CCCVII.—*Influence of Poles and Polar Linkings on the Course pursued by Elimination Reactions. Part V. The Mechanism of Thermal Decomposition of Quaternary Phosphonium Hydroxides.*

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PRESENT knowledge regarding the thermal decomposition of quaternary phosphonium hydroxides is derived exclusively from two early researches, together covering five examples. Cahours and Hofmann (*Annalen*, 1857, **104**, 1) established the formation of a tertiary phosphine oxide, and either methane or ethane, from tetramethyl-, tetraethyl-, and triethyl*iso*amyl-phosphonium hydroxides, and Collie (*Phil. Mag.*, 1887, **24**, 27; J., 1888, **53**, 636) observed the analogous decompositions, leading to toluene, of benzyltriethyl- and dibenzyldiethyl-phosphonium hydroxides.

The striking contrast which these observations present to the olefinic degradation of quaternary ammonium hydroxides has often been remarked. The point at issue is four-fold, involving the mechanism of the olefinic degradation, the reason for its non-appearance in the decompositions of phosphonium hydroxides, the mechanism of the paraffinic degradation of these substances, and the reason for its non-appearance in the ammonium series.

The mechanism of the olefinic degradation of ammonium hydroxides is already known in outline. However, the results establishing it (Parts I and II, J., 1927, 997; 1928, 3125) raise the second of the above questions in a still more acute form; for, in the first place, the mechanism is such that there is no obvious reason why it should not be applicable to "-onium" compounds generally, and, secondly, it has been experimentally (Parts III and IV, J., 1928, 3127; preceding paper) shown to apply to compounds as different from ammonium hydroxides as sulphones, wherefore its apparent inability to function in the phosphonium hydroxide series seems the more surprising. Our answer to this point is that actually the mechanism *is* able to function in that series, and that the reason for the non-appearance of olefinic degradation in the simple cases previously studied (in all of which the olefin which might have been formed is ethylene) is the intervention of the paraffinic degradation at a lower temperature than that which olefin-elimination would require. The mechanism of the paraffinic decomposition will be considered later: the only point which need now be noted is that, in most of the examples which have come within our experience, the reaction proceeds rapidly at temperatures in the neighbourhood of 130°. Now it is an essential feature of the mechanism of the olefinic degradation that the reaction is facilitated by the internal electron-attraction of the -onium group. The relative electron affinities of various -onium groups are inferable, in some cases theoretically, and in all cases from suitable studies on orientation in aromatic substitution : observations in this field (Ingold, Shaw, and Wilson, J., 1928, 1280) establish the order $\overset{\oplus}{N}R_3 > \overset{\oplus}{P}R_3$. Since the temperatures favourable to the formation of simple aliphatic olefins from quaternary ammonium hydroxides are all considerably higher than that named above, it appears that corresponding degradations of phosphonium hydroxides would require temperatures in still greater excess of that at which reaction proceeds in a different direction. It is, however, a further consequence of the mechanism of the olefinic degradation that the facility of the process depends also on the extent to which the β-hydrogen atom eliminated from the kation is activated or de-activated by the β-substituents of the group forming the olefin. Electron-repelling alkyl groups de-activate, and, accordingly, phosphonium hydroxides in which the only olefins which might be formed are simple aliphatic olefins, do not, for the reason indicated, constitute favourable cases for the observation of olefinic degradation. On the other hand, electron-absorbing or -attracting groups such as phenyl or nitroxyl promote the reaction (Part I, *loc. cit.*) and therefore reduce the region of favourable temperatures to an extent which may be illustrated for the phenyl group by the observation that the formation of styrene from quaternary ammonium hydroxides containing a β-phenylethyl radical attached to the nitrogen atom proceeds with facility even at 100°. We therefore examined the thermal decomposition of β-phenylethyltriethylphosphonium hydroxide and found that the formation of styrene and triethylphosphine attained an appreciable speed at the temperature of the paraffinic decomposition, which, however, was still the main reaction. It was then an obvious step to activate the β-hydrogen atom still further by the introduction of a second β-phenyl group, and, proceeding accordingly, we found that ββ-diphenylethyltri-*n*-butylphosphonium hydroxide yielded *as*-diphenylethylene and tri-*n*-butylphosphine as the main products of its decomposition; the simultaneous paraffinic degradation was only just discernible. Thus we are able to record clear cases, proving, not only the possibility of olefinic degradation in the phosphonium hydroxide series, but also that the conditions for its facilitation are similar to those already established for the ammonium series.

