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36. **Tyunosin Ukita,* Kinzo Nagasawa,* and Masachika Irie*** : Organic Phosphates. III.[4] Studies on Alcoholysis of Several Cyclic Phosphates.

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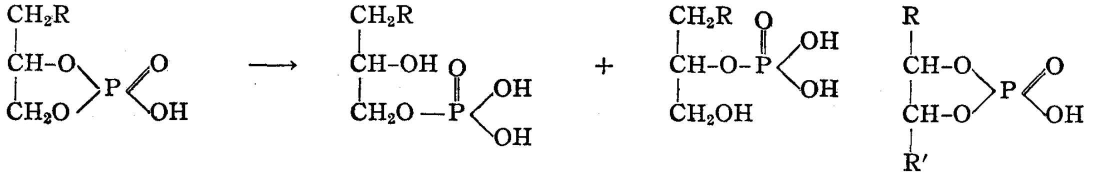
Recently Ukita, Bates, and Carter[2] observed that on treatment of glycerol 1,2-cyclic phosphate (GCP)[1] (I) with absolute ethanol or benzyl alcohol and trifluoroacetic acid, (I) formed alkyl esters of glycerophosphates having alkyl groups corresponding to the alcohols used. Thus benzyl glycerophosphate which showed Rf_1 0.77[6] was isolated as its barium salt from the alcoholysate of GCP with benzyl alcohol.

Tener and Khorana[3] also reported the results of similar alcoholysis reactions for cyclic nucleotides with several alcohols using hydrochloric acid as a catalyst, and from the reaction mixtures, they separated both 2′- and 3′-benzylnucleotides in the case of the reaction with benzyl alcohol.

In the previous papers of this series,[4,5] the present authors observed that on acid hydrolysis, 1,2-propanediol cyclic phosphate (PCP) (Ⅱ) gave only 2-hydroxypropyl phosphate (Ⅲ) in contrast with the case of GCP which gave both α- and β-glycerophosphate (Ⅳ and Ⅴ).



(Ⅰ R=OH
(Ⅱ) R=H

(Ⅲ) R=H
(Ⅳ) R=OH

(Ⅴ) R=OH

(Ⅵ) R=R′=H
(Ⅶ) R=R′=CH_3

It is of interest whether a similar difference as in the hydrolysis of GCP and PCP might also be observed in the alcoholysis of these compounds.

This paper deals with the results of their alcoholysis together with those for ECP (Ⅵ) and BCP (Ⅶ), the syntheses of which were reported in the first paper of this series.[4]

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[1] The following abbreviations are used : GCP, glycerol 1,2-cyclic phosphate; PCP, 1,2-propanediol cyclic phosphate; ECP, ethyleneglycol cyclic phosphate; BCP, 2,3-butanediol cyclic phosphate; EP, ethyleneglycol phosphate; BP, 2,3-butanediol phosphate; GP, glycerophosphate; PP, 1,2-propanediol phosphate (preceded by alkyl or cation substituted or number of the position of hydroxyl group concerned with phosphoryl ester where necessary). TFA, trifluoroacetic acid, TCA, trichloroacetic acid.

[2] T. Ukita, N. A. Bates, H. E. Carter : J. Biol. Chem., **216**, 867(1955).

[3] G. M. Tener, H. G. Khorana : J. Am. Chem. Soc., **77**, 5349(1955).

[4] T. Ukita, K. Nagasawa, M. Irie : This Bulletin, **5**, 121(1957). The author's name misspelled as Tyunoshin Ukita should read Tyunosin Ukita.

[5] T. Ukita, K. Nagasawa, M. Irie : *Ibid.*, **5**, 127(1957).

