toluene in a Soxhlet apparatus for 2 hr. The product was precipitated by the addition of ligroin to the extracts and crystallized twice from toluene to give 0.1 g., 20%, of yellow needles, m.p. 268°. Absorption maxima occur at: 1705, 1650, 1600, 1550, 1487, 1448, 1355, 1110, 1142, 1120, 1103, 963, 890, 838, 813, 778, 753, 724 and 683 cm.$^{-1}$ in the infrared and at 265 mμ (log ϵ 4.27) and 365 mμ (log ϵ 4.56) in the ultraviolet.

Anal. Calcd. for $C_{23}H_{16}O_2$: C, 85.16; H, 4.97. Found: C, 85.46; H, 4.96.

3-(*p*-Methoxyphenyl)-6-phenyl-2-pyrone.—A catalyst mixture was prepared in the same manner as that used in the synthesis of 3,6-diphenyl-2-pyrone and diluted to 100 ml. with distilled water; 5 ml. of this catalyst was added to a solution of 0.5 g. of 2-(*p*-methoxyphenyl)-5-phenylpenten-2-yne-4-oic acid in 50 ml. of methanol. The reaction was kept at 45–50° for 48 hr. and the methanol evaporated. The precipitate was filtered, washed with distilled water and crystallized two times from ethanol to give 0.1 g., 20%, of yellow plates, m.p. 170°. Absorption maxima occur at: 1700, 1625, 1610, 1575, 1550, 1510, 1490, 1450, 1358, 1305, 1290, 1250, 1175, 1110, 1083, 1047, 1027, 965, 900, 840, 806, 777, 763 and 683 cm.$^{-1}$ in the infrared and occur at 250 mμ (log ϵ 4.00) and 370 mμ (log ϵ 4.10) in the ultraviolet.

Anal. Calcd. for $C_{18}H_{14}O_3$: C, 77.68; H, 5.07. Found: C, 77.50; H, 5.10.

Infrared absorption spectra were obtained on potassium bromide pellets using a Baird Associates double beam recording infrared spectrophotometer with sodium chloride optics. Ultraviolet absorption spectra were obtained using 1.00-cm. silica cells in a Beckman DU spectrophotometer. Absolute methanol was used as solvent except as noted.

LOUISVILLE 8, KENTUCKY

[CONTRIBUTION FROM AVERY LABORATORY, UNIVERSITY OF NEBRASKA]

Pyrolysis of Alkyl Phosphates

BY HENRY E. BAUMGARTEN AND ROBERT A. SETTERQUIST[1]

RECEIVED NOVEMBER 26, 1956

The preparation of amyl dimethyl, dimethyl hexyl, dimethyl octyl, dioctyl methyl and cyclohexyl dimethyl phosphates is described. These five alkyl phosphates and three others have been pyrolyzed to give olefins in high yield. The pyrolyses were accompanied by extensive rearrangement of the olefinic double bond.

In the preparation of olefins by the pyrolysis of esters, it is becoming increasingly apparent that a considerable variation in the nature of the acid moiety is allowable. A recent review[2] has cited numerous examples of olefin formation by pyrolysis in the liquid and vapor phases of esters of many different organic acids, and to these examples may be added the pyrolyses of esters of the inorganic acids, boric acid[3] and sulfurous acid.[4–6] Although no systematic study of the pyrolysis of the esters of phosphorus acids has been reported, isolated examples of the thermal decomposition of such substances to olefins have been described. For example, Gerrard[7] reported that *n*-octyl phosphorodichloridite decomposed to give octylene at 150°. Arbuzov and Valitova[8] obtained olefinic products by heating tertiary alkyl phosphites with methyl iodide in a sealed tube at 200°. Cronje[9] reported that the pyrolysis of dihydrogen dialkyl pyrophosphates at 180° yielded olefins. Other workers have reported obtaining olefinic by-products during the preparation or reaction of various organophosphorus esters but, in most instances, the immediate precursor of the olefin has not been identified and in many may not have been an organophosphorus compound. The present communication describes the preparation and pyrolysis of a number of alkyl phosphates and is the first of a series to be devoted to the pyrolysis of various phosphorus derivatives.

