[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF COLORADO]

Alkaline and Neutral Hydrolysis of 2-Octyl Nitrate[1]

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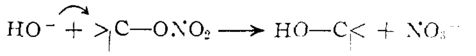
The rates of bimolecular hydrolysis of 2-octyl nitrate with sodium hydroxide in 92.6 wt. % aqueous ethanol and of neutral hydrolysis in 70 vol. % aqueous acetone have been measured at 62.3°. The configurational relationship between optically active 2-octyl nitrate and 2-octanol has been established by hydrogenolysis of the nitrate ester. Alkaline hydrolysis of active 2-octyl nitrate in ethanol led to a mixture of 2-octanol and ethyl 2-octyl ether (as well as 2-octanone) of which mixture 33% resulted from displacement on carbon and 67% from displacement of the nitrogen–oxygen bond. With alkali in aqueous dioxane, the resulting 2-octanol had 71% retention of configuration and 29% inversion of configuration. On the other hand, neutral hydrolysis in aqueous acetone led to 85% inversion of configuration. These results indicate that nitrate esters are borderline compounds, with reasonably comparable abilities to undergo alkyl-oxygen cleavage like sulfonate esters and nitrogen–oxygen cleavage, analogous to carboxylic esters.

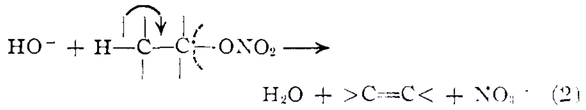
In previous papers by Baker and Easty[2] studies of the hydrolytic decomposition of esters of nitric acid were described; three simultaneous hydrolytic modes of decomposition of nitrate esters were postulated. These are illustrated below with hydroxide ion and may be extended to neutral hydrolysis with water considered as the nucleophilic agent

(a) nucleophilic substitution



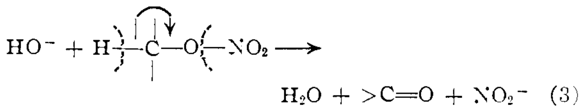
$$HO^- + >C{-}ONO_2 \longrightarrow HO{-}C< + NO_3^- \qquad (1)$$

(b) β-hydrogen elimination of nitric acid



$$HO^- + H{-}C{-}C{-}ONO_2 \longrightarrow H_2O + >C{=}C< + NO_3^- \qquad (2)$$

(c) α-hydrogen elimination of nitrous acid



$$HO^- + H{-}C{-}O{-}NO_2 \longrightarrow H_2O + >C{=}O + NO_2^- \qquad (3)$$

In their work, Baker and Easty found that alkaline treatment of isopropyl nitrate gave 70–80% of isopropyl alcohol, 11–14% of propylene (equation 2) and 8–14% of acetone (equation 3), while the neutral hydrolysis gave only alcohol. Our interest lies in the question of the nature of the alcohol-producing reactions.

Baker and Easty proposed that the base-promoted alcohol-producing reaction involved a nucleophilic displacement on carbon (equation 1), similar to displacement reactions of alkyl halides.[3] The tests which they applied were the effect upon rate of varying the alkyl group in the nitrate ester, effect of changes in nucleophilic reagent and effect of changes in medium. There was a close correspondence of causes and effects in alkyl nitrates and alkyl halides and this led them to postulate that the base-promoted second-order process was as given in equation 1, and in addition that there was a base-independent, carbonium-ion process, available in part for the neutral hydrolysis of isopropyl nitrate and utilized entirely for *t*-butyl nitrate, *viz.*

$$RONO_2 \longrightarrow R^+ + ONO_2^- \qquad (4)$$

$$R^+ + H_2O \longrightarrow RO^+H_2, \text{ etc.} \qquad (5)$$

Baker and Easty apparently did not consider an attractive alternative mechanism for the hydrolysis—that is, the one analogous to that usually utilized by carboxylate esters,[4] where there would occur nitrogen–oxygen cleavage as in (6) rather than alkyl–oxygen cleavage as would be expected for the process described in equation 1.

$$HO^- + O_2N{-}OR \longrightarrow HONO_2 + OR^- \longrightarrow NO_3^- + ROH \qquad (6)$$

To distinguish between these possibilities we have subjected optically active 2-octyl nitrate to both alkaline and neutral hydrolysis. Alkaline hydrolysis was conducted in 92.6 wt. % ethanol, where competition with ethoxide ion must be considered,[5,6] and in 64% aqueous dioxane, where this difficulty is eliminated. Neutral hydrolysis was carried out in 70 vol. % aqueous acetone in the presence of calcium carbonate.