Our explanation of the paraffinic degradation of phosphonium hydroxides utilises Sidgwick's hypothesis regarding the relation between atomic number and the maximal number of electrons that can find accommodation in the valency shell of an element. According to this hypothesis, for which a large body of evidence has been advanced by its author ("The Electronic Theory of Valency," Chapter IX), the nitrogen octet is constitutionally incapable of expansion by the inclusion of additional electrons, whereas the phosphorus octet can, under favourable conditions, add on two, and sometimes four, more electrons. The phosphonium ion, therefore, unlike the ammonium ion, should be capable of co-ordinating with a sufficiently basic anion to give a neutral complex with a shared decet, and, since the hydroxide ion is strongly basic, we assume that quaternary phosphonium hydroxides can act in this way—in other words, that they are not infinitely strong electrolytes. Granting this, the remaining stages are obvious : the associated hydroxide, $R_4P\cdot OH$, has the constitution of a weak acid, and, since it is formed in the presence of a large excess of hydroxide ions, will yield its anion ; and the latter can, in a single step, recover both its neutrality and its octet by the ejection of an alkyl radical as an anion, $\overset{\curvearrowleft}{R}\!-\!PR_3\leftarrow\overset{\ominus}{O}$, which, of course, is at once converted into a hydrocarbon :

$$[\overset{(8)}{R_4P}]^{\oplus} + OH^{\ominus} \rightleftharpoons \overset{(10)}{R_4P\cdot OH} \underset{H_2O}{\overset{OH'}{\rightleftharpoons}} [\overset{(10)}{R_4PO}]^{\ominus} \longrightarrow \overset{(8)}{R_3PO} + R^{\ominus}.$$

$$R^{\ominus} + H_2O \longrightarrow RH + OH^{\ominus}.$$

If the four radicals, here represented as R_4, are different, the one ejected will be that which has the greatest toleration for a negative charge.

The above mechanism contains an automatic explanation of the failure of the paraffinic degradation in the ammonium series, and is susceptible to further tests, which in due course will be applied, relating to the degradation of -onium compounds of other elements ; in the meantime we have utilised it in the interpretation of experiments undertaken with the object of ascertaining the relative anionic stabilities of different types of hydrocarbon radicals, that is, their relative affinities for a negative charge. Our procedure was to ascertain the relative progress of the competing reactions

$$[R_nR'_{n'}P]^{\oplus}\,OH^{\ominus} \longrightarrow \begin{cases} R_{n-1}R'_{n'}PO + RH \\ R_nR'_{n'-1}PO + R'H \end{cases} (n + n' = 4)$$

by analysis of the mixture of hydrocarbons, RH and R'H, evolved on decomposition of phosphonium hydroxides containing any two of the series of radicals under comparison. The phosphine oxides were usually examined qualitatively, but their physical characteristics, and those of most of these salts, rendered them unsuitable for quantitative study. The results are recorded in the following table; the analytical data from which the compositions are calculated will be found in the experimental portion.

Decomposition of Quaternary Phosphonium Hydroxides $(R_nR'_{n'}P)^{\oplus}OH^{\ominus}$.

Expt. No.	Constitution of kation.				Composition of hydrocarbons.				
	R.	n.	R′.	n'.	RH (p mols. %).	R′H (p' mols. %).	$\frac{p}{n}$.	$\frac{p'}{n'}$.	$\frac{pn'}{p'n}$.
1, 2*	Methyl	4	—	—	100	—	—	—	—
15	Benzyl	1	Phenyl	3	100	0	100	0	∞
13	Phenyl	1	Methyl	3	100	0	100	0	∞
14	Benzyl	1	,,	3	100	0	100	0	∞
5, 6	Methyl	1	Ethyl	3	100	0	100	0	∞
3, 4	,,	3	,,	1	100	0	33	0	
17†	$\beta\beta$-Diphenylethyl	1	n-Butyl	3	10	0	10	0	>50
16‡	β-Phenylethyl	1	Ethyl	3	88	7	88	2·3	38
9, 10	Ethyl	1	n-Propyl	3	23	77	23	26	0·9
7, 8	,,	3	,,	1	73	27	24	27	
18, 19	n-Propyl	1	n-Butyl	3	26	74	26	25	1·0
11	,,	3	,,	1	76	24	25	24	
12	n-Propyl	3	n-Octyl	1	77	23	26	23	1·1
20	Carbethoxymethyl	1	Methyl	3	100	0§	100	0	∞

* Benzyl alcohol added; no toluene formed (contrast Expt. 14).

† *as*-Diphenylethylene, 90%, formed.

‡ Styrene, 5%, formed.

§ Too small to be estimated.

Expt. 2 was performed in order to eliminate at the outset the rather unlikely possibility that the paraffins arising in these decompositions are secondary products formed by thermal fission of the hydroxide into a tertiary phosphine and an alcohol (compare the degradation of quaternary ammonium salts), and the reduction of the latter by the former. The result was as indicated in the note below the table, notwithstanding that benzyl alcohol was expected to undergo reduction much more readily than methyl alcohol. The formation of styrene and *as*-diphenylethylene in Expts. 16 and 17 has already been discussed. The purpose of Expt. 20 will be mentioned later.

