phosphonium salts, after separation, were hydrolysed to the corresponding phosphine oxides with aqueous sodium hydroxide.

6-Hydroxyhexyltriphenylphosphonium iodide (I; n = 6, X = I) reacted with sodium hydride in a melt to give a mixture containing products derived from the betaine (III; n = 6) formed initially. The chief products were hex-5-en-1-ol (29%; identified as the phenylurethane) and triphenylphosphine (32%), possibly formed by an internal cyclic elimination:

² A. R. Hands and A. J. H. Mercer, *J. Chem. Soc.*, 1965, 6055. ³ A. R. Hands and A. J. H. Mercer, *J. Chem. Soc.* (C), 1967, 1099.

¹ A. Hoffmann, J. Amer. Chem. Soc., 1921, **43**, 1684; 1930, **52**, 2995; M. Grayson, J. Amer. Chem. Soc., 1963, **85**, 79; G. Aksnes, Acta Chem. Scand., 1961, **15**, 438.

⁴ G. Wittig and U. Schöllkopf, Chem. Ber., 1954, 87, 1318.

$$\begin{array}{c} H_{2} \\ Ph_{3}P - CH_{2} \overline{C}CH \\ H \\ H \\ CH_{2} \\$$

The betaine also underwent an intermolecular nucleophilic attack to give 6-phenoxyhexyltriphenylphosphonium (IV; n = 6) and 6-oxohexyldiphenylphosphine (V; n = 6) ions. The former reacted with another molecule of base to give the phosphorane (VI; n = 6), identified by its conversion by acetone to triphenylphosphine oxide (19%) and 7-methyl-1-phenoxyoct-6-ene (VII; n = 6; 9%) in a Wittig reaction.



The cation (IV; n = 6) could also react with the anion (V; n = 6) to give 6-phenoxyhexyldiphenylphosphine (VIII; n = 6) (3%). An alternative reaction leading to the same product is the attack of the anion (V; n = 6) on the original betaine (III; n = 6).

Attack of a hydride anion on the betaine (III; n = 6) could also lead to a pentacovalent phosphorus intermediate (X; n = 6) which could break down to form an anion (V; n = 6) and benzene.

After addition of water to the reaction mixture, 6-hydroxyhexyldiphenylphosphine (IX; n = 6) (14%) was isolated due to protonation of the anion (V; n = 6).

6-Phenoxyhexyldiphenylphosphine (VIII; n = 6) was identified by oxidation to the phosphine oxide (XI; n = 6) which was synthesised independently. 6-Hydroxyhexyldiphenylphosphine (IX; n = 6) was identified by

$$\begin{array}{ccc} \operatorname{Ph}_{2}\mathbf{P}(\mathcal{O})(\mathcal{CH}_{2})_{n}\mathcal{O}\mathcal{P}h & \operatorname{Ph}_{2}(\mathcal{M}e)\overset{+}{\mathbf{P}}(\mathcal{CH}_{2})_{n}\mathcal{X} & \mathbf{I}^{-1}\\ (\mathcal{X}\mathcal{I}) & (\mathcal{X}\mathcal{I}\mathcal{I}) \\ & & \mathcal{P}h(\mathcal{M}e)\mathbf{P}(\mathcal{O})(\mathcal{CH}_{2})_{n}\mathcal{X} \\ & & (\mathcal{X}\mathcal{I}\mathcal{I}\mathcal{I}) \end{array}$$

quaternisation with methyl iodide to the phosphonium salt (XII; n = 6, X = OH) which was hydrolysed to 6-hydroxyhexylmethylphenylphosphine oxide (XIII; n = 6, X = OH). 7-Methyl-1-phenoxyoct-6-ene (VII; n = 6) was identified from its n.m.r. and mass spectra and by independent synthesis.

11-Hydroxyundecyltriphenylphosphonium bromide (I; n = 11, X = Br) reacted with sodium hydride in a melt to give a mixture of 11-phenoxyundecylidenetriphenylphosphorane [(VI; n = 11) identified by its conversion by acetone to triphenylphosphine oxide (37%) and 12methyl-1-phenoxytridec-11-ene (VII; n = 11) (25%)], 11-phenoxyundecyldiphenylphosphine (VIII; n = 11, 22%) and 11-hydroxyundecyldiphenylphosphine (IX; n = 11 (15%). The formation of these products can be rationalised by the initial formation of a betaine (III; n = 11) (cf. the 6-hydroxyhexyl salt, in the Scheme), which is unlikely to break down by an internal cyclic elimination as this would involve a twelve-membered cyclic-transition state. The alternative elimination by abstraction by hydride ion of a proton from the carbon β to phosphorus may be disfavoured by the alkoxide anion.

11-Phenoxyundecyldiphenylphosphine (VIII; n =11) was identified by oxidation to the phosphine oxide (XI; n = 11) which had been prepared independently. The structure of the phosphine (VIII; n = 11) was confirmed by methylation to the phosphonium salt (XII; n = 11, X = OPh) which was hydrolysed to the phosphine oxide (XIII; n = 11, X = OPh). 11-Hydroxyundecyldiphenylphosphine (IX; n = 11) was identified by quaternisation with methyl iodide to the phosphonium salt (XII; n = 11, X = OH) which was hydrolysed to the phosphine oxide (XIII; n = 11, X = OH). 12-Methyl-1-phenoxytridec-11-ene (VII; n = 11) was identified from its n.m.r. and mass spectra and by independent synthesis. Mass spectrometry showed that there were impurities of 1-phenoxyundecane and 1-phenoxyundec-10-ene (m/e 248 and 246, respectively) in the tridecene $(m/e\ 288)$. Both compounds were synthesised independently and standard mixtures with 12-methyl-1-phenoxytridec-11-ene were made for comparative g.l.c. to estimate the quantities of these impurities (1.8% and 3.0% respectively). 1-Phenoxyundecane was formed by nucleophilic attack of hydride ion on the carbon atom α to phosphorus and 1-phenoxyundec-10-ene by abstraction of a proton by hydride ion from the carbon atom β to phosphorus.

