## **136.** *Influence of Poles and Polar Linkings on the Course pursued by Elimination Reactions. Part XVII. Thermal Decomposition of Phosphonium Ethoxides.*

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It has been shown that quaternary phosphonium hydroxides may decompose in two directions, to give either a paraffin and a phosphine oxide or an olefin and a phosphine (Part V, J., 1929, 2342). When the alkyl group eliminated is devoid of a β-hydrogen atom (methyl), paraffinic degradation is naturally the sole reaction. When a β-hydrogen atom is present, but is not internally activated by adjacent electron-releasing groups (ethyl), the paraffin reaction is still the exclusive mode of decomposition. When, however, the hydrogen atom is activated by a single adjacent phenyl group (β-phenylethyl), olefinic degradation becomes appreciable, and when two such activating groups are present (ββ-diphenylethyl) the olefin reaction predominates.

The decomposition of phosphonium alkoxides has not previously been investigated. We thought that, since the paraffin reaction of hydroxides involves the separation of the constituents of the hydroxide ion, the replacement of this ion by an alkoxide ion might cause a more extensive supersession of the paraffin by the olefin reaction than is displayed by the results summarised above. There was also a possibility of the formation of ethers by analogy with the corresponding reaction of ammonium alkoxides (Part XV, this vol., p. 523).

We have studied four examples, in which the groups eliminated are those to which reference was made in the first paragraph. Tetramethylphosphonium ethoxide passed smoothly into propane and trimethylphosphine oxide; no ether, no phosphine, and naturally no olefin, was formed. Similarly tetraethylphosphonium ethoxide gave *n*-butane and triethylphosphine oxide, but no ethylene or triethylphosphine. From β-phenylethyltriethylphosphonium ethoxide the main products were *n*-butylbenzene and triethylphosphine oxide, whilst styrene and triethylphosphine were formed in small amount. Finally, ββ-diphenylethyltriethylphosphonium ethoxide gave *αα-diphenyl-*n*-butane* and triethylphosphine oxide in small proportion only, the main products being *as*.-diphenylethylene and triethylphosphine. The following table summarises these results, together with those relating to the corresponding phosphonium hydroxides :

| $\{RR'_3P\}^{\oplus}OH^{\ominus}$. | | Olefin ($R - H_\beta$), | Paraffin ($R + X_\alpha$), | $\{RR'_3P\}^{\oplus}OX^{\ominus}$. | | | Olefin ($R - H_\beta$), | Paraffin ($R + X_\alpha$), |
|---|---|---|---|---|---|---|---|---|
| R. | R′. | %. | %. | R. | R′. | OX. | %. | %. |
| $CH_3\cdot$ | Me | 0 | 100 | $CH_3\cdot$ | Me | OEt | 0 | 100 |
| $CH_3\cdot CH_2\cdot$ | Et | 0 | 100 | $CH_3\cdot CH_2\cdot$ | Et | OEt | 0 | 100 |
| $CH_2Ph\cdot CH_2\cdot$ | Et | 5 | 95 | $CH_2Ph\cdot CH_2\cdot$ | Et | OEt | 10 | 90 |
| $CHPh_2\cdot CH_2\cdot$ | $Bu^{\alpha}$ | 90 | 10 | $CHPh_2\cdot CH_2\cdot$ | Et | OEt | 95 | 5 |

Two conclusions may be drawn with regard to the mechanism of the paraffinic degradation of phosphonium compounds.

(1) In Part V the hypothesis was advanced that the paraffin reaction of phosphonium hydroxides depends on the formation of compounds containing quinquecovalent phosphorus, and the complete process was formulated as follows :

$$\{R_4\overset{(8)}{P}\}^{\oplus}OH^{\ominus} \longrightarrow R_4\overset{(10)}{P}\cdot OH \longrightarrow R_4\overset{(10)}{P}O^{\ominus} + H^{\oplus} \longrightarrow R_3\overset{(8)}{P}O + R^{\ominus} + H^{\oplus} \longrightarrow R_3\overset{(8)}{P}O + RH$$

It is still possible that this is wholly correct for hydroxides, but since alkoxides undergo the same reaction, the postulated ionic dissociation of the quinquecovalent phosphorus complex cannot be thought of as an *essential* step without which the reaction cannot proceed, and the simpler formulation,

$$\{R_4P\}^{\oplus}OX^{\ominus} \longrightarrow R_4\overset{(10)}{P}\cdot OX \longrightarrow R_3PO + RX,$$

the adoption of which is necessary for the reaction of alkoxides, is also a possible variant of the mechanism.

