

saturated with salt. It was then extracted with five 50-ml. portions of ether. The aqueous solution was again diluted with 400 ml. of water and extracted twice with 50-ml. portions of ether. The ether fractions were combined and washed twice with 200-ml. portions of water. The ether solution was dried overnight over anhydrous magnesium sulfate. The ether was evaporated and the residue distilled under vacuum. The product weighed 1 g. and had the following properties: b.p. 53–63° (5 mm.),  $n_D^{20}$  1.4207,  $d_4^{20}$  0.8117,  $\alpha_D^{20} + 0.01^\circ$ .

*Anal.* Found: active H, 0.35; excess Grignard consumed, 0.31.

To 0.0983 g. of phthalic anhydride (m.p. 132°) in a small test-tube, 0.235 g. of the mixture produced in this experiment was added.<sup>8</sup> If 45% alcohol was present, this would be about 0.81 mmole of alcohol. The test-tube was sealed and placed in a bath of boiling acetic acid (111°) for 16.5 hours. The reaction mixture was poured into a solution of 0.2 g. of sodium carbonate in 7 ml. of water, and the water solution was extracted with ether to remove any 2-octanone and 2-octyl ether. The water solution was acidified and an oil formed which slowly crystallized. The solid was washed with petroleum ether, b.p. 60–70°, and all fractions obtained were combined. The m.p. was 64.5–70.5°. The total weight of the 2-octyl phthalate was 0.130 g., which

was a 65% yield based on the amount of phthalic anhydride used. The product had  $[\alpha]_D^{20} + 36.5^\circ$  (*c* 0.038 g./ml., 95% ethanol).

**Alkaline Hydrolysis of Optically Active 2-Octyl Nitrate in Aqueous Dioxane.**—To 350 ml. of sodium hydroxide (0.18 *M*) in water-dioxane (64 vol. % dioxane, 36 vol. % water) was added 7.87 g. (0.045 mole) of optically active 2-octyl nitrate,  $[\alpha]_D^{20} - 17.35^\circ$ . This solution was placed in a sealed tube and the temperature was maintained at  $140 \pm 5^\circ$  for 72 hours.

After the tube was cooled, the solution was removed and water was added to give 600 ml. of solution. This solution was saturated with salt and extracted twice with 100-ml. portions of ether. The ether layers were combined and washed twice with 400-ml. portions of water, and then dried overnight over anhydrous magnesium sulfate. The ether was then removed under vacuum and the product was distilled, b.p. 55–56° (2.8 mm.). The product weighed 2.42 g. which was a 41% yield if all of the product was 2-octanol and 2-octanone. The physical properties of the product were as follows:  $d_4^{21}$  0.8307,  $n_D^{22}$  1.4240,  $\alpha_D^{20} - 3.13^\circ$ ,  $[\alpha]_D^{20} - 3.77^\circ$ .

*Anal.* Found: N, 0.29%; active hydrogen, 0.63; additional Grignard consumption, 0.21.

BOULDER, COLORADO

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

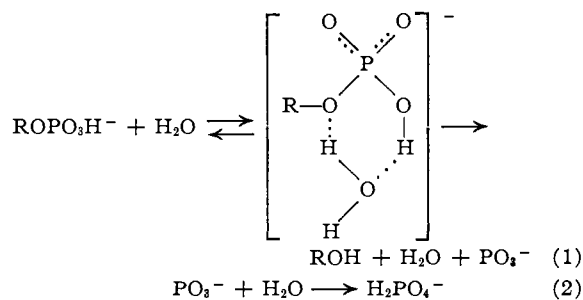
## The Hydrolysis of Mono- and Dibenzyl Phosphates

BY JUNJI KUMAMOTO<sup>1</sup> AND F. H. WESTHEIMER

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The *pH*-rate profiles for the hydrolysis of mono- and dibenzyl phosphates at 75.6° have been determined. The monoanion,  $\text{ROPO}_3\text{H}^-$ , of monobenzyl phosphate hydrolyzes much more readily than does the corresponding monoanion,  $(\text{RO})_2\text{PO}_2^-$ , of dibenzylphosphate. The mechanism for the hydrolysis of phosphate esters, which was advanced in a previous paper, is consistent with these facts.