The relative ease with which the various reactions of sodium hydride with hydroxyalkylphosphonium salts take place was determined in the case of 2,3-dihydroxypropyltriphenylphosphonium iodide, which was shown to react preferentially to give triphenylphosphine oxide and allyl alcohol, no oxa-phosph(v)olan being formed. The iodide reacted with aqueous sodium hydroxide to give 2,3-dihydroxypropyldiphenylphosphine oxide (17%), formed by the normal breakdown of phosphonium hydroxides,⁵ triphenylphosphine oxide (14%), allyl alcohol (7%), and triphenylphosphine (22%). Tri-⁵ G. W. Fenton and C. K. Ingold, J. Chem. Soc., 1929, 2342. phenylphosphine oxide and allyl alcohol could be formed by initial abstraction of the proton from the 2-hydroxygroup followed by breakdown of the resulting betaine in the Wittig manner.⁴ Abstraction of the proton by hydroxide ion on the carbon atom β to phosphorus followed by elimination of triphenylphosphine would give hydroxyacetone which would polymerise under the basic conditions.

The reaction of sodium hydride with two ω -hydroxyalkylarsonium salts was investigated. The reaction with 6-hydroxyhexyltriphenylarsonium iodide (XIV; n = 6, X = I) gave triphenylarsine (89%) and hex-5en-1-ol (61%) via the betaine Ph₃As(CH₂)₆O⁻ which broke down by an internal cyclic elimination (cf. the phosphorus analogue). This mechanism predominates for arsenic over the alternative nucleophilic attack seen with phosphorus, because triphenylarsine is a better leaving group than triphenylphosphine.

$$\frac{Ph_{3}As[CH_{2}]_{n}OH X}{(XIV)} Ph(Me)_{2}N[CH_{2}]_{n}OH X}$$

11-Hydroxyundecyltriphenylarsonium bromide (XIV; n = 11, X = Br) and sodium hydride on being heated together gave mainly triphenylarsine (30%) and undec-10-en-1-ol (29%). This was formed by abstraction of a proton by hydride ion from the carbon atom β to arsenic followed by elimination of triphenylarsine:

$$PhAs - CH_2 CH [CH_2], OH \rightarrow PhAs + CH_2 = CH [CH_2], OH$$

 $H \cap H$ + H₂

In addition, 11-phenoxyundecyldiphenylarsine (ca. 20%), which could not be separated from triphenylarsine by repeated chromatography on alumina, and 11-hydroxyundecyldiphenylarsine (25%) were formed by mechanisms similar to those postulated for the corresponding phosphonium salt. The approximate composition of the mixture of triphenylarsine and 11-phenoxyundecyldiphenylarsine was determined by n.m.r. and mass spectrometry.

Two reactions of sodium hydride with ω -hydroxyalkylammonium salts were investigated. 3-Hydroxypropyldimethylphenylammonium iodide (XV; n = 3, X = I) gave dimethylaniline (83%) and allyl alcohol (72%). This reaction is interpreted either as a breakdown of the initial betaine by an internal elimination:

$$Ph(Me)_2 N - CH_2 - CH - CH_2 \rightarrow PhNMe_2 + CH_2:CHCH_2OH$$

 $H = \int_{H}^{H} \int_{O}^{-1} O$

or by a normal intermolecular elimination.

11-Hydroxyundecyldimethylphenylammonium bromide (XV; n = 11, X = Br) reacted with sodium hydride to give 11-methoxyundecylmethylphenylamine 4 N (XVI; 71%) which was identified by conversion to the methiodide. This reaction is interpreted as intermolecular nucleophilic attack between two molecules of the initially formed betaine to give a cation (XVII) and an anion (XVIII) which react to give the amine (XVI):

$$\begin{array}{c} 2Ph(Me)_{2}\overset{+}{N}[CH_{2}]_{11}O^{-} \xrightarrow{} Ph(Me)N[CH_{2}]_{11}O^{-} + Ph(Me)_{2}\overset{+}{N}[CH_{2}]_{11}OMe \\ (XVIII) & (XVII) \\ Ph(Me)N[CH_{2}]_{11}OMe \\ (XVI) \end{array}$$

EXPERIMENTAL

N.m.r. spectra were recorded in deuteriochloroform with tetramethylsilane as internal standard on a Perkin-Elmer R10 spectrometer. I.r. spectra were recorded (Nujol mulls) with a Perkin-Elmer Infracord 137 spectrophotometer, and mass spectra with an A.E.I. MS9 mass spectrometer. Gas chromatograms were obtained using a Pye Argon gas chromatograph with a 2.5% SE10 silicone column at 135°. 'Evaporation ' means evaporation under reduced pressure at 35°.

Chromatographic Alumina.—Alumina (Spence type H; 2 kg.) was shaken with aqueous acetic acid (10% w/v; 100 ml.) for 20 min.

Reaction of Hydroxymethyltriphenylphosphonium Iodide with Sodium Hydride.—The iodide (21.0 g.; prepared by the method of Horner and Hoffmann ⁶), sodium hydride (1.2 g.), and tetrahydrofuran (150 ml.) were heated under reflux for 1 hr. under a stream of nitrogen. The gas was passed through an aqueous solution of dimedone (50% w/v; 30 ml.) to give a precipitate of formaldehyde dimedone (10.3 g., equivalent to 71% formaldehyde).

The residue in the flask was evaporated to dryness and extracted with ether $(2 \times 100 \text{ ml.})$ and the extracts were evaporated to give triphenylphosphine (13.2 g., 100%), m.p. and mixed m.p. $80-81^{\circ}$.

Reaction of 2-Hydroxyethyltriphenylphosphonium Iodide with Sodium Hydride.—The iodide (21.7 g.; prepared by the method of Hands and Mercer ²), sodium hydride (1.2 g.), and tetrahydrofuran (100 ml.) were heated under reflux for 6 hr. under a stream of nitrogen. The gas was passed through bromine water to give ethylene dibromide which was converted into ethane-1,2-bis(isothiouronium)picrate (13.0 g., equivalent to 41% ethylene), m.p. and mixed m.p. 260°.

The residue in the flask was evaporated to give a solid which was partitioned between chloroform (200 ml.) and water (200 ml.). The chloroform layer was separated, dried (MgSO₄), evaporated, and the residue was recrystallised from acetone to give triphenylphosphine oxide (13·2 g., 95%), m.p. and mixed m.p. $154-155^{\circ}$.

