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Decomposition of Tetrabutylphosphonium Acylates[1]

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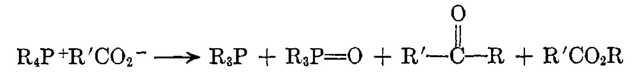
Letts and Collie[2] reported that tetraethylphosphonium acetate and benzoate decompose according to the following general equation. Although they were able



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

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.

[2] E. A. Letts and N. Collie, *Phil. Mag.*, **22**, 183 (1886).

[3] E. L. Eliel and R. P. Anderson, *J. Am. Chem. Soc.*, **74**, 547 (1952).

[4] M. Grayson and P. T. Keough, *ibid.*, **82**, 3919 (1960).

[5] R. L. Shriner and R. C. Fuson, "Identification of Organic Compounds," J. Wiley and Sons, Inc., New York, N. Y., 1940, p. 221.

Hydrolysis of Fluorinated Ethers

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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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[1] (a) J. A. Young and P. Tarrant, *J. Am. Chem. Soc.*, **71**, 2432 (1949); (b) J. L. Rendall and W. H. Pearlson, U. S. Patent 2,795,601 (June 11, 1957); (c) A. M. Lovelace, D. A. Rausch, and W. Postelnak, "Aliphatic Fluorine Compounds," Reinhold Publishing Corp., New York, N. Y., 1958, pp. 206–207, 234.

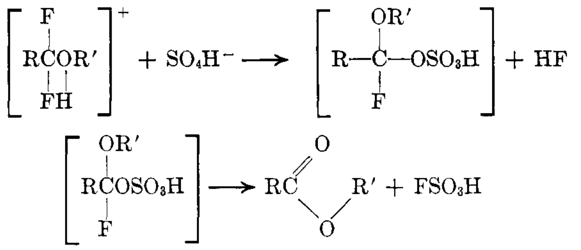
[2] J. D. Park, H. L. Cummings, and J. R. Lacher, *J. Org. Chem.*, **23**, 1785 (1958).

the addition of two moles of 96% sulfuric acid for each mole of ether at 10°, preferably in glass equipment. Yields vary from 55 to 83% and higher temperatures are reported to give undesirable side reactions with correspondingly lower yields.

We have found that α,α-difluoro ethers react with glass or silica gel, at temperatures of 70 to 160° to give the corresponding ester and silicon tetrafluoride, in yields of greater than 90% with no apparent side reactions.[3] The reaction is autocatalytic when the ether is heated in sealed glass ampoules without an added acid catalyst, but the addition of small amounts of sulfuric acid eliminates a prolonged induction period. Phosphoric acid (85%) and 2,2,3,3,3-pentafluoropropionic acid were ineffective as catalysts.

For preparative purposes the reaction is best carried out by refluxing[4] the ether along with approximately four mole percent of concentrated sulfuric acid in the presence of crushed glass until the reaction temperature becomes constant.

No satisfactory mechanism for the replacement of the fluorine atoms has been proposed. The mechanism for the hydrolysis of alkyl ethers suggested by Hammett[5] involving the formation of an alcohol and a carbonium ion is not applicable, since hydrolysis takes place without rupture of the C—O—C bond.[1a] It is suggested that the reaction may take place according to the following scheme.



The hydrogen fluoride and fluorosulfonic acid formed can react with silica to produce silicon tetrafluoride and regenerate the sulfuric acid. A direct reaction of the protonated ether with silica cannot, however, be ruled out.

Experimental

Methyl Bromofluoroacetate.—2-Bromo-1,1,2-trifluoroethyl methyl ether (200 g.) and 95.5% sulfuric acid (1 ml.) were charged to a 300-ml. flask containing silica gel (128 g., 6–12 mesh) and equipped with a reflux condenser and thermometer. The mixture was heated at reflux until the reaction temperature reached 133°, about 6 hr. The crude ester was extracted with diethyl ether. Rectification of the ethereal solution gave 19 g. of the starting ether, b.p. 88°, and 138 g. (78%) of methyl bromofluoroacetate, b.p. 130–134°, n^{25}_D 1.4195. The conversion of ether was 81% and the over-all yield 90%.[6]

Anal. Calcd. for $C_3H_4BrFO_2$: C, 21.05; H, 2.36; Br, 46.74. Found: C, 21.05; H, 2.83; Br, 45.88.