[6] Techniques in paper chromatography : 10～40 γ of phosphorus was applied to Toyo Roshi No. 3 paper and run ascendingly 15 hrs. with one of following solvent systems : (1) *iso*-PrOH+5*N* NH_4OH (2:1); (2) *iso*-PrOH + *t*-BuOH + conc. NH_4OH + H_2O (40:20:1:39); (3) *t*-BuOH + water + picric acid (80:20:4 g); (4) pyridine + *iso*-PrOH + H_2O (5:70:30). P was detected by the method of Bandurski and Axelrod (J. Biol. Chem., **193**, 405(1951)). In this paper, the Rf values of phosphorus compounds found for each of these solvent systems are represented with the abbreviations Rf_1, Rf_2, Rf_3, and Rf_4, respectively.

Experimental

Alcoholysis of Ba-GCP in Benzyl Alcohol with CF_3COOH—A mixture of 0.8 g. of Ba-GCP, 30 cc. of benzyl alcohol, and 2 cc. of trifluoroacetic acid was kept for 24 hrs. at room temperature. From the reaction mixture, after addition of 150 cc. of distilled water, excess of benzyl alcohol was extracted with ether. The aqueous layer was adjusted to pH 9.0 with $Ba(OH)_2$ and excess of the reagent removed with CO_2. After removal of $BaCO_3$ by centrifugation, the supernatant was lyophilized to obtain a vitreous phosphate which showed two phosphate spots with Rf_1 0.78 and Rf_1 0.23 on paper chromatogram.6) The phosphate mixture was dissolved in 3 cc. of MeOH and placed on the top of Solka-Floc column (1.5 × 45 cm.) prepared in MeOH, eluted with the same solvent at a flow rate of 0.4 cc./min., and 4-cc. fractions were collected.

Phosphate with Rf_1 0.77 was detected in Tubes 15 to 34.*7) The fractions in Tubes 22 to 34 were combined**7) and concentrated to ca. 2 cc. at 30° under a reduced pressure. The syrup thus obtained was streaked on 24 sheets of filter paper (16 × 40 cm.) (Toyo Roshi No. 3) and developed ascendingly with the solvent system (1). The zones of papers with Rf_1 0.77 were collected and eluted with 150 cc. of distilled water. The eluate was passed through a column of Amberlite IRC-50 (Ba^{++} type) and the effluent was lyophilized to give 70 mg. of a white powder.***7) This powder was reprecipitated from aqueous solution with acetone. On drying over $CaCl_2$ under 12 mm. the powder once turned into an oil and again solidified by further drying over P_2O_5 *in vacuo* at 75°. The sample for analysis was thus dried to constant weight. *Anal.* Calcd. for $(C_{10}H_{14}O_6P)_2Ba \cdot H_2O$: C, 35.42; H, 4.43; P, 9.20. Found : C, 35.06; H, 4.35; P, 9.12; Rf_1 0.78; Rf_2 0.70.

Periodate oxidation of the Product—2 mg. of the Ba salt was dissolved in 2 cc. of distilled water. To the solution was added a saturated aqueous solution of $(NH_4)_2SO_4$ and the precipitated $BaSO_4$ was centrifuged off. The precipitate was washed twice with 1 cc. of water and the washings were combined with the supernatant. To this solution 5 cc. of periodate solution (0.6250 g. of KIO_4 in 500 cc. of 0.1*N* H_2SO_4) was added and the mixture was adjusted to 10 cc. with water. Each cc. of the solution was taken at intervals and titrated with 0.004*N* $Na_2S_2O_3$ solution up to the constant consumption of the reagent.8) 0.53 mole of periodate was used for the oxidation of 1 mole of the salt [Calcd. for $(C_{10}H_{14}O_6P)_2Ba \cdot H_2O$].

Ethanolysis of GCP with Several Acidic Catalysts—Each tube containing 1 mg. of Ba-GCP dissolved at 0.5 cc. of dehyd. EtOH was added with 0.05~0.1 cc. of CF_3COOH, CCl_3COOH, CH_3COOH, conc. H_2SO_4, or 20 mg. of Amberlite IR-120 (H^+-type) (dried over $CaCl_2$ after washing with dry acetone). One of the tubes was saturated with dry HCl and after 24 hrs. at room temperature, solutions were tested by paper chromatography. The results are shown in Table I.