Before reviewing the conclusions, to which these results lead, regarding the anionic stabilities of the various radicals, it is necessary to consider the evidence which the data afford for the assumption, implicit in our view of the mechanism of the reaction, that the facility of elimination of a given radical is essentially a property of the radical, and is not affected (except, possibly, to a minor extent in certain cases) by the other alkyl groups in the phosphonium complex. The truism that, if W_a and W_b are the respective probabilities that, during a small time-interval, a molecule suffers mutually exclusive changes in groups *a* and *b*, the chance that, in the same interval of time, it suffers either change is $W_a + W_b$ must clearly hold if *a* and *b* are merely imaginary labels applied to groups which in reality are identical when the total probability of reaction becomes $2W_a$; and since, in this case, the two partial reactions are of the same order with respect to each participating component, a similar statement will apply statistically to the substance in bulk, and after integration with respect to time; wherefore we are enabled to express the relative probabilities of elimination of each of the four radicals in a phosphonium complex by dividing the molar proportion of each hydrocarbon by the number of groups of corresponding kind originally present in the phosphonium kation. This calculation is included in the table, the data being expressed in the last three columns, the headings of which are self-explanatory. Now it is clear that the above statistical reasoning relates only to alternative modes of reaction of a given structure, and cannot on any *a priori* grounds be carried over from one structure to another. If, therefore, it is found by specific observations that the relative probabilities of elimination (calculated as described) of two or more groups are independent of the constitution of the phosphonium hydroxide from which they are derived, then this would show that (within the limits of the same observations) the relative facility of elimination of the groups is dependent only on the groups eliminated, and is not an orientation effect of the other radicals present in the phosphonium complex. We have carried out this test for the groups ethyl, *n*-propyl, and *n*-butyl, for which the probabilities of elimination are sufficiently similar to give an accurate meaning to the analytical results; and it will be seen (Expts. 7, 8, 9, 10, 11, 18, 19) that the relationship indicated ($pn'/p'n$ constant, for the same R and R′) holds to within the limits of analytical error. If certain theoretical expectations relating to the *n*-octyl group be admitted as relevant evidence, then Expt. 12 provides further confirmation. It may, therefore, be inferred that the tendency of each of these radicals to elimination is indeed a property of the radical, as the mechanism assumes; or, in other words, that, provided the conditions of decomposition are sufficiently nearly identical, which they certainly must be in the observations considered, the simple statistical treatment illustrated takes sufficient account of the varying structures of the phosphonium ions. Finally, it is necessary to repeat that complete generalisation is not implied; for example, one case in which we should not be surprised to observe considerable deviations from the simple relationship is that in which aryl groups are directly joined to phosphorus; for the power of aryl groups to stabilise intrinsically unstable electronic systems in an attached atom (Ingold, *Ann. Reports*, 1928, **25**, 152; Burton and Ingold, *Proc. Leeds Phil. Soc.*, 1929, **1**, ix, 421) must confer on an aryl group in an arylphosphonium complex the ability to influence the ejection of other groups as well as itself. We have not yet encountered any example suitable for the investigation of possible effects of the kind here anticipated.

On the basis just explained, the tabulated results lead to the following sequence for the order of ease of elimination of the various hydrocarbon radicals studied :

$C_6H_5{\cdot}CH_2 > C_6H_5 > CH_3 > C_6H_5{\cdot}CH_2{\cdot}CH_2 > CH_3{\cdot}CH_2$, higher alphyls.

The more facile elimination of benzyl than of ethyl is inferable from Collie's results (*loc. cit.*), but, if *iso*amyl is similar to the higher alphyl groups examined by us, Cahours and Hofmann (*loc. cit.*) should have obtained nearly 25% of *iso*pentane in the hydrocarbons evolved from triethyl*iso*amylphosphonium hydroxide.

According to our hypothesis of the mechanism of the paraffinic degradation the above order is also the order of the anionic stabilities of the radicals. Independent evidence of the truth of this inference was furnished by the study of a tetramethylphosphonium hydroxide in which a hydrogen atom in one of the methyl groups was replaced by a radical, namely, carbethoxyl, the strong electron affinity of which is very well established. The effect of this substitution should evidently be to increase the toleration of the corresponding group for a negative charge; and, accordingly, we found that the carbethoxylated radical was eliminated to the almost entire exclusion of the unsubstituted methyl groups.

Confirmatory evidence is provided by the series of hydrocarbon radicals. The relatively high stability of the benzyl anion, for instance, is supported both by indirect and by direct evidence : it accords with the theory that ionic stability generally is augmented by decentralisation of the charge (Burton and Ingold, *loc. cit.*), and with the applications of that theory to the stability of free radicals (*idem, ibid.*), to aromatic side-chain reactivity (Ingold and Rothstein, J., 1928, 1217), and to the facilitation of prototropy (Ingold and Shoppee, this vol., pp. 447, 1199), and of reduction (Burton and Ingold, this vol., p. 2023), by aryl groups; it is directly confirmed by the isolation of the benzyl anion in the form of its electrovalent sodium and tetramethylammonium salts (Schlenk and Holtz, *Ber.*, 1917, **50**, 262, 274). Schlenk and Holtz have shown that the anionic stabilities of phenyl, methyl, ethyl and the higher alphyls are all much smaller, but their results do not enable these anions to be placed in order amongst themselves. Our order for methyl and ethyl is in agreement with the established inductive effect of alkyl groups, and the difference is so marked that the very close grouping of ethyl with the higher alphyls is a little surprising. The position of β-phenylethyl is normal; for just as the substitution of phenyl for hydrogen in methyl produces an increase of anionic stability, so the introduction of a β-phenyl group into ethyl should cause the same change, but less markedly, because only that part of the anionic charge which passes by inductive transmission through a single linking reaches the position from which tautomeric distribution in the aromatic ring is facile. It is noteworthy that the position of phenyl between benzyl and methyl is different from its position in the kationic stability sequence (Part I), namely, $C_6H_5{\cdot}CH_2 > CH_3 > C_6H_5$. Benzyl heads *both* series because its electron-distributing mechanism based on the principle of the preservation of atomic octets is reversible, and thus can act for a charge of either sign; on the other hand, the order as between phenyl and methyl becomes inverted on passing from one series to the other, and this suggests that, apart from any reversible mechanism which the aromatic ring may possess for leading away a charge acquired by one of the *nuclear* atoms, the phenyl group has a stronger permanent electron affinity than the methyl group, as, indeed, is indicated by the accepted direction of the molecular polarity of toluene.