The rates of reaction of 2-octyl nitrate with sodium hydroxide in the ethanolic solvent at 62.3° were followed by titration for base, and good second-order rate constants were observed up to 70% completion. These rate constants represent the sum of the rate constants for at least eight reactions, those represented by equations 1, 2, 3 and 6, plus analogous reactions involving ethoxide ion. These rate constants are listed in Table I. It was observed that 2-octyl nitrate was stable toward solvolysis in this solvent in the absence of alkali, over the time of these experiments. The results are compared in Table I with those found by Baker and Easty[2] for isopropyl nitrate. Rates of neutral solvolysis in 70% acetone are also given in Table I, and compared with data of Baker and Easty for isopropyl nitrate in 60% ethanol. It may be noted that the constants are of comparable magnitude and that it appears likely that stereochemical results with 2-octyl nitrate may probably be typical of nitrate esters of saturated secondary alcohols of comparable steric requirements.

When (+)-2-octanol was treated with a mixture of nitric acid and sulfuric acid, it was converted to (+)-2-octyl nitrate. The fact that the nitration did not involve loss or inversion of configuration

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[1] This work was presented in part before the Division of Organic Chemistry at the Spring 1954 meeting of the American Chemical Society at Kansas City, Missouri.

[2] (a) J. W. Baker and D. M. Easty, *Nature*, **166**, 156 (1950); (b) *J. Chem. Soc.*, 1193 (1952); (c) *ibid.*, 1208 (1952).

[3] E. D. Hughes, C. K. Ingold and S. Masterman, *ibid.*, 1196 (1937); E. D. Hughes, C. K. Ingold and A. D. Scott, *ibid.*, 1201 (1937); E. D. Hughes, *Trans. Faraday Soc.*, **37**, 603 (1941).

[4] (a) J. N. E. Day and C. K. Ingold, *ibid.*, **37**, 686 (1941); (b) B. Holmberg, *Ber.*, **45**, 1997 (1912).

[5] J. W. Baker and A. J. Neale, *Nature*, **172**, 583 (1953).

[6] E. F. Caldin and G. Long, *ibid.*, **172**, 583 (1953).

TABLE I

DATA AND REACTION RATE CONSTANTS FOR HYDROLYSIS OF 2-OCTYL NITRATE AT 62.3°

Alkaline hydrolysis: solvent, 92.6 wt. % aqueous ethanol; base, sodium hydroxide.

Compound	Octyl nitrate, *M*	Base, *M*	$10^6 k_2$, l./sec./mole
2-Octyl nitrate	0.0797	0.1162	6.77
	.0655	.1162	7.15
Isopropyl nitrate[a]	....	....	8.80[a]

Neutral hydrolysis: solvent, 70 vol. % aqueous acetone

Compound	Octyl nitrate, *M*	$10^7 k_2$, sec.$^{-1}$
2-Octyl nitrate	0.0493	1.59
	.0570	1.60
Isopropyl nitrate[b]	....	4.8[b]

[a] Interpolated from data of Baker and Easty.[2] This solvent was 90 vol. % ethanol. [b] Data of Baker and Easty.[2] Temperature, 60.3°; solvent, 60 vol. % ethanol.

was demonstrated by hydrogenolysis of (+)-nitrate to (+)-alcohol over platinum oxide. There was no significant decrease in rotation in this cycle, which thus relates the configuration of the alcohol and its nitrate ester. A similar demonstration has been reported with (−)-2,3-butanediol.[7]