Bailly<sup>2</sup> and later Desjobert<sup>3</sup> noted that the rate of hydrolysis of a simple monoester of phosphoric acid is slow in alkaline solution, rises to a maximum around *pH* 4, falls to a minimum at *pH* 1–2, and then rises again in strong acid solution. The rate maximum occurs where the monoanion  $\text{ROPO}_3\text{H}^-$  is present in greatest concentration. In a previous article,<sup>4</sup> it was suggested that the transfer of a proton from the phosphate to the ester oxygen (and cleavage to the alcohol ROH) is an integral part of the hydrolytic process.



A similar mechanism is unavailable to the monoanion of a diester of phosphoric acid. (For alternative mechanisms, see the previous paper.)<sup>4</sup>

An investigation of the rates of hydrolysis of monobenzyl phosphate and of dibenzyl phosphate

revealed the following facts: (1) The monoanion of monobenzyl phosphate hydrolyzes much more readily than does the monoanion of the diester, and (2) the strong acid hydrolysis of the benzyl phosphates is much more pronounced than that for simple aliphatic phosphates. These facts are consistent with the mechanism of equations 1 and 2.

### Experimental

**Materials.**—Tribenzyl phosphate,<sup>5</sup> prepared from sodium benzyloxide and  $\text{POCl}_3$ , melted at 64°. Dibenzylphosphoric acid could be prepared from the triester by the method of Lossen and Kohler<sup>5</sup> or of Clark and Todd<sup>6</sup>; it melted at 78–79°. Monobenzyl dihydrogen phosphate was prepared as the di-(cyclohexylammonium) salt by the procedure of Todd and Curry.<sup>7</sup> We wish to acknowledge gratefully Professor Todd's kindness in sending us both these directions and a sample of his material. About 8 g. of dibenzyl hydrogen phosphate was dissolved in 250 cc. of 50% aqueous alcohol and hydrogenated at atmospheric pressure with 0.4 g. of palladium oxide as catalyst. In about four hours, one equivalent of hydrogen was absorbed, and the process was interrupted. The product was extracted from the filtered solution with two 100-cc. portions of chloroform. The di-cyclohexylammonium salt separated from the concentrated chloroform solution (20 cc.) on addition of excess cyclohexylamine; yield 4.75 g. of colorless needles melting at 233°. A mixed melting point with the sample sent us by Professor Todd showed no depression.

*Anal.* Calcd. for  $\text{C}_{19}\text{H}_{25}\text{PO}_4\text{N}_2 \cdot \text{H}_2\text{O}$ : C, 56.39; H, 9.23; N, 6.93. Found: C, 56.3; H, 9.22; N, 6.88.

(5) von W. Lossen and A. Kohler, *Ann.*, **262**, 209 (1891).

(6) V. M. Clark and A. R. Todd, *J. Chem. Soc.*, 2023 (1950).

(7) A. R. Todd and A. S. Curry, private communication. On drying at 100° and  $10^{-2}$  mm., the salt loses water and cyclohexylamine, to yield monocyclohexylammonium monobenzyl hydrogen phosphate.

(1) Sinclair Oil Company Fellow, 1951–1953.

(2) M. C. Bailly, *Bull. soc. chim.* [5] **9**, 314 (1942).

(3) A. Desjobert, *ibid.*, [5] **14**, 809 (1947).

(4) W. Butcher and F. H. Westheimer, *THIS JOURNAL*, **77**, 2420 (1955).

**Method.**—The kinetic experiments were carried out at 75.6°. The rate determinations at 1.0, 0.5 and 0.1 *M* acid were made using an automatic pipet<sup>8</sup> with an ungreased Teflon plug. All the slower "runs" were made under nitrogen in sealed tubes. The ionic strength was maintained at 1.0 *M* by the addition of twice recrystallized NaClO<sub>4</sub>. The composition of the buffers used is shown in Table I.