EXPERIMENTAL.

Preparation of Tertiary Phosphines.—Trimethylphosphine was prepared in ethereal solution with the aid of zinc methyl (Renshaw and Greenlaw, *J. Amer. Chem. Soc.*, 1920, **42**, 1472; Renshaw and Bell, *ibid.*, 1921, **43**, 916). Triethylphosphine was prepared by the Grignard method (Hibbert, *Ber.*, 1906, **39**, 161), which was also used for the remaining phosphines. Tri-*n*-propylphosphine was obtained by a method almost identical with that recorded by Davies, Pearse, and Jones (this vol., p. 1264), the main difference being that we distilled the Grignard product (metal-bath raised to 300°; pressure 40 mm.) instead of decomposing it with ammonium chloride solution; * our product had b. p. 72—73°/12 mm. Tri-*n*-butylphosphine was prepared by a method similarly related to that recently described by Davies and Jones (this vol., p. 33), and had b. p. 121—122°/16—17 mm. Phenyldimethylphosphine, b. p. 74—75°/12 mm., was obtained as described by Ingold, Shaw, and Wilson

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* It is not implied that this is an improvement. Our preparative work was done before the publication of the methods elaborated by Jones and his collaborators.

(J., 1928, 1280), except that a slight excess of the Grignard reagent was used, and triphenylphosphine (m. p. 79°) as described by Pfeiffer (*Ber.*, 1904, **37**, 4620) excepting that the reaction was conducted in an atmosphere of hydrogen, as in the other preparations.

Preparation and Decomposition of Phosphonium Hydroxides.

Tetramethylphosphonium Hydroxide.—(Expt. 1) The iodide, prepared from ethereal trimethylphosphine and methyl iodide, crystallised from alcohol in iridescent leaflets (Found : I, 57·8. Calc. : I, 58·2%). The corresponding *picrate*, prepared from the iodide and aqueous sodium picrate, separated from water in long needles, which are lemon-yellow in the cold, deep orange at 100°, and do not melt at 290° (Found : C, 37·6; H, 4·1. $C_{10}H_{14}O_7N_3P$ requires C, 37·6; H, 4·4%). The iodide was converted into the hydroxide with silver oxide, prepared with the aid of barium hydroxide, and the carbonate-free hydroxide solution was distilled in an atmosphere of oxygen-free nitrogen. The side arm of the flask was fitted with a condenser jacket and delivered the product into a small receiver which communicated through a tap with a large receiver below, which was kept under reduced pressure, the object of this arrangement being to reduce the volume of apparatus to be swept out with nitrogen. The upper part of the small receiver communicated with a succession of traps, two containing hydrochloric acid, two containing bromine, one water, and one potassium hydroxide solution; the last was joined to an aspirator. Decomposition commenced when the solution had attained a syrupy consistency, and proceeded smoothly at 115—125° (bath temperature). The distillate and contents of the acid traps were partly fractionated, and the first few c.c. of distillate treated with *p*-nitrobenzoyl chloride and pyridine; no methyl *p*-nitrobenzoate was obtained. The undistilled portion of the contents of the acid traps was basified and distilled in a current of ether vapour; the dried ethereal distillate yielded no salt with ethereal picric acid. The contents of the bromine traps on treatment with ice and sulphur dioxide yielded no oil. The gas in the aspirator was shown by analysis to contain methane and nitrogen, together with a trace of hydrogen.* The residue in the distillation flask had b. p. 210—212°, m. p. 140—141° (Collie records m. p. 137° for trimethylphosphine oxide). Most of its salts were very soluble and hygroscopic, but a non-hygroscopic salt was found in *hydroxytrimethylphosphonium trichloroacetate*, which separated from concentrated aqueous solution and, after being dried, crystal-

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* The gas analyses recorded in this paper were made with Bone and Wheeler's apparatus, the hydrogen being burnt on copper oxide at 280—300° before the hydrocarbons were burnt on the same reagent at red heat.

lised from ligroin in leaflets, m. p. 64° (Found : C, 23·5; H, 4·0. $C_5H_{10}O_3Cl_3P$ requires C, 23·8; H, 3·9%).

(Expt. 2) The previous experiment was repeated, but benzyl alcohol (1·5 mols.) was added to the concentrated hydroxide solution just before decomposition commenced. The volatile products were the same as before, and no toluene could be detected in the distillate receiver or the first acid trap.