A sample of (+)-2-octyl nitrate, $[\alpha]^{25}\text{D}$ +16.65°, was heated at reflux with excess ethanolic sodium hydroxide (10%) for about 50 hours, and the fraction boiling in the alcohol–ether range was collected. Infrared analysis (qualitative) of the product showed bands in the infrared spectrum indicating the presence of hydroxyl, carbonyl and ether linkages. The sample had zero optical rotation. The product was analyzed by the Grignard procedure and gave the following results: 2-octanol, 45.6%; ketone, 39.8%; ether 14.6% (by difference). A portion of the mixture was treated with phthalic anhydride and the crude acid phthalate which was isolated had a specific rotation of +36.5°. This implies[8] that the alcohol which resulted was 76% (+)2-octanol and 24% *racemic*-2-octanol or 88% (+)2-octanol and 12% (−)2-octanol. It is to be noted that the alcohol has principally the *retained* configuration. The results in this experiment, and others analogous to it, are obscured by the possibility of reactions (7) and (8).

$$\text{EtO}^- + {>}\overset{|}{\underset{|}{\text{C}}}\text{—ONO}_2 \longrightarrow \text{EtO}\underset{|}{\text{C}}{<} + \text{NO}_3^- \quad (7)$$

$$\text{EtO}^- + \text{O}_2\text{N—OR} \longrightarrow \text{EtONO}_2 + {}^-\text{OR} \quad (8)$$

Reaction (7) will give inverted ethyl 2-octyl ether, which would therefore have rotation opposite to that of the parent nitrate ester, while (8), like reaction (6), would give alcohol of *retained* configuration. The fact that rotation in this sample and in others like it were low or zero (but always of the same rotation as the parent nitrate, if observable) indicates that the major proportion of the hydrolysis reaction involved nitrogen–oxygen cleavage as in (6) and (8), rather than carbon–oxygen cleavage as in (1) and (7). This is based upon the fact that the pure ether has a rotation about 1.6 times that of the alcohol.[9] Assuming that the analysis is correct and that the composition of the alcohol results entirely from equations 1, 6 and 8 and none by racemization of active alcohol,[10] the fraction of processes involving attack on carbon (inversion) may readily be shown to be 33% and that of retention (processes) 67%.

In order to remove a portion of the ambiguity of these experiments, a hydrolysis experiment was conducted with levorotatory nitrate ester and excess sodium hydroxide in 64% aqueous dioxane. The product was submitted to nitrogen analysis and to analysis on the Grignard machine. The data obtained give the following analysis: 2-octanol nitrate, 3.6%; 2-octanol, 82%; 2-octanone, 19%. The product had $[\alpha]\text{D}$ −3.77°; of this rotation, −0.62° is due to the nitrate and −3.15° to the alcohol. Thus the alcohol appears to be a mixture of 42% of (−)-2-octanol and 58% of racemic alcohol or 71% of (−)2-octanol (retention of configuration in hydrolysis) and 29% of (+)2-octanol (inversion of configuration).

Although one might assume that the inverted alcohol resulted from racemization,[10] it seems more likely that it results, at least in part, from a displacement as in (1). This conclusion is based upon the experiment in ethanol, where this type of reaction did obtain, as noted by the formation of ether. Thus, with hydroxide and ethoxide, it appears that reactions involving attack on carbon and on nitrogen are of comparable importance with 2-octyl nitrate, the ratios of reaction (6) + (8) to (1) + (7) being about 2 to 1 under both conditions studied.

On the other hand, when dextrorotatory 2-octyl nitrate was solvolyzed with 78% aqueous acetone in the presence of calcium carbonate, the resulting product was levorotatory. Analysis by infrared and refractive index procedures indicated that the product was 13% 2-octanone and 87% 2-octanol. A comparison of the rotation of the product with that of the alcohol from which the nitrate was prepared indicates that the alcohol was 71% (−)2-octanol and 29% *racemic*-2-octanol, or that the process yielded 85% of the inverted alcohol and 15% of the alcohol with retained configuration.

The net inversion of configuration in the neutral hydrolysis leads, of course, to the rejection of the process analogous to (6) for the reaction of 2-octyl nitrate with water. Instead the major reaction may be a nucleophilic displacement on carbon by water, analogous to equation 1, combined with the reactions analogous to (6) or to (4) and (5) to accommodate the partial small amount of retention, or alternatively, the process may be described entirely in terms of reactions (4) and (5).[11] In any case, 2-octyl nitrate appears to react principally like a typical ester in alkaline hydrolysis[4] and principally like an alkyl halide or sulfonate ester in neutral hydrolysis.[12] The results observed are

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(6) A. F. McKay, R. H. Meen and G. F. Wright, THIS JOURNAL, **70**, 430 (1948).