TABLE I  
COMPOSITION OF BUFFERS

pH	Potassium acid phthalate <i>M</i>	HClO <sub>4</sub> <i>M</i>	NaClO <sub>4</sub> <i>M</i>
2.40	0.050	0.040	0.91
3.01	.050	.020	.93
2.99	.10	.040	.86
3.50	.050	.008	.94
	NaOAc <i>M</i>	HOAc <i>M</i>	NaClO <sub>4</sub> <i>M</i>
3.91	0.150	0.700	0.85
4.58	.350	.350	.65
4.58	.700	.700	.30
5.88	.700	.035	.30
	NH <sub>4</sub> OAc <i>M</i>		
7.00	1.00		

The first ionization constant of phthalic acid<sup>9</sup> at 75° and at an ionic strength<sup>10</sup> of unity was estimated as  $1.60 \times 10^{-3}$ . The ionization constant of acetic acid,<sup>10,11</sup> under the same conditions, was estimated as  $2.64 \times 10^{-5}$ .

The rates of hydrolysis were determined by measuring the amount of benzyl alcohol produced; a few experiments were checked by a determination of the quantity of inorganic phosphate formed. An aliquot of reaction mixture was added to an excess of sodium carbonate solution, and the mixture extracted with methylene chloride. Only benzyl alcohol was extracted by the organic solvent; the sodium salts of the phosphate esters remained in the aqueous layer. The extraction coefficient for benzyl alcohol in 1 *M* sodium perchlorate solution was found to be 7.9.

In a typical experiment, 10 cc. of reaction solution was added to excess sodium carbonate in a 30-cc. separatory funnel, and the solution extracted with 5 or 10 cc. of methylene chloride. The stopcock was lubricated with a mixture of washed bentonite and glycerol. This special lubricant was necessary because all available stopcock greases contained constituents which extracted into methylene chloride and interfered with the spectrophotometric determination of benzyl alcohol. The extinction coefficient for benzyl alcohol, measured with a Beckman quartz model DU spectrophotometer was found to be 186 at 258.5 m $\mu$ .

The analysis for inorganic phosphate was made by the method of Murray and Ashley.<sup>12</sup>

**Ionization Constants.**—The ionization constants of dibenzyl hydrogen phosphate and of monobenzyl dihydrogen phosphate were determined by an indicator method<sup>13</sup> under the same conditions (ionic strength of 1, *T* = 75.6°) at which the kinetic experiments were made. The results of these determinations are shown in Tables II–VI.

**Kinetic Equations.**—The hydrolysis of dibenzyl phosphate consists of two successive reactions which proceed at comparable rates. The analysis for benzyl alcohol measures the sum of the product formed in both steps; analysis for inorganic phos-

(8) F. H. Westheimer and R. P. Metcalf, *THIS JOURNAL*, **63**, 1339 (1941).

(9) W. J. Hamer, G. D. Pinching and S. F. Acree, *J. Research Natl. Bur. Standards*, **36**, 539 (1945).

(10) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York, N. Y., 1950, p. 523.

(11) H. S. Harned and R. W. Ehler, *THIS JOURNAL*, **55**, 652 (1933).

(12) W. M. Murray, Jr., and S. E. Q. Ashley, *Ind. Eng. Chem., Anal. Ed.*, **10**, 1 (1938).

(13) H. H. Willard, L. L. Merritt, Jr., and J. A. Dean, "Instrumental Methods of Analysis" D. Van Nostrand Co., Inc., New York, N. Y., 1949, p. 139.

TABLE II  
INDICATOR CONSTANT FOR META CRESOL PURPLE AT 75.6°  
AND  $\mu = 1$

HClO <sub>4</sub> , <i>M</i>	Optical density, <i>D</i> , 532 m $\mu$	<i>K'</i> <sub>ind</sub> × 10 <sup>3</sup> , m./l. <sup>a</sup>
1.20	0.762	
0.0496	.526	2.53
.0199	.352	2.60
.0199	.342	2.81
.00993	.235	2.73
.00993	.230	2.78
.000993	.060	2.89
Phthalate buffer, pH 5	.035	

Average *K'*<sub>ind</sub> =  $2.72 \times 10^{-2}$  m./l.