Trimethylethylphosphonium Hydroxide.—(Expt. 3) The iodide was prepared in ethereal solution from trimethylphosphine and ethyl iodide, and crystallised from alcohol in leaflets (Found : I, 54·6. Calc. : I, 54·7%). The *picrate*, prepared from the iodide and aqueous sodium picrate, separated from water in long needles, m. p. 290°, which showed the same change of colour on heating as the tetramethylphosphonium salt (Found : C, 39·6; H, 4·5. $C_{11}H_{16}O_7N_3P$ requires C, 39·7; H, 4·8%). The iodide was converted into the hydroxide, and the solution distilled as described above. Examination of the distillate and of the contents of the various traps proved the absence of detectable amounts of alcohols, tertiary phosphines, and unsaturated hydrocarbons. Analysis of the gas indicated : CO_2,CO,O_2, 1·4; H_2, 1·2; CH_4, 32·9; C_2H_6, 0·0; N_2, 64·5 vols. %, the yield of methane being 88% calculated on the iodide. The residual dimethylethylphosphine oxide, b. p. 223—225°, m. p. about 73—75°, was very hygroscopic and yielded an oily salt with trichloroacetic acid.

(Expt. 4) In the preceding experiment the apparatus was not swept out *exhaustively*, because the object was to ascertain the composition of the hydrocarbons evolved, and it was undesirable to dilute the product too largely with nitrogen; furthermore, the silver salts were not washed exhaustively, as a large bulk of liquid was inconvenient. In a duplicate experiment the concentration of the hydroxide solution was determined by titration, and the apparatus was swept out thoroughly after the decomposition. Analysis gave : CO,CO_2,O_2, 0·7; H_2, 0·5; CH_4, 14·6; N_2, 84·2 vols. %, the yield of methane being 95%. It appears, therefore, that there is a definite but minor side-reaction ($<5\%$) in which hydrogen is formed.

Methyltriethylphosphonium Hydroxide.—(Expts. 5 and 6) The iodide was prepared from triethylphosphine and methyl iodide in ether, and crystallised from absolute alcohol in small leaflets (Found : I, 48·6. Calc. : I, 48·8%). The *picrate*, prepared from the iodide and aqueous sodium picrate, separated from alcohol in prisms, m. p. 239° (Found: C, 43·0; H, 5·3. $C_{13}H_{20}O_7N_3P$ requires C, 43·2; H, 5·5%). Distillation of the hydroxide gave no detectable quantities of tertiary phosphines, alcohols or unsaturated hydrocarbons. Triethylphosphine oxide was identified by the b. p. 238—240°, m. p. about 46°, and the m. p. 99—100° of its chromate (Pickard and Kenyon, J., 1906, **89**, 264). Analysis of the gases gave: CO_2, O_2, CO, 2·2, 2·0; H_2, 0·0, 0·0; CH_4, 38·5, 38·7; C_2H_6, 0·0, 0·0; N_2, 59·5, 59·3 vols. %, the yield of methane calculated on the original iodide being 88, 89%.

*Triethyl-*n*-propylphosphonium Hydroxide.*—(Expts. 7 and 8) The *iodide* was prepared from *n*-propyl iodide and triethylphosphine in absolute alcohol (over-night at 30°), precipitated by the addition of ether, and crystallised from alcohol, from which it separated in colourless needles (Found: I, 43·9. $C_9H_{22}IP$ requires I, 44·1%). The *picrate*, obtained from the iodide and sodium picrate, separated from alcohol in rosettes of foliated needles, m. p. 91° (Found: C, 46·0; H, 6·3. $C_{15}H_{24}O_7N_3P$ requires C, 46·3; H, 6·2%). Distillation of the hydroxide yielded neither phosphines nor olefins, and the gas gave the following results on analysis: CO, 1·0, 1·0; H_2, 0·9, 0·6; hydrocarbons, 28·5, 28·4; N_2, 69·6, 70·0 vols. %; 1 vol. of the hydrocarbons gave 2·271, 2·277 vols. CO_2, which corresponds to C_2H_6, 72·9, 72·3; C_3H_8, 27·1, 27·7 vols. %. The yield of hydrocarbons is 90% calculated on the iodide used. The phosphine oxides had b. p. 245—247°, m. p. about 37° (Found: C, 55·4; H, 11·3. Calc. for Et_3PO: C, 53·7; H, 11·2%. Calc. for Et_2Pr^aPO: C, 56·8; H, 11·5%).

*Ethyltri-*n*-propylphosphonium Hydroxide.*—(Expts. 9 and 10) Tri-*n*-propylphosphine and ethyl iodide were allowed to react in alcohol at the ordinary temperature; the *iodide*, precipitated with ether, crystallised from alcohol–ethyl acetate in needles (Found: I, 40·1. $C_{11}H_{26}IP$ requires I, 40·2%). The *picrate*, prepared from the iodide and aqueous sodium picrate, separated from benzene–ligroin in needles, m. p. 64° (Found: C, 48·7; H, 6·9. $C_{17}H_{28}O_7N_3P$ requires C, 48·9; H, 6·7%).