(8) H. Pickard and J. Kenyon, *J. Chem. Soc.*, **91**, 2057 (1907).

(9) H. Phillips, *ibid.*, **127**, 2552 (1925).

(10) W. von E. Doering and T. C. Aschner, THIS JOURNAL, **71**, 838 (1949).

(11) Our data of course offer no clue as to the question of whether the so-called "unimolecular" or "solvolytic" processes, particularly of secondary compounds, occur by one, two or more processes.

(12) H. Phillips, *J. Chem. Soc.*, **123**, 44 (1923); **127**, 2552 (1925).

thus analogous to those on the solvolysis of β-lactones.[13]

When hydrolysis was conducted in the presence of dilute sulfuric acid, no apparent catalysis of hydrolysis occurred. With concentrations of 70–90% sulfuric acid, 2-octanone was obtained and oxides of nitrogen were evolved.

Addendum on 2-Octyl Nitrite.—When optically active 2-octyl nitrite was allowed to react with either ethanolic sodium hydroxide or with 10% sulfuric acid in the presence or absence of urea, 2-octanol of at least 99% *retention* of configuration was formed. This work[14] is not being reported in detail here as it simply confirms a portion of the elegant work reported recently[15] on the hydrolysis of nitrite esters.

Acknowledgments.—The authors wish to acknowledge support of this work by the U. S. Naval Ordnance Test Station Inyokern of the U. S. Navy Bureau of Ordnance and by the Office of Ordnance Research of the U. S. Army. They wish further to acknowledge a helpful discussion with Professor Howard J. Lucas, who informed them of corresponding work on the alkaline hydrolysis of *sec*-butyl nitrate, done in collaboration with Pierre J. Leroux (Ph.D. thesis, California Institute of Technology, 1951). Analyses were conducted by Clark Microanalytical Laboratories and Galbraith Laboratories, and infrared analyses were conducted by Mrs. Patricia S. Ramey.

Experimental

The resolution of 2-octanol was carried out according to Kenyon.[16] Upon treatment of (–)2-octanol, $[\alpha]^{25}\mathrm{D}$ $-9.57°$, with nitric acid and sulfuric acid according to the procedure of Shriner and Parker,[17] 2-octyl nitrate was produced in 60–75% yields. Our product had the following physical properties: b.p. 55–56° (2 mm.), 95–97° (18 mm.); d^{20}_{4} 0.950; $n^{20}\mathrm{D}$ 1.4253; $M\mathrm{D}$ calcd., 47.29; found, 47.13; $[\alpha]^{25}\mathrm{D}$ $-17.64°$ (neat). Shriner and Parker report b.p. 95–97° (20 mm.); d^{20}_{20} 0.954; $n^{20}\mathrm{D}$ 1.4301; $M\mathrm{D}$ calcd. 47.69; found, 47.39; $[\alpha]^{25}\mathrm{D}$ $+14.59$.

Hydrogenolysis of 2-Octyl Nitrate.—A solution of 10 g. (0.057 mole) of (–)2-octyl nitrate, $[\alpha]^{25}\mathrm{D}$ $-15.94°$, in 150 ml. of 95% ethanol was subjected to hydrogenation at 2 atmospheres pressure over 120 mg. of platinum oxide catalyst. The absorption of hydrogen was quantitative and fairly rapid. After the hydrogenation was complete, the catalyst was removed by filtration and the alcohol was distilled. The odor of ammonia was strong. The product, (–)2-octanol, $[\alpha]^{25}\mathrm{D}$ $-9.52°$ (neat), boiling at 86° (20 mm.), was obtained in 63–75% yield. Similar results were obtained with the dextrorotatory isomer.