<sup>a</sup> Calculated on the assumption that the ratio (I<sup>-</sup>)/(HI) = (0.776 - *D*)/(*D* - 0.035).

TABLE III  
IONIZATION CONSTANT OF DIBENZYL HYDROGEN PHOSPHATE  
AT 75.6° AND  $\mu = 1$

Dibenzyl hydrogen phosphate, <i>M</i> × 10 <sup>3</sup>	HClO <sub>4</sub> , <i>M</i> × 10 <sup>3</sup>	<i>D</i> , obsd.	(H <sup>+</sup> ), calcd., <i>M</i> × 10 <sup>3</sup>	<i>K'</i> × 10 <sup>3</sup> , m./l.
14.2		0.274	12.8	12.1
7.1	24.8	.424	29.9	7.5
6.0	29.7	.447	33.8	7.4

Average *K'* =  $9 \times 10^{-2}$  m./l.

TABLE IV  
FIRST IONIZATION CONSTANT OF MONOBENZYL DIHYDROGEN  
PHOSPHATE AT 75.6° AND  $\mu = 1$

Di-(cyclohexyl-ammonium) monobenzyl phosphate, <i>M</i> × 10 <sup>3</sup>	HClO <sub>4</sub> , <i>M</i> × 10 <sup>2</sup>	<i>D</i> , obsd.	(H <sup>+</sup> ), calcd., <i>M</i> × 10 <sup>3</sup>	<i>K'</i> <sub>1</sub> × 10 <sup>2</sup> , m./l.
11.08	1.986	0.177	6.40	2.34
9.31	1.986	.208	8.22	2.46
8.20	2.100	.243	10.60	2.89

Average *K'*<sub>1</sub> =  $2.56 \times 10^{-2}$  m./l.

TABLE V  
INDICATOR CONSTANT FOR BROM CRESOL GREEN AT 75.6°  
AND  $\mu = 1$

Buffer	Optical density, <i>D</i> , 617 m $\mu$	<i>K'</i> <sub>ind</sub> × 10 <sup>5</sup> , m./l. <sup>a</sup>
1.006 <i>M</i> HClO <sub>4</sub>	0.006	
0.000437 <i>M</i> HClO <sub>4</sub>	.060	2.53
Acetate buffer, pH 4.58	.560	2.77
Acetate buffer, pH 4.58	.564	2.65
1.0 <i>M</i> NaCO <sub>3</sub>	1.120	

Average *K'*<sub>ind</sub> =  $2.65 \times 10^{-5}$  mole/liter

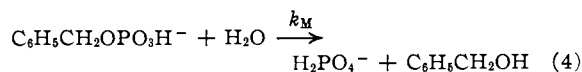
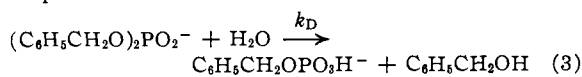
<sup>a</sup> Calculated on the assumption that the ratio (I<sup>-</sup>)/(HI) = (*D* - 0.006)/(1.120 - *D*).

TABLE VI  
SECOND IONIZATION CONSTANT OF MONOBENZYL DIHYDRO-  
GEN PHOSPHATE AT 75.6° AND  $\mu = 1$

Di-(cyclohexyl-ammonium) monobenzyl phosphate, <i>M</i> × 10 <sup>3</sup>	HClO <sub>4</sub> , <i>M</i> × 10 <sup>3</sup>	<i>D</i> , obsd.	(H <sup>+</sup> ), calcd., <i>M</i> × 10 <sup>3</sup>	<i>K'</i> <sub>2</sub> × 10 <sup>5</sup> , m./l.
12.54	9.93	1.008	2.79	7.33
12.34	9.93	.989	3.35	8.13
12.23	9.93	.999	3.24	7.51

Average *K'*<sub>2</sub> =  $7.66 \times 10^{-7}$  m./l.

phate measures only the product from the second step.