Methyl Dichloroacetate.—2,2-Dichloro-1,1-difluoroethyl methyl ether (342 g.) was refluxed with silica gel (141 g., 6–12 mesh) and 95.5% sulfuric acid (1 ml.). The reaction was terminated when the temperature reached 142°. The crude ester was distilled away from the silica gel under vacuum. Distillation of the crude ester through a 4-in. Heli-Pak filled column gave 268 g. (91%) of methyl dichloroacetate, b.p. 62–63° (4 mm.), n^{25}_D 1.4425. No unchanged ether was found. Redistillation of a portion of the product gave a center cut boiling at 143°, n^{25}_D 1.4414 [lit.,[7] b.p. 142.79° (760 mm.), n^{25}_D 1.4405].

Methyl Chlorofluoroacetate.—2-Chloro-1,1,2-trifluoroethyl methyl ether (138 g.) was heated with crushed "Pyrex" glass (157 g.) and 95.5% sulfuric acid (2 ml.) at 80–83° for 7.5 hr., and then allowed to stand overnight at room temperature. The crude ester was distilled from the glass under vacuum. Distillation gave 20 g. of starting ether, b.p. 66–72°, 7 g. of intercut, b.p. 72–113°, 86 g. (73%) of methyl chlorofluoroacetate, b.p. 113–116°, n^{25}_D 1.3905 (lit.,[1a] b.p. 116°, n^{25}_D 1.3903), and 3 g. of residue. A material balance gave an organic recovery of 95%, conversion of ether of 77%, and yield of 93%.

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(3) E. R. Larsen, Abstracts, 140th National Meeting of the American Chemical Society, September 3–8, 1961, p. 30-M.

(4) The use of a nickel condenser is recommended, since with glass extensive etching, which weakens the condenser, takes place just below the cooling jacket.

(5) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1949, p. 300.

(6) A similar reaction using the procedure of Young and Tarrant[1a] gave a 61% crude yield of ester with no recovered starting ether.

(7) R. R. Driesbach, "Physical Properties of Pure Compounds," Vol. III, Advances in Chemistry Series, no. 29, R. F. Gould, ed., American Chemical Society, Washington, D. C., 1961, p. 446.

New Simple Cyclization of 2-Anilinopropionic Acids to 4-Keto-1,2,3,4-tetrahydroquinolines with Polyphosphoric Acid

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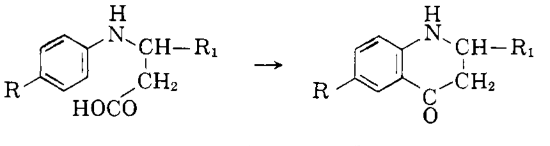
The cyclization of 2-anilinopropionic acids to 4-keto-1,2,3,4-tetrahydroquinolines was first investigated by Clemo and Perkin[1,2] and later by Backeberg.[3] More recently, this subject was thoroughly studied simultaneously by Elderfield[4,5] and by Johnson[6,7] with their collaborators. They concluded that protection of the free hydrogen on the nitrogen of the anilinopropionic acid was a necessary condition for the ring closure. This was accomplished by two separate steps of tosylation prior to ring closure and detosylation afterwards. The cyclization procedure itself, which was carried out with a variety of reagents under various conditions, appeared also quite laborious. The recent report[8] that 2-(2,5-dimethoxyanilino)butyric acid was directly cyclized to the corresponding dihydroquinolone with polyphosphoric acid led to the present investigation of its general applicability.



I. R = Cl; R_1 = H
II. R = Cl; R_1 = CH_3
III. R = CH_3O; R_1 = H

In a preliminary study, three anilino acids which previously were cyclized by Elderfield and Johnson were chosen for our experiments. It was found that these acids could be cyclized readily with polyphosphoric acid to 4-keto-1,2,3,4-tetrahydroquinolines, I, II, and III, in approximately 55% to 65% yield by modification of

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(1) G. R. Clemo and W. H. Perkin, *J. Chem. Soc.*, **125**, 1608 (1924).

(2) G. R. Clemo and W. H. Perkin, *ibid.*, **127**, 2297 (1925).

(3) O. G. Backeberg, *ibid.*, 618 (1933).

(4) R. C. Elderfield, *et al.*, *J. Am. Chem. Soc.*, **68**, 1259 (1946).

(5) R. C. Elderfield and A. Maggiolo, *ibid.*, **71**, 1906 (1949).

(6) W. S. Johnson, *et al.*, *ibid.*, **71**, 1901 (1949).

(7) W. S. Johnson and B. G. Buell, *ibid.*, **74**, 4513 (1952).

(8) J. Koo, *J. Org. Chem.*, **26**, 2440 (1961).