232. *Influence of Poles and Polar Linkings on the Course pursued by Elimination Reactions. Part XIX. Thermal Decomposition of Phosphonium Chlorides.*

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The available information concerning the thermal decomposition of quaternary phosphonium chloride is summarised in the following table (Am = amyl; Bz = benzyl):

No.	R_4 in $(R_4P)^{\cdot}Cl'$.	Products.	Ref.	No.	R_4 in $(R_4P)^{\cdot}Cl'$.	Products.	Ref.
1	Et_4	$C_2H_4+PEt_3,HCl$	(*a*)	6	Me_2Et_2	$C_2H_4+PMe_2Et,HCl$	(*d*)
2	Et_3Bz	$C_2H_4+PEt_2Bz,HCl$	(*b*)	7	Et_3Pr^a	$C_2H_4+PEt_2Pr^a,HCl$	,,
3	Me_4	$C_2H_4+PMe_3,HCl$	(*c*)	8	Et_3Am	$C_2H_4+PEt_2Am,HCl$	,,
4	Me_3Et	$C_2H_4+PMe_3,HCl+$ PMe_2Et,HCl	(*d*)	9	Et_2Bz_2	$C_2H_4+PEtBz_2,HCl$	,,
				10	$EtBz_3$	C_2H_4+Stilbene$+$ $PEt_2Bz,HCl+PBz_3,HCl$	,,
5	$MeEt_3$	$C_2H_4+PMeEt_2,HCl$	,,				

(*a*) Letts and Collie, *Phil. Mag.*, 1886, **22**, 183; (*b*) Collie, *ibid.*, 1887, **24**, 27; (*c*) J., 1888, **53**, 636; (*d*) *Idem*, *ibid.*, p. 714.

In examples 1, 2, and 4—10, an ethyl group is present and is eliminated as ethylene (in reactions 1 and 2 the products indicated are stated to be formed "nearly quantitatively"); it was concluded that the decomposition of phosphonium chlorides proceeds similarly to olefinic degradation of ammonium hydroxides. In examples 3 and 4 a methyl group appears as ethylene and in example 10 a benzyl group as stilbene; in these cases the intermediate formation of a bivalent-carbon compound, *e.g.*, methylene, was presumed.

Although Part V (J., 1929, 2342) was concerned primarily with phosphonium hydroxides, the degradation of phosphonium compounds generally was considered. It was shown that the modes of degradation characteristic of ammonium compounds, together with all the constitutional conditions governing these reactions, should apply in the phosphonium series also, but that, in addition to these forms of reactivity, phosphonium compounds may exhibit yet another form, namely, that which is attributable to the presumed ability of the phosphorus atom to expand its octet and thus temporarily to co-ordinate an anion. The supersession in phosphonium hydroxides of the olefinic type of degradation characteristic of ammonium hydroxides is readily explained on this basis (Part V), which, however, offers no immediate suggestion to account for the alleged reappearance in phosphonium chlorides of olefinic degradation in place of the elimination of an alkyl chloride, which is the normal reaction of ammonium chlorides. On the contrary, the chloride ion, which is insufficiently basic to effect β-proton elimination in the majority of ammonium salts, should be still less able to do this in phosphonium salts, because, first, the inductive effect of the phosphonium pole is less (Part V), and, secondly, in so far as the phosphorus atom is able to co-ordinate it offers an alternative point of attraction for the anion. Thus, theory indicates that phosphonium chlorides, even more than ammonium chlorides, should yield alkyl chlorides rather than olefins, and accordingly we were disposed to doubt the evidence of widely occurring olefinic degradation contained in the records summarised above.

We have revised the first four of these examples. In each case reaction proceeded in substantially one direction, the products being, as expected, an alkyl chloride and a phosphine. In example (2), even the phosphine was different from that reported in the work cited above, but it is consistent with analogy that the benzyl group (Bz), rather than the ethyl group, should suffer elimination in this case.

(1) $(PEt_4)^{\cdot}Cl' \longrightarrow EtCl+PEt_3$ (3) $(PMe_4)^{\cdot}Cl' \longrightarrow MeCl+PMe_3$
(2) $(PEt_3Bz)^{\cdot}Cl' \longrightarrow BzCl+PEt_3$ (4) $(PMe_3Et)^{\cdot}Cl' \longrightarrow MeCl+PMe_2Et$

At present we are not able to account satisfactorily for the differences between our results and those previously recorded.

We have not revised the remaining six examples, because the results just described seem sufficient to show that the decomposition of phosphonium chlorides is normal and not analogous to the olefinic degradation of ammonium hydroxides.

EXPERIMENTAL.