From the many possible simple and mixed alkyl and aryl phosphates three types were selected for study: alkyl dimethyl phosphates (I), dialkyl methyl phosphates (II) and trialkyl phosphates (III).

$$\underset{\mathrm{I}}{\mathrm{RCH_2CH_2OP(O)(OCH_3)_2}} \longrightarrow \mathrm{RCH{=}CH_2 + HOP(O)(OCH_3)_2}$$

$$\underset{\mathrm{II}}{\mathrm{(RCH_2CH_2O)_2P(O)OCH_3}} \longrightarrow \mathrm{2RCH{=}CH_2 + (HO)_2P(O)OCH_3}$$

$$\underset{\mathrm{III}}{\mathrm{(RCH_2CH_2O)_3PO}} \longrightarrow \mathrm{3RCH{=}CH_2 + (HO)_3PO}$$

Preparation of the mixed phosphates (I) was effected by treatment of the appropriate alcohol (IV) with phosphorus oxychloride in the presence of dimethylaniline followed by reaction of the intermediate alkyl phosphorodichloridate (V) with sodium methoxide.

$$\underset{\mathrm{IV}}{\mathrm{RCH_2CH_2OH}} + \mathrm{POCl_3} \xrightarrow{\mathrm{C_6H_5NMe_2}} \underset{\mathrm{V}}{\mathrm{RCH_2CH_2OP(O)Cl_2}} \xrightarrow{\mathrm{CH_3ONa}} \underset{\mathrm{I}}{\mathrm{RCH_2CH_2OP(O)(OCH_3)_2}}$$

The phosphates thus prepared are described in Table I. This procedure was more effective in our hands than the alternative treatment of dimethyl phosphorochloridate with the alkoxide of IV or with IV and a tertiary amine.[10]

Dioctyl methyl phosphate (II, R = C_6H_{13}) was prepared by treating the commercially available dioctyl phosphorochloridate with sodium methoxide in ether or, preferably, with methanol and tri-

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(1) Minnesota Mining and Manufacturing Co. Fellow, 1955–1956.

(2) W. J. Bailey and J. J. Hewitt, *J. Org. Chem.*, **21**, 543 (1956).

(3) G. L. O'Connor and H. R. Nace, THIS JOURNAL, **77**, 1578 (1955).

(4) D. Libermann and A. Rouiax, *Compt. rend.*, **226**, 2151 (1948).

(5) C. C. Price and G. Berti, THIS JOURNAL, **76**, 1207 (1954).

(6) G. Berti, *ibid.*, **76**, 1213 (1954).

(7) W. Gerrard, *J. Chem. Soc.*, 84 (1944).

(8) A. E. Arbuzov and F. G. Valitova, *Izvest. Akad. Nauk, U.S.S.R. Otdel. Khim. Nauk*, 801 (1952); *C. A.*, **47**, 10462 (1953).

(9) J. H. Cronje, *J. S. African Chem. Inst.* [*N.S.*], **2**, 15 (1949).

(10) The choice of the procedure selected was based on a relatively small number of orienting experiments. In view of the results of G. M. Steinburg (*J. Org. Chem.*, **15**, 637 (1950)) the reaction of IV with dimethyl phosphorochloridate (or its precursors, dimethyl phosphite, carbon tetrachloride and triethylamine) could prove to be superior to the method chosen.