Acid Catalysed Alcoholysis of PCP with Various Alcohols—To 0.5 cc. each of MeOH, EtOH, *n*-PrOH, *iso*-PrOH, *t*-BuOH, benzyl alcohol, and 1,2-propanediol were added 1 mg. of Ba-PCP and 0.05~0.1 cc. of CF_3COOH. The mixtures were kept at room temperature (17~20°) and after 48 hrs. the solutions were tested by paper chromatography with the solvent system (1). Similar solutions of Ba-PCP dissolved in the same kinds of alcohol as above were saturated with dry HCl gas and the solutions were kept at room temperature for 23 hrs. and tested similarly by paper chromatography.

Dioxane solution of Ba-PCP and Ba 2-hydroxypropyl phosphate was used as control. The results are shown in Table II.

Ethanolysis of PCP with Several Acidic Catalysts—Ba-PCP was alcoholysed with EtOH using several acidic catalysts, Amberlite IR-120 (H^+-type), CCl_3COOH, CH_3COOH, and conc. H_2SO_4. The amounts of Ba-PCP and catalysts used were the same as in the case of GCP. The reaction products were tested on paper chromatograms after 24 hrs. at room temperature and the results are shown in Table III.

Isolation of the Product of Alcoholysis of PCP with Benzyl Alcohol and its Identification with Benzyl 2-Hydroxypropyl Phosphate—A mixture of 2.05 g. (0.01 mole) of Ba-PCP, 21.6 g. (0.2 mole) of benzyl alcohol, and 5.7 g. (0.05 mole) of CF_3COOH was kept at room temperature for 24 hrs. The mixture was neutralized with $Ba(OH)_2$ and extracted with ether to remove benzyl alcohol. CO_2 was saturated in the aqueous layer to precipitate $BaCO_3$ which was centrifuged off. From the supernatant Ba^{++} was removed with Amberlite IR-120 (H^+-type) and the acid solution obtained was lyophilized. The residual vitreous syrup was treated with NH_3 in *iso*-PrOH and isopropanol-soluble ammonium salt was separated. The aqueous solution of this salt was converted into free acid and

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7) * This mixture showed one additional spot at Rf_1 0.83 with greenish blue tone which was proved to be the spot caused by CF_3COOH by blank test.

** These tubes contained an impurity with Rf_1 0.83 in minor amounts.

*** This powder showed only one phosphate spot with Rf_1 0.77 on paper chromatogram.

8) According to the method reported by L. Voris, G. Ellis, and L. A. Meynard (J. Biol. Chem., **133**, 492(1940)).

Ba salt by successive passage through the columns of Amberlite IR-120 (H^+-type) and IRC-50 (Ba^{++}-type). 1.7 g. of Ba salt of the product (yield 50%) was obtained which was recrystallized from water. *Anal.* Calcd. for $(C_{10}H_{14}O_5P)_2Ba\cdot 2H_2O$: C, 38.23; H, 4.49; P, 9.88. Found : C, 38.24; H, 4.51; P, 9.67. Rf_1 0.84; Rf_2 0.88.

Hydrogenolysis of the Product—To a solution of 20 mg. of the above Ba salt in 10 cc. of 50% EtOH was added 20 mg. of Pd-C. The mixture was shaken in hydrogen atmosphere at room temperature. After 1 hr. consumption of hydrogen ended. The catalyst was removed by filtration and the filtrate was concentrated to a small bulk. An aliquot of the solution was tested on paper chromatogram after removal of Ba^{++} with Amberlite IR-120 (H^+-type). The results are shown in Table V. The solution gave a single phosphate spot with Rf_1 0.27 and Rf_2 0.58.

Acid Catalysed Alcoholysis of ECP and BCP with Several Alcohols—To a series of tubes containing 0.5 cc. of MeOH, EtOH, PrOH, *iso*-PrOH, *t*-BuOH, benzyl alcohol and ethyleneglycol, 1 mg. of Ba-ECP (Series A) was added. Another series of ethanolic solutions of Ba-BCP with similar concentrations was prepared with the exception of replacing ethyleneglycol with 2,3-butanediol (Series B). Both series were kept at room temperature (25~30°) for 48 hrs. after addition of acid catalysts as in the case of alcoholysis for GCP or PCP.