(2) The remarkably close similarity between the results obtained with hydroxides and with ethoxides shows that, whatever may be the effect of the replacement of the hydroxide ion by the ethoxide ion on the olefin reaction, there is also a closely parallel effect on the paraffin reaction. But the facility of the olefin reaction is fundamentally dependent on the basicity of the attacking anion (Part I, J., 1927, 997), and it is known that the replacement of the hydroxide ion by the more basic ethoxide ion is a sufficient change to produce very great facilitation (Part VII, J., 1930, 705). It follows that the paraffin reaction must be similarly dependent on the basicity of the anion, and this shows that the slow (rate-determining) stage of the reaction formulated above is the initial stage, the speed of which, probably proportional to $f_{\pm}^{2}[R_4P^{\cdot}][OX']$, where $f$ is the activity coefficient of the univalent ions, depends *inter alia* on the chemical activity of the unshared electrons of the anion.

## EXPERIMENTAL.

Equiv. amounts of $CH_2Ph{\cdot}CH_2Br$ (prep. from $CH_2Ph{\cdot}CH_2{\cdot}OH$, aq. HBr, and conc. $H_2SO_4$), and $PEt_3$ in $Et_2O$ (Hibbert, *Ber.*, 1906, **39**, 161) were kept at room temp. for several hrs. Most of the $Et_2O$ was removed through a long Dufton column, and the residue was refluxed with $MeNO_2$. The $\{P(CH_2{\cdot}CH_2Ph)Et_3\}^{\cdot}Br'$, pptd. in cryst. form by cautious addition of $Et_2O$, was crystallised from EtOH and dried in vac. over $P_2O_5$. ββ-*Diphenylethyltriethylphosphonium chloride* was similarly prepared from $CHPh_2{\cdot}CH_2Cl$ and $PEt_3$ in $Et_2O$–$MeNO_2$ and crystallised from MeOH (Found: Cl, 10·5. $C_{20}H_{28}PCl$ requires Cl, 10·6%). These and the other phosphonium halides (later paper) were converted into ethoxides by treatment with 1 equiv. of NaOEt in Ca-dried EtOH, and the EtOH solutions of phosphonium ethoxides were distilled in N. In each case decomp. set in at about 100—120° and was completed at about 140° (bath temps.).

The cryst. residue from the distillation of $\{PMe_4\}^{\cdot}OEt'$ had the characteristic physical properties of a phosphine oxide, had b. p. 210° and m. p. 140°, and was definitely identified as $Me_3PO$ by means of the trichloroacetate (Fenton and Ingold, J., 1929, 2350). The alc. distillate had the odour of a phosphine and on treatment with MeI and subsequently with excess of dry $Et_2O$ gave a definitely visible amount of salt, which, however, was insufficient for purification and analysis. This is a possible indication of the incursion of the reaction which leads to an ether, and this form of degradation will be sought in more favourable examples. The gaseous products of the reaction were passed through Br and into the aspirator in a current of N. The Br gave no trace of oil on treatment with ice and $SO_2$. The gas in the aspirator was shown by analysis (Bone–Wheeler) to consist of N and a hydrocarbon which on combustion gave 3·10 vols. of $CO_2$ and was therefore $C_3H_8$.

The cryst. residue from the distillation of $\{PEt_4\}^{\cdot}OEt'$, evidently a phosphine oxide, had b. p. 240° and was identified as $Et_3PO$ by means of its chromate (Pickard and Kenyon, J., 1906, **89**, 264). The alc. distillate had the odour of a phosphine but the quantity was insufficient to yield a visible amount of methiodide. The Br through which the gaseous decompn. products were passed yielded no olefin bromide. The gases collected consisted of N and a hydrocarbon which on combustion gave 4·05 vols. of $CO_2$ and was therefore $C_4H_{10}$ (yield *ca.* 90%).