TABLE I

ALKYL PHOSPHATES

Phosphate	Method[a]	Yield, %	B.p., °C.	Mm.	$n^{25}D$	Composition	Phosphorus, % Calcd.	Phosphorus, % Found	Infrared spectrum,[b] cm.$^{-1}$ P → O stretch	Infrared spectrum,[b] cm.$^{-1}$ P–O–Me stretch	Infrared spectrum,[b] cm.$^{-1}$ P–O–C stretch
Amyl dimethyl	B	66	72–74	0.4	1.4127	$C_7H_{17}O_4P$	15.81	15.59	1283(s)	1190(w)	1135(vs)
Cyclohexyl dimethyl	A	41	106	1.5	1.4417	$C_8H_{17}O_4P$	14.88	14.72	1280(s)	1188(w)	1015(vs) 1035(vs)
Dimethyl hexyl	B	70	100	1.7	1.4180	$C_8H_{19}O_4P$	14.75	14.63	1280(s)	1187(w)	1035(vs)
Dimethyl octyl	A	70	130	1.7	1.4236	$C_{10}H_{23}O_4P$	13.00	12.53	1286(s)	1192(w)	1040(vs)
Dioctyl methyl	[c]	58	162–164	1	1.4362	$C_{17}H_{37}O_4P$	9.21	9.20	1286(s)	1188(w)	1035(vs)

[a] Method A = solid sodium methoxide in ether; method B = methanolic sodium methoxide. [b] L. J. Bellamy ("The Infrared Spectra of Complex Molecules," Methuen and Co., London, 1954, Chap. 18) quotes for the P → O stretching vibration, 1250–1300 cm.$^{-1}$, for the P–O–CH_3 stretching vibration, 1190 ± 3 cm.$^{-1}$, for the P–O–C(aliphatic) stretching vibration, 1000–1500 cm.$^{-1}$. [c] See Experimental section.

TABLE II

OLEFINS FROM THE PYROLYSIS OF ALKYL PHOSPHATES

Phosphate	Amount pyrolyzed, g.	Time, of addn., min.	Temp., °C.	B.p. range, °C.	Yield[a] of olefin, %	Infrared spectrum[b] C=C stretching, cm.$^{-1}$
Amyl dimethyl	10.0	180	500	25–35	85	1638, ~1650
Cyclohexyl dimethyl	14.2	45	350	78–83	66	1648
Dimethyl *n*-hexyl	8.0	120	420	63–70	88	1643, ~1656, ~1667
	14.3	120	350	64–68	97	1642, ~1652, 1667
	11.2	120	300	63–68	90	1643, ~1654, ~1667
	12.6	45	300	60–67	87	
	11.4	120	250	.....	0[c]	
Dimethyl octyl	14.5	60	300	120–125	75	1643, 1666
Dioctyl methyl	12.0	120	300	120–125	99	1645, 1668
Tributyl	10.0	180	500	.....	75	1635
Triisoamyl	17.4	60	350	20–38	67	
Tri-(2-ethyl) hexyl	25.0	93	350	117–121	90	1646, 1670

[a] Based on total possible olefin obtainable. [b] L. J. Bellamy "(The Infrared Spectra of Complex Molecules," Methuen and Co., London, 1954, Chap. 3) quotes the average values for the C=C stretching vibration as, for $CHR{=}CH_2$ 1643 cm.$^{-1}$, for $CHR_1{=}CHR_2$ (*trans*) 1673 cm.$^{-1}$, for $CHR_1{=}CHR_2$ (*cis*) 1657 cm.$^{-1}$. [c] 9.8 g. (86%) of dimethyl *n*-hexyl phosphate recovered.

ethylamine in carbon tetrachloride. All of the simple trialkyl phosphates (III) used in this study were available from other sources.

The phosphates were pyrolyzed by dropping them through a 1-in. Pyrex or Vycor glass tube packed with $^1/_{16}$-in. glass helices and heated to various temperatures by a tube furnace. The results of several typical pyrolyses are given in Table II. Inasmuch as a strong acid (phosphoric acid, its methyl or dimethyl ester or polymeric acids derived from these) should be formed in the elimination reaction, extensive isomerization of the double bond was expected in the olefin formed. Therefore, that part of the pyrolysate which boiled within the temperature range dictated by the boiling points of the expected olefins was collected as product.

In every run some darkening of the pyrolysis tube indicated that carbonization occurred in varying amounts, perhaps adding to the extent of isomerization.[11] As the temperature was increased the extent of the darkened area also increased.