Distillation of the hydroxide yielded only negligible traces of basic volatile products; a perceptible quantity of heavy oil was, however, obtained from the bromine traps, but it was far too small to identify. The gaseous products on analysis gave: CO, 0·5, 0·5; H_2, 0·5, 0·5; hydrocarbons, 29·2, 29·3; N, 69·8, 69·7 vols. %; 1 vol. of the hydrocarbons gave 2·757, 2·773 vols. CO_2, corresponding to C_2H_6, 24·3, 22·7; C_3H_8, 75·7, 77·3 vols. %. Yield of hydrocarbons, 90% calculated on the iodide used. The mixture of phosphine oxides had b. p. 253—257°, but it did not solidify.

*Tri-*n*-propyl-*n*-butylphosphonium Hydroxide.*—(Expt. 11) A mixture of tri-*n*-propylphosphine (8 c.c.), alcohol (16 c.c.), and *n*-butyl iodide (15 g.) was kept at the ordinary temperature over-night and then heated for 1 hour on the steam-bath. The quaternary *iodide*, precipitated with ether, crystallised from ethyl acetate in needles, m. p. 239—240° (Found : I, 36·6. $C_{13}H_{30}IP$ requires I, 36·9%). The *picrate*, prepared from the iodide and sodium picrate, crystallised from dilute acetic acid in small prisms, m. p. 67° (Found : C, 51·0; H, 6·9. $C_{19}H_{32}O_7N_3P$ requires C, 51·2; H, 7·2%). Decomposition of the hydroxide yielded scarcely ponderable traces of volatile basic products and small but definite traces of something which formed a heavy oil with bromine. The phosphine oxides partly crystallised when kept over sulphuric acid in a vacuum, but the crystalline constituent was not isolated because it vanished when air was admitted to the desiccator. The gaseous product on analysis gave : CO_2,O_2,CO, 1·6; H_2, 1·0; hydrocarbons, 23·4; N_2, 74·0 vols. %; 1 vol. of the hydrocarbons gave 3·240 vols. CO_2, which corresponds to C_3H_8, 76·0; C_4H_{10}, 24·0 vols. %. Yield of hydrocarbons, 85% calculated on the iodide used.

*Tri-*n*-propyl-*n*-octylphosphonium Hydroxide*.—(Expt. 12) A solution of tri-*n*-propylphosphine (9 g.) and *n*-octyl bromide (15 g.) in alcohol (20 c.c.) was kept at the ordinary temperature over-night and heated on the steam-bath for 1 hour. The addition of ether precipitated the quaternary bromide as an oil, and the ether and alcohol were therefore evaporated and the excess of *n*-octyl bromide was removed by distillation under reduced pressure. The liquid bromide was converted into the iodide with sodium iodide in alcohol, and into the chloride *via* the hydroxide, but these salts also were liquids; a very fusible, but solid *chloroaurate* was finally obtained, which separated from ligroin–alcohol in prisms, m. p. 38° (Found : C, 32·7; H, 6·2. $C_{17}H_{38}P,AuCl_4$ requires C, 33·2; H, 6·2%). The hydroxide on decomposition gave no detectable traces either of volatile bases or of olefins. The octane was collected as liquid, dried, weighed, and distilled (b. p. 125°). The gaseous product on analysis gave : CO_2,O_2,CO, 1·7; H_2, 0·8; hydrocarbon, 23·4; N_2, 74·1 vols. %. 1 Vol. of the hydrocarbon gave 2·993 vols. CO_2, wherefore it was propane and contained no significant quantity of octane vapour. Yields : octane, 19·8; propane, 66·2; total, 86%; mols. octane/mols. propane = 23/77.

Phenyltrimethylphosphonium Hydroxide.—(Expt. 13) The iodide, crystallised from alcohol, had m. p. 236° (Michaelis, *Annalen*, 1876, **181**, 359, records m. p. 205°), but the picrate prepared from our iodide was pure and its m. p. agreed with that recorded by Ingold, Shaw, and Wilson (*loc. cit.*). The hydroxide solution, prepared at 0°, underwent decomposition from the early stages of concentration at 100°. The products included no perceptible trace either of olefins or of volatile bases, and no gaseous hydrocarbons. Benzene

(b. p. and conversion into *m*-dinitrobenzene) and trimethylphosphine oxide (b. p. and m. p.) were, however, obtained in good yield.

Benzyltrimethylphosphonium Hydroxide.—(Expt. 14) The *bromide*, prepared from trimethylphosphine and benzyl bromide in ethereal solution, crystallised from alcohol–ligroin in needles, m. p. 222° (Found : Br, 32·1. $C_{10}H_{16}BrP$ requires Br, 32·3%). It yielded a picrate agreeing in m. p. with that described by Ingold, Shaw, and Wilson (*loc. cit.*). The decomposition of the hydroxide took place exactly as in the preceding case, and the products were the same except that toluene (b. p. and conversion into trinitro-derivative) replaced benzene.