Determination of Rate Constants.—For the neutral hydrolysis solutions of nitrate in 70 ml. of acetone were made up to 100 ml. with water. The water was distilled and carbonate free, and the acetone was purified by heating it at reflux over potassium permanganate for 24 hours, distilling and drying over anhydrous magnesium sulfate. Samples about 0.05 *M* in nitrate ester were prepared, and aliquots were sealed in tubes and placed in a thermostated bath at 62.34 ± 0.02°. Samples were withdrawn from time to time, were cooled and diluted with water, and were titrated with standard sodium hydroxide for liberated acid. The reactions were followed to 40–50% completion and the data were plotted to give good first-order rate constants. The rate constants are given in Table I. The fact that the hydrolysis was not catalyzed by the liberated acid may be inferred from the fact that good rate constants were observed. Lack of catalysis by dilute acid of the hydrolysis of ethyl nitrate has been reported previously.[18]

For the alkaline hydrolysis the solvent was ordinary commercial ethanol (92.6 wt. % ethanol). Solutions, approximately 0.07 *M* in octyl nitrate and 0.12 *M* in sodium hydroxide, were prepared, and aliquots were sealed in tubes and placed in a thermostated bath at 62.34 ± 0.02°. Samples were withdrawn from time to time and were cooled and diluted with water. The excess sodium hydroxide was estimated by titration with standard hydrochloric acid. Plots of the rate data, using a standard equation for the second-order rate law,[19] gave good straight lines. The rate constants, corrected for expansion of solvent, are given in Table I. The reactions were followed to 60–70% completion. 2-Octyl nitrate was found to be relatively stable in the absence of alkali under similar conditions; this also has been observed with isopropyl nitrate in 90 vol. % ethanol.[2]

Neutral Hydrolysis of Optically Active 2-Octyl Nitrate.—A typical product run on optically active 2-octyl nitrate was as follows: 4.5 g. (0.026 mole) of (+)2-octyl nitrate ($\alpha^{25}\mathrm{D}$ $+16.43°$, d^{20}_{4} 0.950, $[\alpha]^{25}\mathrm{D}$ $+17.29°$, $n^{20}\mathrm{D}$ 1.4250) was added to a combustion tube containing 55 ml. of acetone, 15 ml. of water and 4.0 g. of calcium carbonate. There was 0.84 mole of water present which was about 40 times the amount of 2-octyl nitrate. The combustion tube was sealed and placed in a furnace at 104–106° for 21 days; the combustion tube was then cooled, opened, and the solution in the sealed tube was filtered. The combustion tube was washed with ether which was added to the filtered solution. To the combined filtrate water was added until the ether layer separated. The ether layer was washed with water and dried overnight over anhydrous magnesium sulfate. After removal of the ether by distillation, the product (1.07 g., 32%) was distilled under reduced pressure, and had the following properties: b.p. 54–56° (3 mm.), $n^{25}\mathrm{D}$ 1.4244, $\alpha^{25}\mathrm{D}$ $-4.90°$ (neat), d^{25}_{4} 0.820, $[\alpha]^{25}\mathrm{D}$ $-5.98°$. This product was estimated to be 87% 2-octanol and 13% 2-octanone by refractive index analysis (our observed values for these materials were 1.4256 and 1.4157, respectively) and an identical result was obtained by infrared analysis. The band at 5.83 μ was used for the ketone analysis.

The mode of formation of the ketone is not clear. It may be due to lack of mixing of the calcium carbonate in the tube, so that the product nitric acid may have oxidized a part of the alcohol. There is the alternative that the ketone was formed by a reaction analogous to (3). This type of reaction was not observed at lower temperatures with isopropyl nitrate.[2]

Alkaline Hydrolysis of Optically Active 2-Octyl Nitrate in Ethanol.—A solution of 9.5 g. (0.054 mole) of (+)2-octyl nitrate, $[\alpha]^{25}\mathrm{D}$ $+16.92°$, in 100 ml. of 2 *N* ethanolic sodium hydroxide was heated at reflux for 98 hours. The reaction mixture was poured into water and the separated alcohol fraction was washed with water, dried over anhydrous magnesium sulfate, and distilled at 36–52° (2 mm.). This fraction had $[\alpha]^{25}\mathrm{D}$ $+1.56°$ (neat), as compared with a value of $+9.42°$ for the original alcohol from which the nitrate ester was prepared.