Reaction of 4-Chlorobutan-1-ol with Triphenylphosphine. 4-Chlorobutan-1-ol (3.0 g.) and triphenylphosphine (7.3 g.) were heated at ca. 150° (bath) for 15 min. Tetrahydrofuran (0.90 g., 45%), b.p. 66—72° (lit.,⁷ 64—65°), $n_{\rm D}^{19}$ 1.4081 (lit.,⁷ $n_{\rm D}^{21}$ 1.4076), identified by i.r. spectroscopy, distilled from the mixture. The cooled residue was extracted with ether (4 × 200 ml.) and the extracts were evaporated to give unchanged triphenylphosphine (6.9 g., 95%), m.p. and mixed m.p. 81—82°.

⁶ L. Horner and H. Hoffmann, Chem. Ber., 1958, 91, 52.

7 A. Bourguigon, Bull. Soc. chim. belges, 1908, 22, 87.

A similar reaction between triphenylphosphine (33 g.) and 5-chloropentan-1-ol gave tetrahydropyran (2.5 g., 24%), b.p. 88—89° (lit.,⁸ 88°), $n_{\rm D}^{18}$ 1.4200 (lit.,⁸ $n_{\rm D}^{18-5}$ 1.4195).

6-Iodohexan-1-ol.—6-Chlorohexan-1-ol (21 g.), sodium iodide (34 g.), and acetone (100 ml.) were heated under reflux for 10 hr. The precipitated sodium chloride was filtered off and the solution was evaporated to give an oil which was poured into water (150 ml.) and extracted with ether (2 × 100 ml.). The extracts were dried (Na₂SO₄) and evaporated to give 6-iodohexan-1-ol contaminated with 1,6-di-iodohexane (24 g., 70%), b.p. 122—124°/15 mm. (lit.,⁹ 85—95°/2 mm.) (Found: I, 56·9. Calc. for 6-iodohexan-1-ol containing 6% 1,6-di-iodohexane: I, 56·9%). The *phenylurethane* separated as needles from light petroleum (b.p. 40—60°), m.p. 83° (Found: C, 44·9; H, 5·0; I, 36·4; N, 3·9. C₁₃H₁₈INO₂ requires C, 44·9; H, 5·2; I, 36·6; N, 4·0%).

6-Hydroxyhexyltriphenylphosphonium Iodide.—Triphenylphosphine (55·5 g.), impure 6-iodohexan-1-ol (48·5 g.), and acetone (250 ml.) were heated under reflux for 60 hr. The mixture was cooled and evaporated to give a solid which was extracted with boiling acetone (6 × 500 ml.). The extracts were evaporated to give 6-hydroxyhexyltriphenylphosphonium iodide (52 g., 50%), prisms (from acetone), m.p. 133°, ν_{max} . 3340 cm.⁻¹ (OH) (Found: C, 58·9; H, 5·8; P, 6·5. C₂₄H₂₈IOP requires C, 58·8; H, 5·8; P, 6·3%).

The solid residue from the acetone extraction was recrystallised from ethanol to give *hexane*-1,6-*bis(triphenylphosphonium iodide)* (16·1 g., 18% with respect to triphenylphosphine), needles, m.p. 292° (decomp.) (Found: C, 59·5; H, 5·0; I, 30·2. $C_{42}H_{42}I_2P_2$ requires C, 59·5; H, 4·9; I, 29·5%). The iodide (15·5 g.) was hydrolysed by heating it under reflux with aqueous potassium hydroxide (25% w/v; 50 ml.) for 15 min. to give hexane-1,6-bis(diphenylphosphine oxide) (7·6 g., 63%), needles (from ethanol), m.p. 195° (lit.,¹⁰ 196—197°).

In a similar experiment, triphenylarsine (30.5 g.), 6-iodohexan-1-ol (22.5 g.), and ethanol (200 ml.) were heated under reflux for 250 hr. to give 6-hydroxyhexyltriphenylarsonium iodide (14.6 g., 28%), prisms (from acetone), m.p. 138—139°, ν_{max} . 3330 cm.⁻¹ (OH) (Found: C, 53.6; H, 5.3. C₂₄H₂₈AsIO requires C, 53.9; H, 5.3%), and hexane-1,6-bis-(triphenylarsonium iodide) (1.9 g., 2%), needles (from ethanol), m.p. 233—234° (Found: C, 53.3; H, 4.5; As, 14.4. C₄₂H₄₂As₂I₂ requires C, 53.1; H, 4.5; As, 15.8%).

6-Hydroxyhexyldiphenylphosphine Oxide.—6-Hydroxyhexyltriphenylphosphonium iodide (12·7 g.) and aqueous potassium hydroxide (10% w/v; 50 ml.) were heated under reflux for 20 min. The cooled mixture was extracted with chloroform (100 ml.) and the extracts were dried and evaporated to give the phosphine oxide (7·2 g., 92%), b.p. 225—227°/0·01 mm., m.p. 43—45°, ν_{max} , 3300 (OH) and 1175 cm.⁻¹ (P:O); τ ca. 2·4 (m, 10H), 6·40 (t, J 6 c./sec., 2H), 6·62 (s, 1H, disappears on adding D₂O), 7·76 (quintet, $J_{\rm H, H}$ 6 c./sec., $J_{\rm P, H}$ 12 c./sec., 2H), 8·60 (m, 8H) (Found: C, 71·0; H, 7·8; P, 10·4. C₁₈H₂₃O₂P requires C, 71·5; H, 7·7; P, 10·3%).

Reaction of 6-Hydroxyhexyltriphenylphosphonium Iodide with Sodium Hydride.—(a) The iodide (20 g.) and sodium hydride (1.0 g.) were intimately mixed and heated for 45 min. at $130-150^{\circ}$ (bath) under a stream of nitrogen. The outgoing gas was passed through a liquid nitrogen

⁸ J. S. Allen and Hibbert, J. Amer. Chem. Soc., 1934, 56, 1398.

trap to give benzene (0.5 g., 16%), identified by i.r. spectroscopy.