The results of Table II indicate that alkyl phosphates pyrolyze readily at temperatures of 300° and above to give excellent yields of olefin. From many experiments the optimum temperature appeared to be around 350°, although occasionally good yields were obtained at 300°. It is interesting to note that in the attempted pyrolysis of dimethyl *n*-hexyl phosphate at 250°, no olefin was obtained and 85.5% of the starting material was recovered. Thus, the pyrolysis temperature of the phosphates is intermediate between those of the sulfites (170–260°) and of the acetates (400–550°).[6]

Essentially the stoichiometric amounts of olefin were obtained from II and III, two and three moles of olefin per mole of phosphate, respectively.

Although no attempt was made to determine quantitatively the composition of the olefinic products, the infrared spectra of all olefin fractions were examined for evidence of double bond migration. In all instances in which such migration would be expected, the infrared spectra indicated that migration had occurred. To illustrate, the frequencies of selected bands occurring in the spectrum of the product obtained from dimethyl *n*-hexyl phosphate at 350° are given in Table III together with the characteristic frequencies reported[12] for 1-hexene and *cis*- and *trans*-2-hexene. Comparison of these values indicates that a mixture of olefins was present in the pyrolysate. Inasmuch as the spectrum of the product obtained at 350° differed little from those of olefins formed at various temperatures from 300 to 400°, small variation in temperature apparently had little

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(11) W. J. Bailey and L. Nicholas, *J. Org. Chem.*, **21**, 854 (1956).

(12) N. Sheppard and D. M. Simpson, *Quart. Rev.*, **6**, 1 (1952).

TABLE III

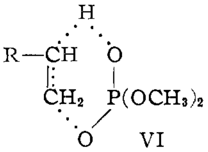
INFRARED SPECTRUM OF HEXENE PYROLYSATE[a]

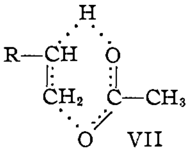
Mode	1-Hexene	*cis*-2-Hexene	*trans*-2-Hexene	Pyrolysate
CH stretching	3083	3010	3026	3080
				3010
C=C stretching	1656	1656	(1670)	1667
				~1652
				1642
CH bending	1416	1408	1299	1408
(in plane)	1297			1297
CH bending	993	694	966	993
(out of plane)	910			966
	632			907
	1820[b]			690
				1820

[a] Values for 1-hexene, *cis*-2-hexene, *trans*-2-hexene from ref. 12. [b] Overtone.

effect on the extent of isomerization, although the isomerization may have been in part thermal in origin. Of the other phosphates pyrolyzed, only cyclohexyl dimethyl phosphate appeared to give a single olefin, substantially free from rearrangement products.

Although a cyclic transition state (VI) can be written for the pyrolysis of alkyl phosphates which resembles that (VII) now commonly accepted for the pyrolysis of acetates and other esters of organic acids,[13] it seems more likely that the reaction


VI


VII

may proceed *via* ionic intermediates either to the exclusion of or in competition with the cyclic mechanism. Much of the argument offered by Berti[6] in support of an ionic type of cleavage for alkyl sulfites appears to be applicable to the cleavage of phosphates as well.

Experimental[14]

Alkyl Dimethyl Phosphates.—Equimolar amounts of the alcohol, phosphorus oxychloride and dimethylaniline and twice the molar amount of sodium methoxide were used. Special care was taken to maintain anhydrous conditions throughout each preparation.

A mixture of dry ethyl ether (100 ml. for each 10 g. of alcohol used), the alcohol and dimethylaniline was treated dropwise with stirring with phosphorus oxychloride in dry ether (100 ml. for each 20 g. of phosphorus oxychloride) while the temperature was maintained below −15°. After the addition was completed the mixture was allowed to stand and come to room temperature. The resulting ethereal solution of alkyl phosphorodichloridate was transferred from the precipitated dimethylaniline hydrochloride through a filter stick into another large, 3-necked, round-bottomed flask. The solid amine hydrochloride was washed with dry ether and the ethereal solution was added to the filtrate. Solid sodium methoxide (method A) or a 10% solution of sodium methoxide in methanol (method B) was added slowly while the cooled (in ice) ether solution was stirred rapidly. The reaction mixture was allowed to stand overnight at room temperature. The precipitated sodium chloride was separated by filtration and the ethereal solution was washed with 100 ml. of 5% aqueous sodium bicarbonate and then dried over anhydrous magnesium sulfate. The product was distilled under reduced pressure through an 18-in. by 0.5-in. Vigreux column.