If the concentration of dibenzyl phosphate is represented by  $D$ , that of monobenzyl phosphate by  $M$ , that of benzyl alcohol by  $B$ , and that of inorganic phosphate by  $P$ , then

$$\frac{B}{D_0} - 2 = \frac{(k_D - 2k_M)e^{-k_D t} + k_D e^{-k_M t}}{k_M - k_D} \quad (5)$$

Substituting  $k_M/k_D = R$ ,  $k_M t = \tau$  and  $B/D_0 = F$

$$F = \frac{(1 - 2R)e^{-\tau/R} + e^{-\tau}}{R - 1} + 2 \quad (6)$$

When  $R = 1$ , eq. 6 is indeterminate, but is equivalent to 7

$$F = -2e^{-\tau} - e^{-\tau} + 2 \quad (7)$$

The family of curves shown in Fig. 1 was plotted from equations 6 and 7. The hydrolysis of monobenzyl phosphate, at any particular acidity, proved to be a simple first-order reaction. From a study of this reaction, the rate constants,  $k_M$ , were determined for the entire range of acidities studied. Then the data for the diester were plotted as  $F$  against  $\tau$  (*i.e.* against  $k_M t$ ); each value of  $R$  (and hence of  $k_D$ ) was determined by fitting the experimental points for a particular acidity to the corresponding curve in Fig. 1. The results were checked, in a few cases, by a determination of inorganic phosphate. The values of  $k_M$  and  $k_D$  were substituted in eq. (8).

$$P/D_0 = 1 - e^{-k_D t} - \frac{k_D}{k_M - k_D} (e^{-k_D t} - e^{-k_M t}) \quad (8)$$

The agreement between the calculated and experimental values of  $P/D_0$  was satisfactory.

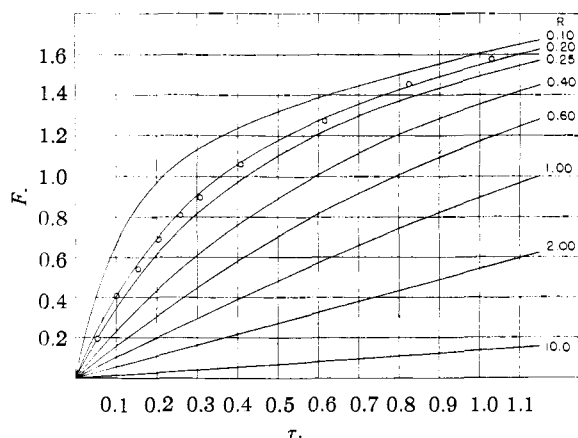


Fig. 1.—Family of curves used to evaluate  $R$  for the hydrolysis of dibenzyl phosphate.

### Results

The  $pH$ -rate profile for the hydrolysis of monobenzyl phosphate is shown in Fig. 2; that for dibenzyl phosphate in Fig. 3; the data are presented in Tables VII and VIII. The half-time for the

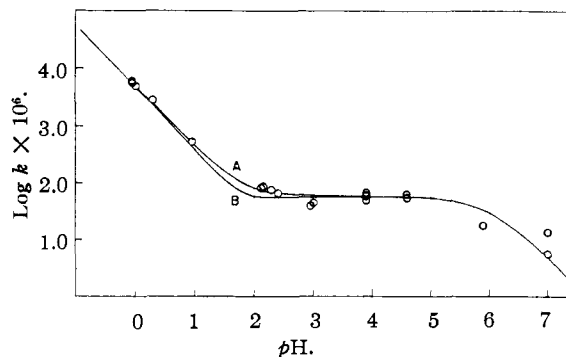


Fig. 2.— $pH$ -rate profile for the hydrolysis of monobenzyl phosphate.

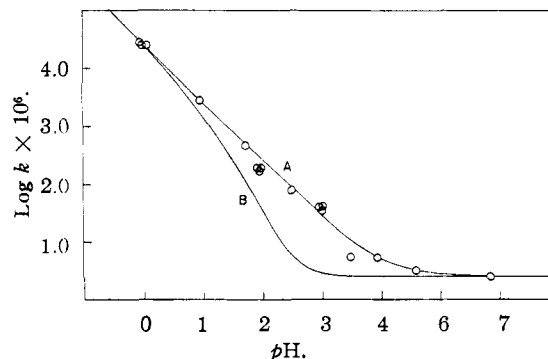


Fig. 3.— $pH$ -rate profile for the hydrolysis of dibenzyl phosphate.

most rapid hydrolysis was about half an hour; the half-time for the slowest about half a year.