The reaction solutions were tested on paper chromatograms. As a control, aqueous Ba-ECP, Ba-EP, and aqueous Ba-BCP, Ba-BP were used for the series A and B, respectively. The results are shown in Table VI.[9]

Ethanolysis of ECP and BCP with Several Acidic Catalysts—Ba-ECP and Ba-BCP were ethanolysed using several acidic catalysts, Amberlite IR-120 (H^+-type), CCl_3COOH, AcOH, and conc. H_2SO_4. The amount of the material, catalyst, and the reaction conditions used were the same as in the similar tests for GCP and PCP. The results obtained are shown in Table VII.

Results and Discussions

The benzyl-GP obtained by trifluoroacetic acid-catalysed alcoholysis of GCP with benzyl alcohol was purified as a Ba salt. Although this product showed a single spot with Rf_1 0.78 and Rf_2 0.70 on paper chromatograms, it was proved from the result of its periodate oxidation to be a mixture of ca. 50% of both Ba benzyl α-glyceryl (VIII) and Ba benzyl β-glyceryl phosphates (XI).

The alcoholysis of GCP with ethanol was tested using various acidic catalysts and, as shown in Table I, of the catalysts tried, TFA, TCA, and hydrochloric acid were found to be active. Glacial AcOH had poor activity and H_2SO_4 hydrolysed GCP to GP.

TABLE I. Ethanolysis of GCP with Several Acidic Catalysts

Solution spotted	Rf_1		
	Product of hydrolysis	Starting material	Product of alcoholysis
Ba-GCP+EtOH (control)		0.60 S	
Ba-GP + 〃 (〃)	0.23 S		
Ba-GCP+ 〃 +IR-120 (H^+)	0.23M	0.60W	0.66M
〃 $+CF_3COOH$	0.23 S		0.66 S
〃 $+CCl_3COOH$	0.23 S		0.66 S
〃 $+CH_3COOH$	0.23W	0.60 S	0.66M
〃 $+H_2SO_4$	0.23 S		
〃 +HCl	0.23 S		0.66 S

Figures indicate the Rf_1 values. S, M, W, etc. represent the sizes and gradations of the tones of spots : S : strong, M : medium, W : week, F : faint.

Alcoholysis of PCP was tested with several alcohols using both TFA and hydrochloric acid as a catalyst. In this case (Table II) TFA more favored the alcoholysis than hydrochloric acid. Of the alcohols used the primary alcohols were most powerful in ester exchange reactions compared with secondary and tertiary ones. An interesting fact is that benzyl alcohol, although it alcoholysed PCP in major amount when catalysed by TFA, gave no spot of alcoholysis product when hydrochloric acid was used as catalyst.

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[9] The porduct of methanolysis of ECP with trifluoroacetic acid was performed in preparative scale. From 1.1 g. of Ba-ECP, after isolation of the product through cellulose column chromatography, pure Ba methyl 2-hydroxyethyl phosphate was obtained in a yield of 250 mg.

Table II. Acid Catalysed Alcoholysis of PCP

Solution spotted	Rf_1			
	Inorganic P	Product of hydrolysis	Starting material	Product of alcoholysis
Ba-PCP +dioxane (control)			0.63 S	
Ba-1-PP+ 〃 (〃)		0.27 S		
Ba-PCP + 〃 +TFA	W	0.27 S		
〃 +MeOH +〃	W	0.27 S		0.70 S
〃 +EtOH +〃	W	0.27M		0.74 S
〃 +PrOH +〃	W	0.27M		0.75 S
〃 +*iso*-PrOH +〃	W	0.27M		0.75W
〃 +*t*-BuOH +〃		0.27 S		
〃 +benzyl alcohol +〃	W	0.27M		0.84 S
〃 +propyleneglycol+ 〃	W	0.27M		0.74 S
〃 +dioxane +HCl	W	0.27 S		
〃 +MeOH +〃		0.27 S		0.70M
〃 +EtOH +〃		0.27 S		0.74M
〃 +PrOH +〃		0.27 S		0.75M
〃 +*iso*-PrOH +〃		0.27 S		0.75F
〃 +*t*-BuOH +〃		0.27 S		
〃 +benzyl alcohol +〃		0.27 S		
〃 +propyleneglycol+ 〃		0.27 S		0.74M

Figures and abbreviations are the same as in Table I.