The residue in the flask was cooled, water (30 ml.) was added, and the mixture was steam distilled to give hex-5-en-1-ol (1.2 g., 29%), identified as the α -naphthylurethane, m.p. and mixed m.p. 60-61°. The residual mixture was extracted with chloroform (60 ml.), the extracts were dried (Na_2SO_4) , and evaporated to give an oil which was chromatographed on alumina (700 g.). Elution with light petroleum (b.p. 40-60°; 4 l.) gave triphenylphosphine (3.4 g., 32%), m.p. and mixed m.p. 81-82°. Elution with a mixture of benzene and light petroleum (1:1, v/v; 21)gave 6-phenoxyhexyldiphenylphosphine (0.4 g., 3%) which was oxidised with hydrogen peroxide and aqueous sodium hydroxide in acetone to give 6-phenoxyhexyldiphenylphosphine oxide, prisms (from acetone), m.p. 100-102°, vmax. 1255 (CH₂·OPh), 1180 cm.⁻¹ (P:O), $\tau 2.0$ —3.2 (m, 15H), 6.08 (t, J 6 c./sec., 2H), 7.5-8.6 (m, 10H) (Found: C, 75.8; H, 7.3. C₂₄H₂₇O₂P requires C, 76.2; H, 7.2%), M (mass spectrum) 378.

Elution with benzene-ether (1 : 1, v/v; 5 l.) gave 6-hydroxyhexyldiphenylphosphine (1.7 g., 14%), b.p. $152^{\circ}/0.1$ mm., v_{max} . 3350 cm.⁻¹ (OH) (Found: C, 76.0; H, 8.3. C₁₈H₂₃OP requires C, 75.5; H, 8.0%).

Elution with ether (5 l.) gave triphenylphosphine oxide $(2\cdot3 \text{ g.}, 19\%)$, m.p. and mixed m.p. $153-154^{\circ}$.

(b) The iodide (10 g.) and sodium hydride (0.5 g.) were heated for 40 min. under nitrogen. The mixture was cooled and acetone (5 ml.) was added. The mixture was chromatographed on alumina (350 g.). Elution with light petroleum (b.p. 40-60°; 3 l.) gave a mixture of 7-methyl-1-phenoxyoct-6-ene and 6-phenoxyhexyldiphenylphosphine which was heated under reflux with methyl iodide (10 ml.) and ethanol (50 ml.) for 3 hr. to quaternise the phosphine. The mixture was cooled, evaporated, and the resulting oil was extracted with ether (2×50 ml.). The extracts were evaporated to give 7-methyl-1-phenoxyoct-6-ene (0.4 g., 9%) whose i.r. and n.m.r. spectra were identical with those of an authentic sample.

6-Phenoxyhexyltriphenylphosphonium Bromide.— 1-Bromo-6-phenoxyhexane (23 g.), triphenylphosphine (24 g.), and ethanol (150 ml.) were heated under reflux for 24 hr. The mixture was cooled, evaporated, and the resulting oil was extracted with ether (5 × 500 ml.) to give the bromide (42 g., 89%), needles (from acetone), m.p. 149— 150°, v_{max} . 1225 cm.⁻¹ (CH₂·OPh) (Found: C, 68·9; H, 6·1; Br, 16·0; P, 6·1. C₃₀H₃₂BrOP requires C, 69·4; H, 6·2; Br, 15·4; P, 6·0%).

6-Phenoxyhexyldiphenylphosphine Oxide.—6-Phenoxyhexyltriphenylphosphonium bromide (4·2 g.) and aqueous sodium hydroxide (10% w/v; 20 ml.) were heated under reflux for 15 min. The mixture was cooled and extracted with chloroform (50 ml.), the extracts were dried (Na₂SO₄) and evaporated to give 6-phenoxyhexyldiphenylphosphine oxide (2·7 g., 88%), m.p. 104—105°, mixed m.p. with material from reaction of 6-hydroxyhexyltriphenylphosphonium iodide with sodium hydride, 100—102°.

7-Methyl-1-phenoxyoct-6-ene.—A solution of 6-phenoxyhexyltriphenylphosphonium bromide (20 g.) in tetrahydrofuran (50 ml.) was added to a solution of phenyl-lithium prepared from lithium (0.7 g.), bromobenzene (7.5 g.), and tetrahydrofuran (40 ml.). The mixture was stirred under nitrogen at room temperature for 1 hr. Acetone (10 ml.) ¹⁰ G. M. Kosolapoff and R. F. Struck, J. Chem. Soc., 1959, **3950**.

⁹ A. Scaglia, Boll. chim. farm., 1959, 98, 464.

was added and the mixture was heated under reflux for 1 hr., cooled, and evaporated to give a paste. This was extracted with light petroleum (b.p. 40—60°; 2×125 ml.) to give an oil which was chromatographed on alumina (150 g.). Elution with light petroleum (b.p. 40—60°; 1 l.) gave 7-methyl-1-phenoxyoct-6-ene (5·1 g., 61%), b.p. 167— 168°/12 mm., $n_{\rm D}^{22}$ 1·5045, $n_{\rm D}^{30}$ 1·5025, $v_{\rm max}$ 1240 cm.⁻¹ (CH₂·OPh), τ 2·6—3·2 (m, 5H), 4·88 (t, J 5 c./sec., 1H), 6·08 (t, J 6 c./sec., 2H), 8·30 (s, 3H), 8·39 (s, 3H), 7·9—8·7 (m, 10H) (Found: C, 83·0; H, 10·2. C₁₅H₂₂O requires C, 82·5; H, 10·2%), M (mass spectrum) 218.

11-Hydroxyundecyltriphenylphosphonium Bromide.—11-Bromoundecan-1-ol (70 g.), triphenylphosphine (72 g.), and ethanol (450 ml.) were heated under reflux for 60 hr. The mixture was cooled and evaporated to give an oil which was extracted with boiling ether (4 × 500 ml.); the residue recrystallised from acetone to give the bromide (109 g., 77%), m.p. 90—91°, v_{max} . 3350 cm.⁻¹ (OH) (Found: C, 67.4; H, 7.5; Br, 15.6; P, 6.4. C₂₉H₃₈BrOP requires C, 67.8; H, 7.5; Br, 15.6; P, 6.0%).