TABLE VII  
RATE OF HYDROLYSIS OF MONOBENZYL PHOSPHATE AT 75.6°  
AND IONIC STRENGTH 1

$\text{HClO}_4$ , $M$	$pH$	Monobenzyl phosphate, <sup>a</sup> $M \cdot 10^4$	$10^4 k$ , $\text{min}^{-1}$
1.120	-0.05	8.99	545
1.125	- .05	8.96	599
0.988	.005	45.4	498
.490	.31	12.3	284
.113	.95	12.2	53
.0088	2.13	11.2	86
.0089	2.11	10.4	84
.0078	2.28	20.8	77
	2.40	8.65	66
	3.01	8.20	45
	2.99	10.4	38
	3.91	11.2	57
	3.91	44.8	63
	3.91	12.4	48
	4.58	11.2	62
	4.58	11.2	51
	5.88	8.6	17
	7.00	10.4	5.3
	7.00	8.9	13.4

<sup>a</sup> As dicyclohexylammonium salt.

The rate equation for the hydrolysis of the phosphate esters can be written as

$$v = k_{\text{obsd.}}(\text{Ester}) = k_1(\text{H}^+)(\text{E}) + k_2(\text{E}) + k_3(\text{E}^-)$$

where  $(\text{E})$  is the concentration of the uncharged es-

TABLE VIII  
RATES OF HYDROLYSIS OF DIBENZYL PHOSPHATE AT 75.6°  
AND IONIC STRENGTH 1

HClO <sub>4</sub> , <i>M</i>	<i>pH</i>	Dibenzyl phosphate, <sup>a</sup> <i>M</i> × 10 <sup>4</sup>	10 <sup>4</sup> <i>k</i> <sub>2</sub> , min. <sup>-1</sup>
1.123	-0.04	23.6	2820
0.988	.005	33.9	2580
.997	.001	11.1	2600
.113	.95	9.45	290
.0145	1.72	56.8	48
.0099	1.97	6.90	21.6
.0099	1.97	5.82	20.3
.0099	1.90	29.1	20.3
	2.50	10.0	7.94
	3.01	6.95	4.1
	2.99	6.95	4.1
	3.00	8.04	4.1
	3.91	8.04	5.3
	3.50	6.95	5.7
	4.58	8.04	0.25
	5.88	8.04	0.25

<sup>a</sup> As the free acid.

ter-acid, and (E<sup>-</sup>) is the concentration of the corresponding monoanion. No hydrolysis could be detected for the dianion, E<sup>=</sup>, of monobenzylphosphate.

The curves marked A in Figs. 2 and 3 were derived using the values for the rate constants *k*<sub>1</sub>, *k*<sub>2</sub> and *k*<sub>3</sub> which are presented in Table IX. The curves marked B in Figs. 2 and 3 were derived by fitting the experimental curves under the assumption that *k*<sub>2</sub> is zero. It is seen that this assumption is approximately valid for monobenzyl phosphate, and that the value of *k*<sub>2</sub> for this ester therefore is very doubtful; however, for dibenzyl phosphate, there can be no question that *k*<sub>2</sub> is real. The plot (Fig. 3) of log *k*<sub>obsd.</sub> against *pH* is reasonably linear from *pH* 0 to about 3.5, but this approximate linearity must be fortuitous, since the first ionization constant of the ester, (RO)<sub>2</sub>PO<sub>2</sub>H, falls at *pK* 1.1 and not at 3.5. Therefore, the molecular species changes, over the range of acidity in question, from the uncharged acid, (C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>O)<sub>2</sub>PO<sub>2</sub>H, to its anion, (C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>O)<sub>2</sub>PO<sub>2</sub><sup>-</sup>. The determination of large ionization constants is difficult, and the value here quoted may well be in error (with a corresponding error in the value given for *k*<sub>2</sub>). But there can be little question that the *pK* value for the diester is approximately correct; it is in reasonable agreement with those independently determined (at 25° and low ionic