Dioctyl Methyl Phosphate. (a) **From Sodium Methoxide.**—To a solution of 170.5 g. (0.5 mole) of dioctyl phosphorochloridate in 200 ml. of ether cooled in ice was added 27 g. (0.5 mole) of sodium methoxide in small portions. The reaction mixture was allowed to stand overnight and the sodium chloride was separated by filtration. The filtrate was washed with 5% aqueous sodium bicarbonate, then several portions of water and dried over magnesium sulfate. The ether was distilled from the product, giving 146 g. (87%) of crude dioctyl methyl phosphate, $n^{25}\text{D}$ 1.4400. Although purification by distillation was possible, in the presence of traces of acid, decomposition took place (even at 0.25 mm.) giving octene, which contaminated the distilled ester (*vide infra*).

(b) **From Methanol and Triethylamine.**—To a stirred solution of 10 g. (0.10 mole) of triethylamine and 3.5 g. (0.11 mole) of methanol in 200 ml. of dry carbon tetrachloride held at 0° in an ice-bath was added over a period of 1 hr. a solution of 33 g. (0.097 mole) of dioctyl phosphorochloridate in 50 ml. of carbon tetrachloride. The mixture was removed from the cold bath and allowed to stand at room temperature protected from moisture until no further precipitate of triethylamine hydrochloride formed.[15] The filtered carbon tetrachloride solution was washed successively with 5% hydrochloric acid, water, 5% aqueous sodium bicarbonate (twice) and water. The solution was dried over magnesium sulfate and then divided into two equal portions. The first half of the solution was distilled through a 24-in. column of the Podbielniak type.[16] Small fractions were collected at frequent intervals, a total of 9.5 g. (58%) of dioctyl methyl phosphate, b.p. 162–164° (1 mm.), $n^{25}\text{D}$ 1.4361–1.4362, being collected before the temperature at the take-off fell (to about 150°). On raising the bath temperature from about 210 to 230°, the remainder of the liquid in the still-pot suddenly and almost instantly decomposed forming octene, 2.5 g. (23%) (which was caught in the cold trap protecting the pump).

The second half of the solution was evaporated on the steam-bath under reduced pressure (down to 0.5 mm.), giving 14.2 g. (87%) of crude dioctyl methyl phosphate, $n^{25}\text{D}$ 1.4378. The infrared spectra of the crude product and of the distillate described above were not perceptibly different, indicating that for most practical purposes the crude material should suffice.

Pyrolysis Procedure.—The apparatus consisted of either a thick walled Pyrex or a Vycor glass tube, 25-mm. o.d. and 24 in. long, inserted in a vertically disposed FD303 Hoskins electric furnace. The tube was packed for 12 in. of its depth with $^1/_{16}$-in. Pyrex glass helices (which were cleaned after each run with a solution of hot concentrated nitric and sulfuric acids and rinsed thoroughly with distilled water). A Hershberg-type dropping funnel,[17] modified to permit the pressure-equalized introduction of nitrogen into the system, was used to introduce the sample. The pyrolysate was collected in a large (50-mm. o.d.) side-arm test-tube immersed in a Dry Ice–methanol-bath. In some experiments the side-arm of the test-tube was connected to a U-tube immersed in Dry Ice–methanol as a precautionary measure, but normally this precaution was not necessary. A slow flow of nitrogen (about 1–2 l. per hour) was introduced into the tube during pyrolysis to sweep the vapors into the receiver and maintain a non-oxidizing atmosphere within the apparatus. All gases not condensed in the cold bath(s) were collected in a gas buret over water.