An ethereal solution of trimethylphosphine was prepared by the aid of dimethylzinc as described by Renshaw and Greenlaw (*J. Amer. Chem. Soc.*, 1920, **42**, 1472) and Renshaw and Bell (*ibid.*, 1921, **43**, 916). Addition of methyl iodide caused the precipitation of tetramethylphosphonium iodide which was crystallised from alcohol (Found : I, 57·8. Calc. : I, 58·2%). The use of ethyl iodide similarly led to trimethylethylphosphonium iodide (Found : I, 54·6. Calc. : I, 54·7%). An ethereal solution of triethylphosphine was prepared by the Grignard method, the whole Grignard product being distilled instead of being decomposed with water (Hibbert, *Ber.*, 1906, **39**, 161). Ethyl bromide was added, and, in order to obtain the best possible yield of tetraethylphosphonium bromide, the reaction was completed by removing part of the ether by distillation with a long Dufton column, adding nitromethane, boiling under reflux for 16 hours, and pouring the solution into excess of ether. The precipitated salt was crystallised from alcohol (Found : Br, 35·0. Calc. : Br, 35·2%). For the preparation of benzyltriethylphosphonium bromide, an ethereal solution of triethylphosphine was allowed to react with benzyl bromide at 30° for 1 hour, and the precipitated salt was washed with ether and crystallised from alcohol–ether (Found : Br, 24·0. Calc. : Br, 24·3%). The phosphonium bromides and iodides were converted, *via* the hydroxides, into the corresponding chlorides which were crystallised from alcohol, and benzyltriethylphosphonium chloride was also prepared by direct interaction of benzyl chloride with triethylphosphine in ether.

1. The chlorides were distilled in oxygen-free nitrogen. In the case of tetraethylphosphonium chloride decomposition commenced above 350° and was completed at 380° (bath temperatures). Triethylphosphine distilled and condensed at the ordinary temperature, and ethyl chloride below—30°. The former was identified by the preparation of its methiodide and thence of its methopicrate, which was compared (m. p. and mixed m. p.) with an authentic specimen. The ethyl chloride was similarly identified by interaction with trimethylamine in alcohol, conversion of the quaternary ammonium chloride into the corresponding picrate, and comparison of this with trimethylethylammonium picrate. A trace of a sublimate, apparently triethylphosphonium chloride, was found on the upper portion of the decomposition flask. Any gases which escaped condensation were passed through liquid bromine, as were also the whole of the nitrogen sweepings. The bromine solution on decomposition with ice and sulphur dioxide yielded an amount of heavy oil, possibly ethylene dibromide, too small for definite identification.

2. Decomposition of benzyltriethylphosphonium chloride commenced above 300° and was completed at 340° (bath temperatures), and the distillate was received in dilute hydrochloric acid. From this distillate the oil was collected and identified as benzyl chloride by its odour, b. p., and conversion by treatment with alcoholic trimethylamine into benzyltrimethylammonium chloride, and thence into the picrate (m. p. and mixed m. p.). The acid solution was basified under ether, and the phosphine identified as triethylphosphine as in the preceding experiment. The bromine through which, as usual, all the gaseous products were passed, yielded only a minute trace of oil after treatment with sulphur dioxide and ice.

3. Decomposition of tetramethylphosphonium chloride proceeded above 360° (bath temperature). The distillate was received in dilute hydrochloric acid at 0°, which, after basification under ether, gave trimethylphosphine. The latter in ethereal solution was converted into the methiodide (Found : I, 58·0. Calc. : I, 58·2%) and thence into the methopicrate, which was compared with tetramethylphosphonium picrate (m. p. and mixed m. p.). The gaseous products were passed through bromine and collected over water, and were finally swept through with nitrogen. The bromine, on the usual treatment, yielded only a very small amount of oil. The gas in the aspirator was slowly passed through a solution of trimethylamine in nitromethane. The precipitation of the tetramethylammonium chloride was completed by adding ether, and the salt was identified by conversion into the picrate (m. p. and mixed m. p.). A small amount of sublimate, evidently trimethylphosphonium chloride, was formed in the upper part of the decomposition flask.

4. The decomposition of trimethylethylphosphonium chloride commenced above 320° and was completed at 360° (bath temperature). The distillate when treated as in the preceding case (acid at 20°), yielded a phosphine, which by treatment with trinitroanisole in ether gave almost pure trimethylethylphosphonium picrate (m. p. and mixed m. p. both before and after crystallis-

ation). The gaseous product on passage through bromine and into a nitromethane solution of trimethylamine gave only trimethylethylammonium chloride, which was identified as the picrate (m. p. and mixed m. p.). The bromine, after the usual treatment, gave a very little heavy oil, but not enough for identification. The neck of the decomposition flask was found to have collected a film of sublimate, which on basification gave the odour of a phosphine.

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