In a similar experiment, triphenylarsine (25 g.), 11bromoundecan-1-ol (24 g.), and ethanol (250 ml.) were heated under reflux for 250 hr. to give 11-hydroxyundecyltriphenylarsonium bromide (8 g., 16%), needles (from acetone), m.p. 84—86°, ν_{max} . 3250 cm.⁻¹ (OH) (Found: C, 62·7; H, 7·1; As, 12·8. C₂₉H₃₈AsBrO requires C, 62·5; H, 6·9; As, 13·4%).

In a similar experiment, dimethylaniline (22 g.), 11bromoundecan-1-ol (41 g.), and ethanol (400 ml.) were heated under reflux for 24 hr. to give 11-hydroxyundecyldimethylphenylammonium bromide (13 g., 21%), needles (from acetone), m.p. 118°, ν_{max} , 3300 cm.⁻¹ (OH) (Found: C, 61·3; H, 8·8; Br, 21·4; N, 3·6. C₁₉H₃₄BrNO requires C, 61·3; H, 9·2; Br, 21·5; N, 3·7%).

11-Hydroxyundecyldiphenylphosphine Oxide.—11-Hydroxyundecyltriphenylphosphonium bromide (41 g.) and aqueous potassium hydroxide (25% w/v; 100 ml.) were heated under reflux for 15 min. The mixture was cooled and extracted with chloroform (2 × 150 ml.); the extracts were dried (Na₂SO₄) and evaporated to give the *phosphine oxide* (26 g., 89%), b.p. 270—272°/0·1 mm., ν_{max} . 3350 (OH) and 1165 cm.⁻¹ (P:O), $\tau 2 \cdot 0$ —2·6 (m, 10H), 6·35 (t, J 7 c./sec., 2H), 7·14 (s, 1H, disappears on adding D₂O), 7·70 (m, 2H), and 8·70 (m, 18H) (Found: C, 73·9; H, 9·1; P, 8·6. C₂₃H₃₃O₂P requires C, 74·1; H, 8·9; P, 8·3%).

Reaction of 11-Hydroxyundecyltriphenylphosphonium Bromide with Sodium Hydride.—(a) The bromide (60 g.) and sodium hydride (3.0 g.) were intimately mixed and heated at 120—140° (bath) under a stream of nitrogen for 45 min. Acetone (5 ml.) was added to the cooled mixture which was chromatographed on alumina (1.3 kg.).

Elution with light petroleum (b.p. 40–60°; 201.) gave an oil (19·2 g.) which was heated under reflux with methyl iodide (70 ml.) and ethanol (50 ml.) for 10 hr. The mixture was cooled, evaporated, and the resulting oil was extracted with ether (4 × 50 ml.). The residue from the extraction gave methyl-11-phenoxyundecyldiphenylphosphonium iodide (15·0 g., equivalent to 11·3 g., 22% 11-phenoxyundecyldiphenylphosphine), needles (from acetone at -15°), m.p. 67–68°, v_{max} . 1240 cm.⁻¹ (CH₂·OPh), τ 1·9–2·4 (m, 10H), 2·6–3·2 (m, 5H), 6·08 (t, J 6 c./sec., 2H), 6·75 (m, 2H), 7·19 (d, $J_{\rm P, H}$ 13 c./sec., 3H), 8·1–8·8 (m, 18H) (Found: C, 63·0; H, 7·2; I, 23·6; P, 5·9. C₃₀H₄₀IOP requires C, 62·7; H, 7·0; I, 22·1; P, 5·4%). The ethereal extracts were evaporated to give 12-methyl-1-phenoxytridec-11-ene

(8.4 g., 25%), b.p. $148-152^{\circ}/0.5$ mm., m.p. and mixed m.p. with authentic sample $7-9^{\circ}$, containing impurities of 1-phenoxyundecane (*ca.* $1\cdot8\%$) and 1-phenoxyundec-10-ene (*ca.* $3\cdot0\%$) identified and estimated by gas chromatography and mass spectrometry.

Elution with benzene (8 l.) gave 11-hydroxyundecyldiphenylphosphine (6·3 g., 15%), prisms (from ether), m.p. 52°, v_{max} , 3400 cm.⁻¹ (OH), τ 2·72 (m, 10H), 6·40 (t, J 5·5 c./sec., 2H), 7·98 (m, 2H), 8·42 (s, disappears on adding D₂O, 1H) 8·73 (m, 18H) (Found: C, 77·6; H, 9·5. C₂₃H₃₃OP requires C, 77·6; H, 9·3%), M (mass spectrum) 356.

Elution with ether (7 l.) gave triphenylphosphine oxide (12 g., 37%), m.p. and mixed m.p. $155-156^{\circ}$.

(b) 11-Hydroxyundecyltriphenylphosphonium bromide [16 g., recrystallised from ethanol-ether (1:1 v/v)] and sodium hydride (0.8 g.) were heated under a stream of nitrogen for 45 min. The mixture was cooled and chromatographed on alumina (700 g.). Elution with light petroleum (b.p. 40-60°; 3 l.) gave an oil (5 g.) which was heated under reflux with methyl iodide (20 ml.) and ethanol for 1 hr. The mixture was cooled, evaporated, and extracted with ether (2×50 ml.). Evaporation of the extracts gave no residue of 12-methyl-1-phenoxytridec-11-ene.

Oxidation of 11-Phenoxyundecyldiphenylphosphine.—The phosphine (1.0 g.), aqueous sodium hydroxide (25% w/v; 1 ml.), hydrogen peroxide (30% w/v; 1 ml.), and acetone (15 ml.) were heated under reflux for 20 min. The mixture was evaporated to give 11-phenoxyundecyldiphenylphosphine oxide (0.8 g., 77%), needles from ether, m.p. 76—77°, v_{max} . 1230 (CH₂·OPh) and 1170 cm.⁻¹ (P:O) (Found: C, 77.9; H, 8.5. C₂₉H₃₇O₂P requires C, 77.6; H, 8.4%), M (mass spectrum), 448.

