Acknowledgment.—The financial support by the Hooker Chemical Corporation of this investigation is gratefully acknowledged.

Decomposition of Tetrabutylphosphonium Acylates[1]

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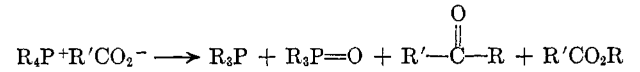
Received October 31, 1962

Letts and Collie[2] reported that tetraethylphosphonium acetate and benzoate decompose according to the following general equation. Although they were able



$$R_4P^+R'CO_2^- \longrightarrow R_3P + R_3P{=}O + R'{-}\overset{\overset{\Large O}{\|}}{C}{-}R + R'CO_2R$$

to identify the various products of these decompositions, no attempt was made to establish the yields or the best reaction conditions. It did appear, though, that the ketones were formed in considerably greater yield than the esters.

It seemed worthwhile to reinvestigate this decomposition with the view of establishing more completely the nature of the reaction. Tetrabutylphosphonium butyrate, benzoate, and acetate were prepared and pyrolyzed. In general the course of the reaction was found to be that suggested by Letts and Collie. Temperatures of 300–340° are required to obtain optimum yields of ketone. The best yields of ketone were obtained when the reaction was conducted under reduced pressure. This is probably due to more rapid removal of the ketone from the hot reaction mixture so that there is less chance for condensation reactions, etc., to occur. Under these conditions tetrabutylphosphonium benzoate gave valerophenone in 39% yield and *n*-butyl butyrate in 12% yield. Table I contains the data obtained from various pyrolysis reactions of this salt. Tetrabutylphosphonium butyrate similarly gave 4-octanone in 39% yield. The ester yield was not determined. In all cases other products were formed in small amount as was shown by gas–liquid chromatographic analysis. These were not identified. The pyrolysis of tetrabutylphosphonium acetate was investigated briefly. Under the conditions used, 325° and atmospheric pressure, 2-hexanone and acetone were the major products. Acetone undoubtedly was formed by condensation of acetate ions.

These reactions may have some value in synthesis. Although the yields of ketone are not high they may be satisfactory for some purposes. The mechanism of the formation of ketone is of interest and may well involve a pentacovalent phosphorus compound as an intermediate. Further work on this aspect of the problem is in progress. The formation of ester undoubtedly involves a typical nucleophilic displacement process.[3]

Table I

Temp., °C.	Pressure, mm.	Time, hr.	Valerophenone, %	Butyl benzoate, %
270	0.05	20	8	2
270	58	8	11	6
	+0.05	24		
300	760	8	22	2
340	760	8	21	16
340	94	1.5	39	12
400	760	15 min.	19	22

Experimental

Preparation of Tetrabutylphosphonium Salts.—Tetrabutylphosphonium bromide, m.p. 107–108° (lit.,[4] 99–101°), 17.0 g. (0.05 mole), in 100 ml. of dry methanol was added with stirring to a suspension of the silver salt of the acid (0.055 mole) in 300 ml. of dry methanol. The mixture was stirred for 24 hr. and filtered with Filter Aid. The filtrate was concentrated *in vacuo* at room temperature. The semicrystalline solid residues were used as such without further treatment.

Pyrolysis of Tetrabutylphosphonium Benzoate.—The pyrolysis reactions were conducted in a distilling flask with a short distillation path. Times are measured from immersion in the hot bath. The yields were calculated on the basis of g.l.c. data. Standard curves were constructed from known samples. The distillates were chromatographed and the percentages of ketone and ester were estimated by comparison with the known chromatograms. Other products found were butyl bromide, tributylphosphine, and tributylphosphine oxide. The infrared spectra of valerophenone and *n*-butyl benzoate obtained on samples isolated by g.l.c. were identical to those of known samples.

Pyrolysis of Tetrabutylphosphonium Butyrate and Acetate.—Essentially the same technique was used. 4-Octanone was identified by collection from a gas–liquid chromatogram and inspection of the infrared spectrum. The yields of ketone and conditions were: 250° (28 mm.) for 10 hr., 28%; 300° (26 mm.) for 2 hr., 39%; 350° (760 mm.) for 30 min., 32%.

Pyrolysis of tetrabutylphosphonium acetate at 325° yielded a distillate which was shown by g.l.c. to be composed of methanol (from the salt preparation), acetone, and 2-hexanone. The ketones were characterized by conversion of fractions from gas-liquid chromatography to 2,4-dinitrophenylhydrazones; thus acetone 2,4-dinitrophenylhydrazone, m.p. 124–126° (lit.,[5] m.p. 126°), and 2-hexanone 2,4-dinitrophenylhydrazone, m.p. 106–108° (lit.,[5] m.p. 106°), were obtained.

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(1) Research supported by the National Science Foundation.

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Hydrolysis of Fluorinated Ethers

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Received September 24, 1962

The hydrolysis of ethers containing the $—CF_2O—$ group by sulfuric acid has been used for the synthesis of the esters of various fluorinated acids[1] and for the determination of the direction of addition of alcohols to fluorinated olefins.[2] Optimum conditions[1a] call for

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