TABLE IX  
THE RATE CONSTANTS FOR THE HYDROLYSIS OF MONO- AND  
DIBENZYL PHOSPHATES AT 75.6° AND *μ* = 1

Ester	<i>k</i> <sub>1</sub> , min. <sup>-1</sup> (m./l.) <sup>-1</sup>	<i>k</i> <sub>2</sub> , min. <sup>-1</sup>	<i>k</i> <sub>3</sub> , min. <sup>-1</sup>
Monobenzyl phosphate	5.22 × 10 <sup>-3</sup>	(0.7 × 10 <sup>-4</sup> )	5.78 × 10 <sup>-5</sup>
Dibenzyl phosphate	2.72 × 10 <sup>-2</sup>	1.9 × 10 <sup>-3</sup>	2.50 × 10 <sup>-5</sup>
Ratio, <i>k</i> <sub>Mono</sub> / <i>k</i> <sub>Di</sub>	0.20	(0.04)	23

strength) for a large number of similar phosphate esters.<sup>14</sup>

### Discussion

The rate of hydrolysis in strong acid is about 100 times greater for monobenzyl phosphate than for 1-methoxypropyl-2-phosphate.<sup>4</sup> If the cleavage at low *pH* may (or must) involve the cleavage of the carbon-oxygen bond, this behavior is that to be expected<sup>15</sup> since benzyl esters are especially reactive both in S<sub>N</sub>1 and in S<sub>N</sub>2 processes. Because of the large rate of hydrolysis in strong acid, the *pH*-rate profile for monobenzyl phosphate necessarily shows a "shelf" rather than the maximum found for other monoesters<sup>3,4</sup>; the region where the uncharged acid is the major species present therefore is somewhat obscured.

The prominent features of the data are these: (1) The rate constant for acid hydrolysis of the diester is five times that for the monoester. (Since there are two benzyl groups which can be removed from the diester, the true ratio of rates, per benzyl group, is about 2.5.) Presumably the same effect which makes diesters stronger acids<sup>14</sup> than monoesters operates here to allow the diester to hydrolyze somewhat more rapidly. (2) The uncharged acids ROPO<sub>3</sub>H<sub>2</sub> and (RO)<sub>2</sub>PO<sub>2</sub>H both undergo hydrolysis somewhat more readily than do the corresponding uncharged acids for simple aliphatic phosphates. Although the value of *k*<sub>2</sub> for monobenzyl phosphate is very uncertain, it appears to be of the same order of magnitude as *k*<sub>3</sub>; if these data are correct, they are in marked contrast to the corresponding data<sup>3,4</sup> for ethyl-, hydroxyethyl-, and 1-methoxypropyl-2-phosphate. Since the benzyl group forms a carbonium ion and enters displacement reactions much more readily than aliphatic groups do, perhaps the hydrolyses of C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>OPO<sub>3</sub>H<sub>2</sub> and of (C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>O)<sub>2</sub>PO<sub>2</sub>H proceed with carbon-oxygen fission. If such proves to be the fact, the contrast between benzyl and ethyl phosphates would be explained. (3) The monoanion for monobenzylphosphate hydrolyzes about twenty times as fast as does the monoanion for dibenzyl phosphate; the statistical correction raises this factor to 40. Although a factor of 40 is not extraordinarily large, it certainly suggests that there is a special mechanism which is operative for the hydrolysis of monoesters. This mechanism probably involves proton transfer, perhaps in the manner indicated in equation 1. In particular, a mechanism which requires the interaction of OH<sup>-</sup> with an uncharged acid is very improbable. Although such a reaction is kinetically indistinguishable from the reaction of the monoanion with water, it cannot account for the fact that the hydrolysis of the monoanion is much faster for the mono- than for the dibenzyl ester of phosphoric acid.

CHICAGO 37, ILL.

(14) W. D. Kumler and J. J. Eiler, *THIS JOURNAL*, **65**, 2355 (1943).

(15) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 154.