Table III. Ethanolysis of PCP with Several Acidic Catalysts

Solution spotted	Rf_1			
	Inorganic P	Product of hydrolysis	Starting material	Product of alcoholysis
Ba-PCP +EtOH (control)			0.63 S	
Ba-1-PP+ 〃 (〃)		0.27 S		
Ba-PCP + 〃 +IR-120 (H^+)	W	0.27 S		0.74 S
〃 + 〃 +TCA	W	0.27 S		0.74 S
〃 + 〃 +CH_3COOH	W	0.27M	0.63 S	0.74M
〃 + 〃 +H_2SO_4	S			0.74F

Figures and abbreviations are the same as in Table I.

PCP was ethanolysed with several acidic catalysts and the results are given in Table III. It shows that TCA was the most desirable catalyst of these acids tested. Amberlite IR-120 (H^+-type) was also available, but from the results of repeated experiments its activity largely depends on the amount of water contained in the resin which was controlled only with difficulty. Sulfuric acid also decomposed PCP in this case.

As shown in Table II, all the paper chromatograms of the alcoholysates of PCP gave one phosphate spot of the alcoholysis products, the Rf values of which differed from one another according to the alcohols used. Of the products of these alcoholysis, those of methanolysis and propyleneglycolysis were compared with authentic, synthesized methyl 2-hydroxypropyl phosphate (IX) and bis(2-hydroxypropyl) phosphate (X), respectively. The results are given in Table IV which shows identities of the products with synthetic specimens on paper chromatograms.

Table IV. Identification of Alcoholysis Product of PCP on Paper Chromatograms

Materials spotted	Rf_1	Rf_2
Product of methanolysis	0.70	0.67
Methyl 2-hydroxypropyl phosphate	0.70	0.67
Product of propyleneglycolysis	0.74	0.81
Bis(2-hydroxypropyl) phosphate	0.74	0.81

However, as was observed in the case of benzyl-GP, the two isomers, benzyl α-glyceryl (VIII) and β-glyceryl phosphate (XI), had the same Rf values for each of the two different solvent systems and their mixture showed only a single spot on a paper chromatogram, so that there is a possibility that methanolysis and propyleneglycolysis products of PCP are methyl 1-methyl-2-hydroxyethyl phosphate (XII) and 1-methyl-2-hydroxyethyl 2′-hydroxypropyl phosphate (XIII) or their mixtures with (IX) and (X).[10]

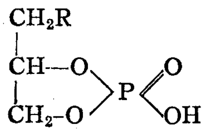
In order to find whether the alcoholysis of PCP occurred to give the mixture of isomeric alkyl hydroxypropyl phosphates, benzyl-PP obtained by TFA-catalysed alcoholysis of PCP with benzyl alcohol was isolated and debenzylated by hydrogenolysis. On detection of the mixture of this reaction products by paper chromatography, the only phosphate spot found was that of 2-hydroxypropyl phosphate (III) with Rf_1 0.27 and Rf_2 0.58 (Table V) and the product gave no trace of the spot for 1-methyl-2-hydroxyethyl phosphate (V) which was known to have Rf_1 0.36 and Rf_2 0.65.[4]

TABLE V. Identification of the Product obtained after Debenzylation of Benzyl Hydroxypropyl Phosphate, the Product of Benzyl-Alcoholysis of PCP, with 2-Hydroxypropyl Phosphate

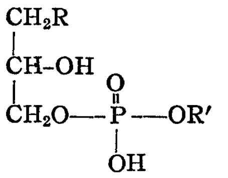
Materials spotted	Rf_1	Rf_2
Product of debenzylation	0.27	0.58
2-Hydroxypropyl phosphate	0.27	0.58

The result reveals that the alcoholysis of PCP with benzyl alcohol occurred to give only benzyl 2-hydroxypropyl phosphate, because there is no possibility for the migration of phosphoryl group in above series of reactions.