Triphenylbenzylphosphonium Hydroxide.—(Expt. 15) The *bromide*, prepared from triphenylphosphine (10 g.) and benzyl bromide (10 g.), crystallised from water or alcohol–ethyl acetate in needles, m. p. 288° (Found : Br, 18·6. $C_{25}H_{22}BrP$ requires Br, 18·5%). The picrate could not be satisfactorily crystallised. The hydroxide solution was prepared at 0°, but the perceptible odour of an aromatic hydrocarbon indicated the commencement of decomposition. The mixture was therefore distilled without filtration from the silver bromide, and toluene (b. p. and oxidation to benzoic acid) passed over in the first portion of the aqueous distillate. The distillation was then stopped, and the liquid in the distilling flask cooled and filtered. Evaporation of the filtrate gave a scarcely perceptible residue. The silver bromide was extracted with acetone in a Soxhlet extractor, and the acetone solution concentrated and poured into water. The precipitate was almost pure triphenylphosphine oxide, m. p. 154—156° (Found : C, 77·3; H, 5·4. Calc. : C, 77·7; H, 5·4%). Evaporation of the aqueous acetone gave a little impure oxide, m. p. about 140°. The recovery of distilled toluene was 70%; that of triphenylphosphine oxide was 100%, of which 92% was almost pure and 8% crude.

β-*Phenylethyltriethylphosphonium Hydroxide.*—(Expt. 16) Triethylphosphine (1 part), β-phenylethyl chloride (2 parts), and alcohol (2 parts) were heated together at 60—70° for 3 hours, and poured into ether. The quaternary salt was extracted with water, and its aqueous solution washed well with ether and evaporated. The syrupy chloride crystallised after being kept for several months over sulphuric acid, but was inconveniently hygroscopic for analysis. The *picrate*, prepared from it with sodium picrate, crystallised with difficulty from chloroform–ligroin in prisms, m. p. 70° (Found : C, 53·1; H, 5·5. $C_{20}H_{26}O_7N_3P$ requires C, 53·2; H, 5·8%). A portion of the hydroxide solution prepared from the chloride and silver oxide was titrated to ascertain its concentration, and the remainder distilled. The contents of the traps containing acid were basified under benzene, and the dried benzene extract treated with trinitroanisole; addition of ligroin precipitated a small amount of solid, which after crystallisation from alcohol was identified as methyltriethylphosphonium picrate. No trace of bromides was obtained from the traps containing bromine. The gaseous product on analysis gave: O_2,CO,H_2, 0·2; hydrocarbons, 10·4; N_2, 89·6 vols. %; 1 vol. of the hydrocarbons gave 2·002 vols. CO_2, wherefore they consisted essentially of ethane. The oily distillate was separated, dried, weighed, treated with bromine until just coloured, and distilled under reduced pressure. The distillate was identified as ethylbenzene (b. p. under ordinary pressure, oxidation to benzoic acid, and analysis: Found: C, 90·4; H, 9·4%), and the residue as styrene dibromide (m. p. and mixed m. p. 73—74°). Yields: styrene, weighed as dibromide, 4·5%; ethylbenzene, by deducting styrene from total liquid hydrocarbons, 84·1%; ethane, 6·6%; total recovery of hydrocarbons, 95·2%. The residue in the distilling flask had the b. p. and approximately the m. p. of triethylphosphine oxide.

ββ-*Diphenylethyltri*-n-*butylphosphonium Hydroxide*.—(Expt. 17) A mixture of tri-*n*-butylphosphine (1 part), ββ-diphenylethyl chloride (2 parts), and alcohol (1 part) was kept at 40—45° for several days, heated for a short time at 60—70°, poured into ether, and extracted with water. The aqueous solution was washed with ether, freed from the solvent by passage of air, and treated with excess of silver oxide. A portion of the hydroxide solution was used for standardisation by titration, and the remainder distilled in nitrogen under reduced pressure in an apparatus modified by the omission of the customary bromine traps and the replacement of the aspirator by an exhausted bulb, communicating with the acid traps by a stop-cock, and having a side arm to facilitate the subsequent transference of the gas to an ordinary holder by filling with water. At the end of the distillation the apparatus was swept out with nitrogen until the pressure in the bulb was slightly less than the atmospheric pressure; liquid bromine was then let in (through the side arm), and a further amount of nitrogen to render the pressure slightly greater than that of the atmosphere. The bromine was drawn off and examined for olefin bromides, with negative results. The residual gas was analysed, but contained neither hydrogen nor hydrocarbons. The distillate was acidified and extracted with ligroin (b. p. 40—45°), and the aqueous solution, combined with the contents of the acid traps, was basified and extracted with ether. The concentrated ethereal solution was treated with methyl iodide, and tri-*n*-butylphosphine was thus identified in the form of its methiodide (m. p. 132—133°. Found: I, 36·6. Calc.: I, 36·8%).