Methyl-11-phenoxyundecylphenylphosphine Oxide.—Methyl-11-phenoxyundecyldiphenylphosphonium iodide (2·2 g.) and aqueous potassium hydroxide (25% w/v; 25 ml.) were heated under reflux for 15 min. The mixture was cooled and extracted with chloroform (100 ml.); the extracts were dried (Na₂SO₄) and evaporated to give the phosphine oxide (0·8 g., 50%), m.p. 69—70°, ν_{max} . 1235 (CH₂·OPh) and 1170 cm.⁻¹ (P:O), τ 2·2—3·2 (m, 10H), 6·06 (t, J 6 c./sec., 2H), 8·31 (d, $J_{P, \text{H}}$ 12 c./sec., 3H), and 8·7 (m, 20H) (Found: C, 73·9; H, 9·1; P, 8·2. C₂₄H₃₅O₂P requires C, 74·6; H, 9·1; P, 8·0%).

11-Hydroxyundecylmethylphenylphosphine Oxide.-11-Hydroxyundecyldiphenylphosphine (4.8 g.), methyl iodide (30 ml.), and ethanol (50 ml.) were heated under reflux for 6 hr. The mixture was cooled, evaporated, and the resulting oil was extracted with ether $(2 \times 50 \text{ ml.})$ to give 11-hydroxyundecylmethyldiphenylphosphonium iodide. $v_{\text{max.}}$ 3300 cm.⁻¹ (OH), as an oil (4.9 g.) which could not be crystallised. The iodide (4.9 g.) was heated under reflux with sodium hydroxide (10% w/v; 25 ml.) for 15 min. The mixture was cooled and extracted with chloroform (100 ml.); the extracts were dried and evaporated to give the phosphine oxide (1.2 g., 30%), prisms (from acetone), m.p. 48°, ν_{max} 3300 (OH) and 1150 cm.⁻¹ (P:O), τ 2·2–2·6 (m, 5H), 6·40 (t, J 6 c./sec., 2H), 7·60 (s, 1H, disappears on adding D₂O), 8·31 (d, J_{P, H} 12·5 c./sec., 3H), and 8·3-8·8 (m, 20H) (Found: C, 69.7; H, 9.8; P, 10.2. C₁₈H₃₁O₂P requires C, 69.7; H, 10.1; P, 10.0%), M (mass spectrum) 310.

1-Phenoxyundecane.—Phenol (4 g.) was dissolved in a solution of sodium (1.0 g.) in dry ethanol (50 ml.), 1-bromoundecane (10 g.) was added and the mixture was heated under reflux for 3 hr. and then cooled; evaporation gave an oil which was partitioned between water (75 ml.) and ether (150 ml.). The ethereal solution was washed with aqueous sodium hydroxide (10% w/v; 100 ml.), dried (Na₂SO₄), and evaporated to give 1-*phenoxyundecane* (7.0 g., 66%), b.p. 131—132°/0.5 mm., m.p. 21°, v_{max} (liq. film) 1240 cm.⁻¹ (CH₂·OPh) (Found: C, 82·3; H, 11·3. C₁₇H₂₈O requires C, 82·3; H, 11·4%), M (mass spectrum) 248.

A similar reaction with phenol (6 g.), sodium (1.5 g.), ethanol (30 ml.), and 1-chloroundec-10-ene (7.2 g.) gave 1-phenoxyundec-10-ene (2.9 g., 31%), b.p. 176—178°/12 mm., m.p. 18—19°, $n_{\rm D}^{20}$ 1.4956, $\nu_{\rm max.}$ (liq. film) 1240 cm.⁻¹ (CH₂·OPh), $\tau 2.7$ —3.4 (m, 5H), 4.24 (m, 1H), 5.07 (m, 2H), 6.19 (t, *J* 6 c./sec., 2H), and 7.9—8.9 (m, 16H) (Found: C, 83.0; H, 10.5. C₁₇H₂₆O requires C, 82.9; H, 10.7%), *M* (mass spectrum) 246.

A similar reaction with phenol (35 g.), sodium (8·2 g.), ethanol (350 ml.), and 11-bromoundecan-1-ol (81 g.) gave 11-phenoxyundecan-1-ol (69 g., 81%), b.p. 278—280°/0·1 mm., m.p. 57—58°, v_{max} 3290 (OH) and 1240 cm.⁻¹ (CH₂·OPh), $\tau 2\cdot 6$ —3·2 (m, 5H), 6·08 (t, J 6 c./sec., 2H), 6·41 (t, J 6 c./sec., 2H), 8·47 (s, 1H, disappears on adding D₂O), 8·7 (m, 18H) (Found: C, 77·8; H, 10·7. C₁₇H₂₈O₂ requires C, 77·3; H, 10·7%), M (mass spectrum) 264.

11-Phenoxyundecyltriphenylphosphonium Iodide .----Thionyl chloride (51 g.) was added to a solution of 11-phenoxyundecan-1-ol (56.5 g.) in chloroform (500 ml.) cooled in an ice-salt bath. The mixture was stirred at room temperature for 2 hr. and heated on a water-bath for 1 hr., cooled, and evaporated. The resulting oil was dissolved in chloroform (600 ml.) and the solution was washed with saturated aqueous sodium hydrogen carbonate (3×100 ml.), dried (MgSO₄), and evaporated to give impure 1-chloro-11-phenoxyundecane as an oil (60 g.). The oil, acetone (400 ml.), and sodium iodide (35 g.) were heated under reflux for 24 hr., the sodium chloride was filtered off, and the acetone was evaporated to give an oil which was poured into water. The resulting mixture was extracted with chloroform (750 ml.), the extracts were dried and evaporated to give impure 1-iodo-11-phenoxyundecane (72 g.) as an oil which was dissolved in ethanol (300 ml.) with triphenylphosphine (55 g.), The mixture was heated under reflux for 30 hr., cooled, and evaporated to give an oil which was extracted with ether (4 imes 500 ml.) and ethyl acetate (8 imes 400 ml.) to give the *iodide* (31 g., 23%) as a glass, v_{max} (liq. film) 1240 cm.⁻¹ (CH₂·OPh) (Found: C, 66·2; H, 6·8; I, 19·8; P, 4.8. C₃₅H₄₂IOP requires C, 66.0; H, 6.6; I, 20.0; P, 4.9%).