The temperature of the tube was determined using a Leeds and Northrup Model 8667 pyrometer and an iron–constantan thermocouple, the thermocouple leads being inserted in a

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(13) J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1956, p. 462.

(14) Boiling points are uncorrected. The alcohols used in this work were obtained from the Matheson Co., Inc. We are indebted to Dr. H. A. Pagel for gifts of tributyl and trikosoamyl phosphate, to the Victor Chemical Works for dioctyl phosphorochloridate and to the Carbide and Carbon Chemicals Co. for tri-(2-ethylhexyl) phosphate.

(15) The quantity of triethylamine hydrochloride precipitated after 4 hr. was 48%, after 16 hr., 79%, after 40 hr., 95%, after 64 hr., 100%.

(16) J. Cason and H. Rapoport, "Laboratory Text in Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1950, p. 237.

(17) "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 129.

well extending about half-way into the packed section of the tube.[18] The temperature was controlled to ±6°.

The optimum rate of addition of phosphate during pyrolysis appeared to be about 0.3 g. of ester per minute, although little change in the yield of olefin occurred when the rate was varied from 0.06 to 0.3 g. per minute. The crude pyrolysate was purified by distillation through an 8-in. Vigreux column. The olefin fraction boiling in the range of temperatures given in the literature[19] for the expected olefin and isomerization products was collected for infrared analysis.[20] No attempt was made to identify other byproducts. After a run the tube was usually clean throughout except for an approximately 2-in. area about 1 in. from the top of the packing, which was black. Etching of the tube in this area took place.

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(18) A number of tube designs, including all-glass construction, have been employed to permit insertion of the thermocouple well and the dropping funnel into the relatively small tube opening. The simplest of these (and the easiest to disassemble and clean) was a tube terminating in an open cup of about 35-mm. o.d. The dropping funnel and thermocouple well were fitted into the cup with a clean rubber stopper. This device was very satisfactory provided that in inserting the pyrolysis tube into the apparatus it was first fitted with a 1.25-in. sleeve of 1-in. copper tubing and a fairly tight-fitting shield formed from a 2-in. square of asbestos cement board (Transite) (to conduct away the heat and to seal off the opening of the furnace, respectively). Otherwise, the rubber stopper charred badly at the higher temperatures.

(19) S. W. Ferris, "Handbook of Hydrocarbons," Academic Press, Inc., New York, N. Y., 1955.

(20) Infrared determinations were made by Mr. E. R. Magnuson with a Perkin-Elmer recording instrument, model 21, employing sodium chloride optics and the neat liquid or gas.

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[CONTRIBUTION FROM THE BEN MAY LABORATORY FOR CANCER RESEARCH AND THE DEPARTMENT OF BIOCHEMISTRY, UNIVERSITY OF CHICAGO]

Phosphonic Acids. IV.[1] Preparation and Reactions of β-Ketophosphonate and Enol Phosphate Esters[2]

BY HERBERT I. JACOBSON, MARTIN J. GRIFFIN, SEYMOUR PREIS AND ELWOOD V. JENSEN

RECEIVED JUNE 18, 1956

In contrast to α-chlorinated ketones which react with triethyl phosphite to form enol phosphate esters, α-iodoketones react "normally" with triethyl phosphite to yield β-ketophosphonate esters. Thus iodoacetone reacts with triethyl phosphite at room temperature to form diethyl β-ketopropylphosphonate (II). Diethyl β-ketopropylphosphonate also may be prepared by the acid-catalyzed ethanolysis of diethyl 3-diethylphosphonoisopropenyl phosphate (IIIb), a substance which is obtained by the smooth reaction of two moles of triethyl phosphite with α,α'-dichloroacetone. Treatment of diethyl 3-diethylphosphonoisopropenyl phosphate (IIIb) with sodium ethoxide in boiling ethanol results in the elimination of the elements of diethyl hydrogen phosphate to form diethyl propynylphosphonate (VI). Hydrogenation of diethyl isopropenyl phosphate (VIII) over palladium yields diethyl isopropyl phosphate (IX), whereas over platinum reductive cleavage of the enol ester linkage takes place to form diethyl hydrogen phosphate (X).