The ligroin was removed from the extract by distillation up to 60° (bath temperature) at 25 mm., and the residue weighed and completely distilled (b. p. 150—155°/24—25 mm.). The product was unsaturated towards bromine and permanganate, and its analysis (Found: C, 93·1, 93·2; H, 6·9, 7·0%) was consistent with the assumption that it was *as*-diphenylethylene (Calc.: C, 93·3; H, 6·7%) but did not exclude the presence of *as*-diphenylethane (Calc.: C, 92·3; H, 7·7%) as a minor constituent. The refractive index was therefore determined with the following results: for an authentic specimen of *as*-diphenylethylene, $n_D^{20^\circ}$ 1·6091; for the above product, $n_D^{21^\circ}$ 1·6059. Since Konowalow and Jatzewitsch record for *as*-diphenylethane, $n_D^{20^\circ}$ 1·5761 (*J. Russ. Phys. Chem. Soc.*, 1905, **37**, 543), the above results indicate the presence of 10% of *as*-diphenylethane. On this assumption the total recovery of hydrocarbons is 91·3%. Definite identification of the constituents was effected by ozonolysis. The product obtained by treatment at 0° in chloroform solution with ozonised oxygen was boiled with water and the volatile products were passed through a trap containing *p*-nitrophenylhydrazine in acetic acid; a copious precipitate of formaldehyde-*p*-nitrophenylhydrazone, m. p. 181—182°, was obtained. The residual oil did not solidify and was therefore not pure benzophenone. It was digested for 2 hours on the steam-bath with a large excess of hydroxylamine hydrochloride and sodium hydroxide in aqueous alcohol, and the product extracted with ether after addition of dilute sulphuric acid. The not quite completely solid mass left after removal of the ether (a long column was used) was washed with a small amount of cold ligroin; it then had m. p. 142—143° and was identified as benzophenoneoxime by mixed m. p. (143—144°). The residue from the ligroin extract distilled almost completely at 20 mm. from a bath at 160—165° (the quantity was insufficient for b. p. determination). The distillate was warmed for a short time with finely powdered aluminium chloride, and the product treated with ice and hydrochloric acid. The precipitate was collected, dried, and sublimed, and 9 : 10-dimethyl-9 : 10-dihydroanthracene was obtained in long yellow needles, m. p. 181° (Radziewanowski, *Ber.*, 1894, **27**, 3228). The formation of this substance established the presence of *as*-diphenylethane (*idem, ibid.*), especially as a control experiment with *as*-diphenylethylene failed to yield the anthracene derivative. The small residue from the distillation of the hydroxide was partly crystalline. After addition of water the solid was collected, dried, and crystallised from benzene–ligroin, from which leaflets separated, m. p. 189—190°. The m. p. and analytical data (Found: C, 93·0; H, 6·7%) agree with those required (Calc.: C, 93·3; H, 6·7%) for Hepp's polymeric *as*-diphenylethylene (*Ber.*, 1874, **7**, 1409), and on this assumption the compound represents another 1·2% of *as*-diphenylethylene. The aqueous filtrate from the solid hydrocarbon, on complete evaporation, left a viscous syrup which may have been tri-*n*-butylphosphine oxide: the amount was too small for identification.

n-*Propyltri*-n-*butylphosphonium Hydroxide.*—(Expts. 18 and 19) A mixture of equal weights of tri-*n*-butylphosphine, *n*-propyl iodide, and alcohol was kept over-night, diluted with ether, and extracted with water. The aqueous solution was extracted with ether, and treated with a stream of air to remove that solvent, and with a suspension of silver oxide. Distillation of the hydroxide solution yielded no volatile basic products, but traces of a heavy oil were obtained from the bromine traps. The residual phosphine oxides did not crystallise and were not examined. The gases which were collected gave on analysis: CO, 1·2, 1·0; H_2, 0·4, 0·9; hydrocarbons, 21·6, 28·3; N_2, 76·8, 69·8 vols. %; 1 vol. of the hydrocarbons gave 3·737, 3·742 vols. CO_2, which corresponds to C_3H_8, 26; C_4H_{10}, 74 vols. %.

ω-*Carbethoxytetramethylphosphonium Hydroxide.*—(Expt. 20) The corresponding chloride was prepared from trimethylphosphine and ethyl chloroacetate in ether–alcohol in the cold, and was precipitated by addition of more ether. It separated from ether–alcohol in hygroscopic needles, m. p. 160° (decomp.). The *picrate*, precipitated by the addition of saturated aqueous sodium picrate to a concentrated solution of the chloride, separated from alcohol in rhombs, m. p. 124—125° (Found: C, 39·7; H, 4·7. $C_{13}H_{18}O_9N_3P$ requires C, 39·9; H, 4·6%). Preliminary tests having shown that the hydroxide solution undergoes rapid hydrolysis as well as the usual decomposition, the product obtained by treating an aqueous solution of the chloride with silver oxide was distilled, without filtration, to two-thirds of its bulk. The apparatus was swept out with nitrogen, but the gas which was collected contained neither hydrogen nor hydrocarbons. The liquid distillate was redistilled, and alcohol detected in the first portion of the distillate by the iodoform reaction and the preparation of ethyl *p*-nitrobenzoate. The residual suspension was acidified with hydrochloric acid, filtered, and distilled to a small bulk; again the collected gas was free from hydrogen and hydrocarbons. The distillate was neutralised and evaporated to dryness, and the residue shown to contain acetate. The undistilled portion was basified with silver oxide, and the filtered solution distilled up to 200° (bath temperature). Analysis of the collected gases gave: CO, 0·4; H_2, 0·5; CH_4, 0·9; N_2, 98·2 vols. %. No basic product was obtained from the acid traps, and no olefin bromides from the bromine solutions. The residue had the b. p. and m. p. of trimethylphosphine oxide and was definitely identified as such by conversion into its trichloroacetate (p. 2349) (Found : C, 23·9; H, 4·0%).

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