In order to demonstrate that the rotation was not due to unreacted nitrate ester, the material was submitted to analysis for nitrogen.[20]

Anal. Calcd. for $C_8H_{18}O$: N, 0.0. Found: N, 0.0. A qualitative infrared analysis of this fraction apparently showed the presence of hydroxyl, carbonyl and ethyl ether groupings. When a sample of (–)nitrate was treated under similar conditions for 12 hours, a product with $[\alpha]^{25}\mathrm{D}$ $-1.68°$ was obtained.

A solution of 6.0 g. (0.034 mole) of optically active 2-octyl nitrate ($[\alpha]^{25}\mathrm{D}$ $+16.65°$) and 5.06 g. of sodium hydroxide in 50 ml. of ethanol was heated at reflux for 47 hours. This solution was cooled, diluted with 400 ml. of water and

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(13) W. A. Cowdrey, E. D. Hughes, C. K. Ingold, S. Masterman and A. D. Scott, *J. Chem. Soc.*, 1264 (1937); A. R. Olson and R. J. Miller, This Journal, **59**, 2144 (1937); A. R. Olson and J. L. Hyde, *ibid.*, **63**, 2459 (1941).

(14) B. Franzus, Ph.D. thesis, University of Colorado, 1954; A. Shadan, M.S. thesis, University of Colorado, 1954.

(15) A. D. Allen, *Nature*, **172**, 301 (1953); *J. Chem. Soc.*, 1968 (1954).

(16) J. Kenyon in H. Gilman and A. H. Blatt, "Organic Syntheses," Coll. Vol. 11, 2nd Edition, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 418.

(17) R. L. Shriner and E. A. Parker, This Journal, **55**, 766 (1933).

(18) S. C. J. Olivier and G. Berger, *Rec. trav. chim.*, **41**, 637 (1922).

(19) S. J. Cristol, This Journal, **67**, 1494 (1945).

(20) Analysis performed by Galbraith Laboratories.

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^{20}_D 1.4207, d^{20}_4 0.8117, α^{25}_D +0.01°.

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.[8] 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 $[\alpha]^{20}_D$ +36.5° (*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, $[\alpha]^{25}_D$ −17.35°. This solution was placed in a sealed tube and the temperature was maintained at 140 ± 5° 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^{21}_4 0.8307, n^{22}_D 1.4240, α^{25}_D −3.13°, $[\alpha]^{25}_D$ −3.77°.

Anal. Found: N, 0.29[20]; 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[1] AND F. H. WESTHEIMER

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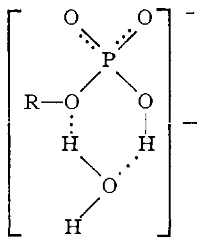
The *p*H–rate profiles for the hydrolysis of mono- and dibenzyl phosphates at 75.6° have been determined. The monoanion, $ROPO_3H^-$, of monobenzyl phosphate hydrolyzes much more readily than does the corresponding monoanion, $(RO)_2PO_2^-$, of dibenzylphosphate. The mechanism for the hydrolysis of phosphate esters, which was advanced in a previous paper, is consistent with these facts.

Bailly[2] and later Desjobert[3] noted that the rate of hydrolysis of a simple monoester of phosphoric acid is slow in alkaline solution, rises to a maximum around *p*H 4, falls to a minimum at *p*H 1–2, and then rises again in strong acid solution. The rate maximum occurs where the monoanion $ROPO_3H^-$ is present in greatest concentration. In a previous article,[4] 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.

$$ROPO_3H^- + H_2O \rightleftarrows$$



$$\longrightarrow ROH + H_2O + PO_3^- \quad (1)$$

$$PO_3^- + H_2O \longrightarrow H_2PO_4^- \quad (2)$$

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

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,[5] prepared from sodium benzyloxide and $POCl_3$, melted at 64°. Dibenzylphosphoric acid could be prepared from the triester by the method of Lossen and Kohler[5] or of Clark and Todd[6]; it melted at 78–79°. Monobenzyl dihydrogen phosphate was prepared as the di-(cyclohexylammonium) salt by the procedure of Todd and Curry.[7] 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 dicyclohexylammonium 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 $C_{19}H_{35}PO_4N_2 \cdot H_2O$: C, 56.39; H, 9.23; N, 6.93. Found: C, 56.3: H, 9.22; N, 6.88.

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[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).

[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.