11-Phenoxyundecyldiphenylphosphine Oxide.—11-Phenoxyundecyltriphenylphosphonium iodide (1.75 g.) and aqueous potassium hydroxide (25% w/v; 15 ml.) were heated under reflux for 15 min., cooled, and extracted with chloroform (2×50 ml.). The extracts were dried (MgSO₄) and evaporated to give the phosphine oxide (1.25 g., 100%), m.p. and mixed m.p. with material from the oxidation of the phosphine 76—77°.

12-methyl-1-Phenoxytridec-11-ene.—A solution of 11-phenoxyundecyltriphenylphosphonium iodide (9 g.) in dry tetrahydrofuran (30 ml.) was added to a solution of phenyllithium prepared from lithium (0.35 g.), bromobenzene ($3\cdot 8$ g.), and tetrahydrofuran (20 ml.). The mixture was stirred under nitrogen at room temperature for 45 min., when a red colour developed. Acetone (10 ml.) was added and the mixture was stirred at room temperature for 30 min., and then heated under reflux for 45 min. during

which time the colour disappeared. The solution was evaporated to give a paste which was extracted with light petroleum (b.p. 40—60°; 150 ml.). The extracts were evaporated to give an oil which was chromatographed on alumina (150 g.). Elution with light petroleum (b.p. 40—60°; 150 ml.) gave the *tridec*-11-*ene* (3·4 g., 83%), b.p. 148—150°/0·5 mm., m.p. 8—9°, v_{max} (liq. film) 1240 cm.⁻¹ (CH₂·OPh), $\tau 2\cdot8$ —3·3 (m, 5H), 4·92 (t, J 6 c./sec., 1H), 6·16 (t, J 6 c./sec., 2H), 8·32 (s, 3H), 8·40 (s, 3H), 7·8—8·8 (m, 18H) (Found: C, 83·0; H, 11·1. C₂₀H₃₂O requires C, 83·3; H, 11·1%), M (mass spectrum) 288.

Hydrogenation of 12-methyl-1-Phenoxytridec-11-ene.—(a) 12-methyl-1-Phenoxytridec-11-ene (2·5 g.), Adams palladium oxide catalyst (0·3 g.), and ethyl acetate (100 ml.) were shaken for 2 hr. under hydrogen (5 atm.). The mixture was filtered and evaporated to give 12-methyl-1-phenoxytridecane (2·3 g., 92%), b.p. 156—160°/0·1 mm., m.p. 22—23°, v_{max} . 1245 cm.⁻¹ (CH₂·OPh), $\tau 2\cdot7$ —3·4 (m, 5H), 6·13 (t, J 6 c./sec., 2H), 8·7 (19H), 9·08 (s, 3H), 9·16 (s, 3H) (Found: C, 82·0; H, 11·9. C₂₀H₃₄O requires C, 82·6; H, 11·8%), M (mass spectrum) 290.

(b) The tridecene (33 mg.), palladium oxide catalyst (2 mg., previously saturated with hydrogen), and methanol (5 ml.) were shaken under hydrogen (1 atmos.) for 2 hr. The uptake of hydrogen was $28 \cdot 2$ ml. (corrected to S.T.P.; 94% calculated for mono-olefin). Filtration and evaporation of the filtrate gave an oil which had i.r. and n.m.r. spectra identical with those of the tridecane prepared in the previous experiment.

2,3-Dihydroxypropyltriphenylphosphonium Iodide.—Triphenylphosphine (262 g.), 3-iodopropan-1,2-diol (170 g., prepared by the method of Glattfield and Klaas¹¹), and ethanol (2 l.) were heated under reflux for 30 hr. The mixture was cooled, evaporated, and the residual oil extracted with ether (2 × 500 ml.) to give the *iodide* (260 g., 60%), needles (from ethanol), m.p. 183°, ν_{max} . 3300 cm.⁻¹ (OH) (Found: C, 54·3; H, 4·8; I, 27·5; P, 6·6. C₂₁H₂₂IO₂P requires C, 54·3; H, 4·8; I, 27·4; P, 6·7%).

Reaction of 2,3-Dihydroxypropyltriphenylphosphonium Iodide with Sodium Hydroxide.—The iodide (150 g.) and aqueous sodium hydroxide (25% w/v; 120 ml.) were heated under reflux for 30 min. under a stream of nitrogen. The outgoing gas was passed through a liquid nitrogen trap to give a mixture of benzene and allyl alcohol (12·4 g.). Phenyl isocyanate (3·1 g.) was added to the mixture which was set aside for 24 hr. The mixture was distilled on a water-bath to give benzene (11·8 g., 47%), b.p. 79—80°, identified by i.r. spectroscopy. The residue was crystallised from light petroleum (b.p. 60—80°) to give allyl phenylurethane (4·0 g., equivalent to 1·3 g., 7% allyl alcohol), m.p. and mixed m.p. 65—66°.

The residue in the flask was cooled and extracted with chloroform (250 ml.); the extracts were dried (Na₂SO₄) and evaporated to give an oil which was chromatographed on alumina (1.7 kg.). Elution with benzene (13 l.) gave triphenylphosphine (18.3 g., 22%), m.p. and mixed m.p. 81—82°. Elution with ether (17 l.) gave triphenylphosphine oxide (12.3 g., 14%), m.p. and mixed m.p. 152—153°. Elution with methanol (6 l.) gave 2,3-dihydroxypropyl-diphenylphosphine oxide (15.0 g., 17%), prisms (from acetone), m.p. 114—115°, v_{max} . 3400, 3200 (OH), and 1182 cm.⁻¹ (P:O), $\tau 2.2$ —2.6 (m, 10H), 5.36 (s, 1H, disappears on adding D₂O), 5.88 (m, 1H), 6.21 (s, 1H, dis-

¹¹ J. W. E. Glattfield and R. Klaas, J. Amer. Chem. Soc., 1933, 55, 1114.

appears on adding D_2O), 6.40 (m, 2H), and 7.49 (m, 2H) (Found: C, 64.5; H, 6.3. $C_{15}H_{17}O_3P$ requires C, 65.2; H, 6.2%), *M* (mass spectrum) 276.