It is of interest that, similar to the different modes of hydrolysis of GCP and PCP, GCP also gave both esters of α-GP and β-GP by alcoholysis in contrast to that for PCP which gave only esters of 2-hydroxypropyl phosphate.

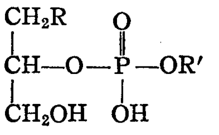


(I) R=OH



$CH_2R-CH(OH)-CH_2O-P(=O)(OH)-OR'$

(VIII) R=OH, R′=benzyl
(IX) R=H, R′=CH_3
(X) R=H, R′=$CH_2CH(OH)CH_3$



$CH_2R-CH(CH_2OH)-O-P(=O)(OH)-OR'$

(XI) R=OH, R′=benzyl
(XII) R=H, R′=CH_3
(XIII) R=H, R′=$CH_2CH(OH)CH_3$

ECP and BCP were similarly alcoholysed with several alcohols applying TFA and hydrochloric acid as a catalyst (Table VI).[9] In these cases not so large differences were observed for the catalytic activity of these two acids. However, the larger reactivity of primary alcohols in ester exchange reactions than secondary or tertiary ones was also observed.

ECP gave no spot for the product of alcoholysis with benzyl alcohol when the reaction was catalysed by hydrochloric acid but it gave the spot when TFA was used as the catalyst, and this result was similar to PCP (Table II).

On alcoholysis of BCP with 2,3-butanediol, two products with Rf_1 0.72 and Rf_1 0.79 were observed. The yield of the former product was larger than that of the latter with hydrochloric acid as catalyst, but the ratio of the yields of these two products seemed to be reverse when TFA was used as the catalyst. However, in this stage, it is not clear which of these two spots is that of the true alcoholysis product.

Tests for several other kinds of acidic catalysts for the ethanolysis of both ECP and BCP did not reveal better catalyst than TFA or hydrochloric acid as in the results of similar tests for GCP and PCP (Table VII).

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[10] The possibility of bis(1-methyl-2-hydroxyethyl) phosphate for the alcoholysis product of PCP with propyleneglycol could be omitted because the alcoholysis occurs more actively with primary alcohol group than secondary one.

TABLE VI. Acid-catalysed Alcoholysis of ECP and BCP

Solution spotted	Rf₁		
	Product of hydrolysis	Starting material	Product of alcoholysis
Ba-ECP + H_2O (control)		0.55 S	
Ba-EP + 〃 (〃)	0.22 S		
Ba-ECP + dioxane + TFA	0.22 S		
〃 + MeOH + 〃	0.22 S		0.63 S
〃 + EtOH + 〃	0.22 S		0.68 S
〃 + PrOH + 〃	0.22 S		0.71 S
〃 + *iso*-PrOH + 〃	0.22 S		0.71 F
〃 + *t*-BuOH + 〃	0.22 S		
〃 + benzyl alcohol + 〃	0.22 S		0.82 S
〃 + ethyleneglycol + 〃	0.22 S		0.55 S
〃 + MeOH + HCl	0.22 S		0.63 S
〃 + EtOH + 〃	0.22 S		0.68 S
〃 + PrOH + 〃	0.22 S		0.71 S
〃 + *iso*-PrOH + 〃	0.22 S		0.71M
〃 + *t*-BuOH + 〃	0.22 S		
〃 + benzyl alcohol + 〃	0.22 S		
〃 + ethyleneglycol + 〃	0.22 S		0.57 S
Ba-BCP + H_2O (control)		0.65 S	
Ba-BP + 〃 (〃)	0.31 S		
Ba-BCP + dioxane + TFA	0.31 S		
〃 + MeOH + 〃	0.31 S		0.73 S
〃 + EtOH + 〃	0.31 S		0.78 S
〃 + PrOH + 〃	0.31 S		0.82 S
〃 + *iso*-PrOH + 〃	0.31 S		0.82 F
〃 + *t*-BuOH + 〃	0.31 S		
〃 + benzyl alcohol + 〃	0.31 S		0.86M
〃 + 2,3-butanediol + 〃	0.31 S		0.72M, 0.79 F
〃 + MeOH + HCl	0.31M		0.72 S
〃 + EtOH + 〃	0.31M		0.78 S
〃 + PrOH + 〃	0.31 S		0.82 S
〃 + *iso*-PrOH + 〃	0.31 S		0.82M
〃 + *t*-BuOH + 〃	0.31 S		
〃 + benzyl alcohol + 〃	0.31 S		0.86 S
〃 + 2,3-butanediol + 〃	0.31 S		0.72 F, 0.79M