It has long been recognized that the reaction of α-chloroketones with sodium diethyl phosphonate[3] and with triethyl phosphite[4] gives rise to unusual products which, although originally formulated as β-ketophosphonates, do not react with the usual carbonyl reagents and which, on acid hydrolysis, undergo cleavage to produce a ketone and inorganic phosphate. The reason for this behavior became clear when it was demonstrated that the reaction of triethyl phosphite with α-chlorinated aldehydes[5] and ketones[6,7] takes place in a manner different from that of simple alkyl halides to yield predominantly enol phosphate esters rather than β-ketophosphonate esters. The most reasonable explanation proposed for this phenomenon is that the polarization induced by the electronegative halogen atoms causes the attack of triethyl phosphite to take place not on the carbon atom bearing the halogen but rather on the carbon atom of the carbonyl group with subsequent concerted rearrangement.[8]

In connection with the synthesis of phosphonate analogs of certain phosphorylated intermediates of metabolism,[1] a method was desired for the preparation of authentic β-ketophosphonate esters. If it is assumed that chloro and polyhaloketones react abnormally in the Arbuzov reaction because of the polarization induced on the carbonyl group by the electronegative halogen atoms, it was considered that an iodoketone might react normally since the less electronegative iodine atom would exert a smaller polarization effect as well as being more reactive toward simple displacement. Accordingly, the reaction of iodoacetone (I) with triethyl phosphite was investigated and found to proceed exothermically at room temperature to produce diethyl β-ketopropylphosphonate (II), with only a small amount of diethyl isopropenyl phosphate being formed.[9] This β-ketophosphonate (II) forms the expected 2,4-dinitrophenylhydrazone derivative, and its infrared spectrum shows strong carbonyl absorption at 1717 cm.$^{-1}$ and

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(1) Paper III, S. Preis, T. C. Myers and E. V. Jensen, THIS JOURNAL, **77**, 6225 (1955).

(2) This investigation was supported in part by a grant from the National Institutes of Health, Public Health Service (RG-3053).

(3) P. Nylen, Dissertation, Uppsala, 1930, p. 59; I. S. Bengelsdorf, Ph.D. Dissertation, University of Chicago, 1951, p. 18.

(4) B. A. Arbuzov, B. P. Lugovkin and N. P. Bogonostseva, *Zhur. Obshchei Khim.*, **20**, 1468 (1950); *C. A.*, **45**, 1506 (1951).

(5) (a) W. Perkow, *Ber.*, **87**, 755 (1954); (b) W. Perkow, E. W. Krockow and K. Knoevenagel, *ibid.*, **88**, 662 (1955).

(6) (a) J. F. Allen and O. H. Johnson, THIS JOURNAL, **77**, 2871 (1955); (b) J. F. Allen, S. K. Reed, O. H. Johnson and N. J. Brunsvold *ibid.*, **78**, 3715 (1956).

(7) (a) A. N. Pudovik and N. M. Lebedeva, *Doklady Akad. Nauk S.S.S.R.*, **101**, 889 (1955); *C. A.*, **50**, 3219 (1956); (b) A. N. Pudovik, *Zhur. Obshchei Khim.*, **25**, 2173 (1955); *C. A.*, **50**, 8486 (1956); (c) A. N. Pudovik, *Doklady Akad. Nauk S.S.S.R.*, **105**, 735 (1955); *C. A.*, **50**, 11230 (1956).

(8) M. S. Kharasch and I. S. Bengelsdorf, *J. Org. Chem.*, **20**, 1356 (1955).

(9) Since the completion of this work, Pudovik[7b,c] has reported the reaction of iodoacetone with triethyl phosphite in boiling diethyl ether to produce diethyl β-ketopropylphosphonate (II) accompanied by small amounts of diethyl isopropenyl phosphate. No mention is made of the formation of the higher boiling phosphate-phosphonate ester III.