Reaction of 2,3-Dihydroxypropyltriphenylphosphonium Iodide with Sodium Hydride.—The iodide (22.0 g.), sodium hydride (1.2 g.), and tetrahydrofuran (100 ml.) were heated under reflux under a stream of nitrogen for 1 hr. The outgoing gas was passed through a liquid nitrogen trap to give a mixture of allyl alcohol and tetrahydrofuran. Phenyl isocyanate (3.5 g.) was added to the mixture which was set aside for 1 hr. and then extracted with light petroleum (b.p. $60-80^{\circ}$) to give allylphenylurethane (1.7 g., equivalent to 21% allyl alcohol), m.p. and mixed m.p. $64-65^{\circ}$.

Water (100 ml.) was added to the cooled residue in the flask and the mixture was extracted with chloroform (100 ml.). The extracts were dried (Na_2SO_4), evaporated, and the resulting oil was chromatographed on alumina (300 g.). Elution with ether (2 l.) gave triphenylphosphine oxide (6.6 g., 51%), m.p. and mixed m.p. 152—153°.

Reaction of 6-Hydroxyhexyltriphenylarsonium Iodide with Sodium Hydride.—The iodide (19.5 g.) and sodium hydride (1.0 g.) were intimately mixed and heated at 140—160° under a stream of nitrogen for 40 min. The gas was passed throuth a liquid nitrogen trap to give hex-5-en-1-ol (1.2 g.) identified as the α -naphthylurethane, m.p. and mixed m.p. 60—62°. The residue in the flask was cooled, water (10 ml.) was added, and the mixture was steam distilled to give more hex-5-en-1-ol (1.0 g., giving a total of 2.2 g., 61%). The residue in the flask was partitioned between chloroform (150 ml.) and water (100 ml.), the chloroform layer was separated, dried (Na₂SO₄), and evaporated to give an oil which was chromatographed on alumina (500 g.). Elution with light petroleum (b.p. 40—60°; 5 l.) gave triphenylarsine (9.9 g., 89%), m.p. and mixed m.p. 51—52°.

Reaction of 11-Hydroxyundecyltriphenylarsonium Bromide with Sodium Hydride.-The bromide (7.9 g.) and sodium hydride (0.4 g) were intimately mixed and heated at 140— 160° under a stream of nitrogen for 30 min. The gas was passed through a liquid nitrogen trap to give undec-10-en-1-ol (0.7 g., 29%) identified as the phenylurethane, m.p. and mixed m.p. 54-55°. The residue in the flask was cooled, water (30 ml.) was added, and the mixture was extracted with chloroform (50 ml.). The extracts were dried (Na_2SO_4) and evaporated to give an oil which was chromatographed on alumina (160 g.). Elution with light petroleum (b.p. $40-60^{\circ}$; 1 l.) gave a mixture of triphenylarsine and 11-phenoxyundecyldiphenylarsine shown by n.m.r. and mass spectrometry to be ca. 1:1 by weight (2.7 g., ca. 30% and 20% respectively). Elution with benzene (1 l.) gave 11-hydroxyundecyldiphenylarsine (1.3 g.,

25%), needles (from ether), m.p. 52—53°, v_{max} 3420 cm.⁻¹ (OH), τ 2·70 (m, 10H), 6·39 (t, J 7 c./sec., 2H), 8·00 (t, J 8 c./sec., 2H), 8·68 (s, 1H, disappears on adding D₂O), and 8·72 (m, 18H) (Found: C, 69·1; H, 8·3; As, 18·6. C₂₂H₃₃AsO requires C, 69·0; H, 8·3; As, 18·7%), M (mass spectrum) 400.

3-Hydroxypropyldimethylphenylammonium Iodide.—Dimethylaniline (24·2 g.), 3-iodopropan-1-ol (37·2 g.), and ethanol were heated under reflux for 6 hr. The mixture was cooled and evaporated to give an oil which was extracted with ether (3×500 ml.) to give the *iodide* (22 g., 36%), needles (from ethanol), m.p. 130—131°, v_{max} . 3300 cm.⁻¹ (OH) (Found: C, 43·2; H, 5·8; I, 41·7; N, 4·7. C₁₁H₁₈INO requires C, 43·0; H, 5·9; I, 41·3; N, 4·6%).

Reaction of 3-Hydroxypropyldimethylphenylammonium Iodide with Sodium Hydride.—The iodide (22 g.) and sodium hydride (1.75 g.) were intimately mixed and heated under a stream of nitrogen at 140—160° for 20 min. The gas was passed through a liquid nitrogen trap to give allyl alcohol (3.0 g., 72%), n_p^{20} 1.4134 (lit.,¹² 1.41345), identified as the phenylurethane, m.p. and mixed m.p. 65—66°. The residue in the flask was cooled and water (30 ml.) was added. The mixture was extracted with chloroform (60 ml.), the extracts were dried (Na₂SO₄) and evaporated to give dimethylaniline (7.2 g., 83%), identified as the picrate, m.p. and mixed m.p. 161—162°.

Reaction of 11-Hydroxyundecyldimethylphenylammonium Bromide with Sodium Hydride.—The bromide (19.0 g.) and sodium hydride (2.0 g) were intimately mixed and heated under a stream of nitrogen at 140-160° for 30 min. The mixture was cooled, water (50 ml.) was added, and the mixture extracted with chloroform (200 ml.). The extracts were dried (Na₂SO₄) and evaporated to give 11-methoxyundecylmethylphenylamine (10.5 g., 71%), b.p. 180-182°/5 mm., $n_{\rm p}^{20}$ 1.5088, $\nu_{\rm max.}$ 1110 cm.⁻¹ (CH₂·OMe), τ 2.8-3.4 (m, 5H), 6.68 (t, $J 6 \overline{c./sec.}$, 4H), 6.71 (s, 3H), and 8.7(m, 18H) (Found: C, 78·1; H, 11·0; N, 5·0. C₁₉H₃₃NO requires C, 78.3; H, 11.3; N, 4.8%), M (mass spectrum) 291. The amine was converted to the methiodide, needles (from acetone), m.p. 60-61° (Found: C, 55.7; H, 8.2; I, 29.5; N, 3.4. $C_{20}H_{36}INO$ requires C, 55.5; H, 8.3; I, 29.3; N, 3.2%).

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¹² J. W. Brühl, Annalen, 1879, 200, 174.