Figures and abbreviations are the same as in Table I.

TABLE VII. Ethanolysis of ECP and BCP with several Acidic Catalysts

Solution spotted	Rf₁		
	Product of hydrolysis	Starting material	Product of alcoholysis
Ba-ECP + EtOH (control)		0.55 S	
Ba-EP + 〃 (〃)	0.22 S		
Ba-ECP + 〃 + IR-120 (H^+)	0.22 S		0.68 S
〃 + 〃 + CCl_3COOH	0.22 S		0.68 S
〃 + 〃 + CH_3COOH	0.22W	0.55M	0.68M
〃 + 〃 + H_2SO_4	0.22 S		
Ba-BCP + 〃 (control)		0.65 S	
Ba-BP + 〃 (〃)	0.31 S		
Ba-BCP + 〃 + IR-120 (H^+)	0.31 S	0.65 F	0.78 S
〃 + 〃 + CCl_3COOH	0.31 S	0.65 F	0.78M
〃 + 〃 + CH_3COOH	0.31 S	0.65 S	0.78M
〃 + 〃 + H_2SO_4	0.31 S		

Figures and abbreviations are the same as in Table I.

The methanolysis products of ECP and BCP as well as the alcoholysis product of ECP with ethyleneglycol were identified on paper chromatograms with authentic, synthesized methyl 2-hydroxyethyl, methyl 1-methyl-2-hydroxypropyl, and bis(2-hydroxyethyl) phosphate, respectively.[11]

TABLE VIII. Identifications of Alcoholysis Products of ECP and BCP on Paper Chromatograms

Materials spotted	Rf_1	Rf_2
Methanolysis product of ECP	0.63	0.66
Methyl 2-hydroxyethyl phosphate	0.63	0.66
Ethyleneglycolysis product of ECP	0.55	0.59
Bis(2-hydroxyethyl) phosphate	0.55	0.59
Methanolysis product of BCP	0.72	0.78
Methyl 1-methyl-2-hydroxypropyl phosphte	0.72	0.78

Summary

Four 1,2-diol cyclic phosphates, glycerol 1,2-cyclic phosphate (GCP), 1,2-propanediol cyclic phosphate (PCP), 2,3-butanediol cyclic phosphate (BCP) and ethyleneglycol cyclic phosphate (ECP) were studied on their acid-catalysed alcoholysis reaction with several alcohols.

For PCP, acid-catalysed alcoholysis was found to occur selectively at its phosphate bond concerned with the secondary hydroxyl group to give only alkyl 2-hydroxypropyl phosphate. Under similar conditions, the phosphate bonds of GCP at α- and β-positions were alcoholysed nonselectively giving 50% each of both alkyl α- and β-glyceryl phosphate.

Primary alcohols were found to alcoholyse cyclic phosphates most actively compared with secondary and tertiary ones. The most effective acid catalyst for this reaction was trifluoroacetic acid or hydrochloric acid among the several catalysts tested.

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[11] The synthesis of these authentic specimens will be reported in the next paper of this series.