When $\{P(CH_2{\cdot}CH_2Ph)Et_3\}^{\cdot}OEt'$ was decomposed, the gas swept by N into the aspirator contained insufficient hydrocarbon to permit accurate analysis, and the Br, placed to collect any unsatd. gaseous hydrocarbons, yielded no olefin bromide on decompn. with ice and $SO_2$. The alc. distillate was poured into $H_2O$ and extracted with $CCl_4$, and the extract was dried and treated with sufficient $CCl_4$ solution of Br to give a faint permanent colour. Evaporation of the solvent yielded styrene dibromide (comparison; m. p. and mixed m. p.) in yield of 10%. The residue in the decomposition flask was extracted with $H_2O$, and the oil identified as butylbenzene by its b. p. (182°) and by oxidation to $Ph{\cdot}CO_2H$. The aq. extract on evaporation gave $Et_3PO$, identified as in the previous expt. In another expt., part of the alc. distillate was treated with MeI and then with excess of $Et_2O$; the $\{PMeEt_3\}^{\cdot}I'$ was collected and identified by conversion into picrate (comparison; m. p. and mixed m. p.). The remainder was poured into $H_2O$ and extracted with $CCl_4$, and the styrene estimated by titration with standard Br in $CCl_4$. The residue in the flask was distilled in steam, the distillate extracted with $CCl_4$, and the extract similarly titrated. The total estimated amount of styrene was 10·6%.

The distillation of $\{P(CH_2{\cdot}CHPh_2)Et_3\}^{\cdot}OEt'$ was conducted in N under reduced press., and any products uncondensed at 0° were passed through dil. aq. HCl and into an exhausted bulb, communicating with the acid trap through a stop-cock and having a side arm to facilitate the transference of gas to an ordinary holder by filling with $H_2O$. At the end of the distillation, the apparatus was swept out with N until the press. in the bulb was slightly less than 1 atm.; Br was then let in (through the side arm), and a further quantity of N to raise the press. slightly above 1 atm. The Br was then drawn off and examined for olefin bromides, with negative results. The residual gases were transferred through aq. KOH to an ordinary holder and analysed; but they contained no hydrocarbons. The distillate was poured into dil. HCl, combined with above-mentioned HCl soln., and extracted with $CCl_4$. The residue in the decomposition flask was also extracted with $H_2O$ and $CCl_4$, and the combined $CCl_4$ extracts dried and distilled. The bulk of the distillate had b. p. 134—139°/14—16 mm., was unsatd. to $KMnO_4$ and Br, and was proved to be $CPh_2{:}CH_2$ by analysis (Found : C, 92·9; H, 6·7. Calc. : C, 93·3; H, 6·7%), refractive index, $n_D^{20^\circ}$ 1·6085, and by ozonolysis to $CH_2O$ (*p*-nitrophenylhydrazone, m. p. and mixed m. p. 181°) and $CPh_2{:}O$ (oxime, m. p. and mixed m. p. 142—144°). There was also a small fraction of b. p. *ca.* 170—175°/15 mm., and a residue which decomposed. The fraction was *αα-diphenyl*-n-*butane*, probably slightly impure (Found : C, 91·7; H, 8·5. $C_{16}H_{18}$ requires C, 91·4; H, 8·6%), because on oxidation with warm alk. $KMnO_4$ it gave $CPh_2{:}O$, which was isolated by extraction with $Et_2O$ after effecting complete solution of the Mn oxides by passage of $SO_2$; the partly-solid mass which was left after removal of the $Et_2O$ was digested with $NH_2OH,HCl$ and 1 equiv. of NaOH in aq. EtOH, and the product, extracted with $Et_2O$ after addition of dil. $H_2SO_4$, was identified (comparison; m. p. and mixed m. p.) as benzophenone-oxime. The aq. HCl soln. was basified under $Et_2O$ and the $Et_2O$ extract therefrom dried and treated with MeI; the methiodide was converted into the methopicrate which was identified as methyltriethylphosphonium picrate (comparison; m. p. and mixed m. p.). The aq. extract from the decomposition flask was evaporated, but the hygroscopic syrup obtained did not suffice for distillation. It was, however, converted into the characteristic chromate of $Et_3PO$.

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