Table VIII. Amounts of 3-Methyl-2-benzothiazolinethione (Vc) and 2-Methylthiobenzothiazole (VIc) adsorbed

Amount of Compd. added mole/mole AgCl	Amount adsorbed (%)		Amount of Compd. added mole/mole AgCl	Amount adsorbed (%)	
	(Vc)	(VIc)		(Vc)	(VIc)
1×10^{-1}	31	5.2	2.5×10^{-2}	23	10
5×10^{-2}	33	7.2	1×10^{-2}	41	13.5

Results of adsorption experiment indicate that that adsorbability of thione compounds is larger than that of corresponding thio-ether compound, as shown in Table VIII.

The author wishes to express his grateful thanks to Dr. Eiji Ochiai, Professor Emeritus of the University of Tokyo, for his kind guidance, and to Dr. Yoshihiko Kashida for his valuable advice and encouragement. He is also indebted to Dr. Yasushi Ohyama, the Chief of the Research Section of this Division, for his kind guidance in making this investigation. Thanks are also due to Mr. Katsuo Hojoh for his assistance in carrying out many laboratory experiments.

Summary

The effect of benzazoles and related compounds (I to VII; 25 in all) on the color of the developed silver image was examined with a liquid silver chloride emulsion developed by a dilute Phenidone-hydroquinone developer. Blue-black toning effect was found to be related strictly to adsorbability of the compound. Relative importance of acidic dissociation constant of benzimidazoles (I) was recognized.

(Received October 17, 1960)

UDC 547.636'118.5.07

97. Tyunosin Ukita[*1] and Ryuzo Takeshita[*2]: Organic Phosphates. XV.[*3] Synthesis and Alcoholysis Reaction of 4,4'-Dinitrohydrobenzoin Cyclic Phosphate.[*4]

(*Faculty of Pharmaceutical Sciences, University of Tokyo*[*1])

As has been reported in the previous paper[1)] of this series, the alcoholysis of hydrobenzoin cyclic phosphate and subsequent hydrogenolysis or acid hydrolysis of the reaction products gave the monophosphate of the alcoholic compounds used. Thus, this cyclic phosphate was found to be available as a novel phosphorylation agent for hydroxylic compound. However, this type of reaction was found most appropriate for primary alcohols which have relatively simple structure, while some polyfunctional hydroxylic compounds, i.e. erythritol and carbohydrates such as hexose, did not alcoholyse this cyclic phosphate under the condition used.

In the present work, as a further study on this type of reaction, 4,4'-dinitrohydro-

---

[*1] Hongo, Tokyo (浮田忠之進).

[*2] Present Address: Institute of Public Health, Shirokane-Daimachi, Minato-ku, Tokyo (竹下隆三).

[*3] Part XIV: This Bulletin, **9**, 544 (1961).

[*4] From the thesis of Ryuzo Takeshita for the degree of Doctor of Pharmaceutical Sciences, University of Tokyo, 1959.

1) T. Ukita, K. Nagasawa, M. Irie: J. Am. Chem. Soc., **80**, 1373 (1958).

benzoin cyclic phosphate was synthesized and its behavior in the alcoholysis reaction was investigated.

Di-O-acetylhydrobenzoin (meso-type) (I) was nitrated with fuming nitric acid to give a crystalline di-O-acetyl-4,4′-dinitrohydrobenzoin (II), $C_{18}H_{16}O_8N_2$, m.p. 232°, in 71% yield. (II) was deacetylated with ethanolic sulfuric acid to 4,4′-dinitrohydrobenzoin (III), $C_{14}H_{12}O_6N_2$, as colorless crystals which melted at 231° (Chart 1).

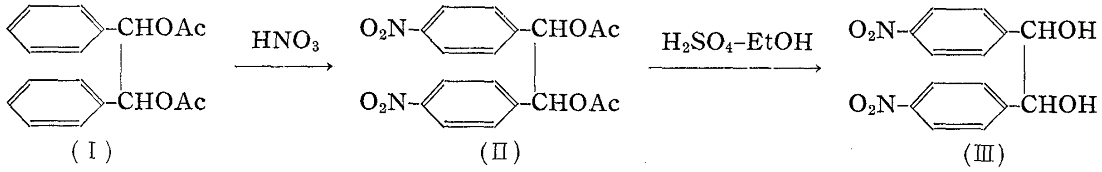

Chart 1.

The structure of (III) was verified by its oxidation with lead tetraacetate to an only product of *p*-nitrobenzaldehyde in a good yield and by the conversion of the latter to its *p*-nitrophenylhydrazone of m.p. 249°. The compound (III) and phosphoryl chloride were reacted by the method similar to that used in the previous work[1] for the synthesis of hydrobenzoin cyclic phosphate and the product (IV) was isolated as the ammonium salt, $C_{14}H_{14}O_8N_3P$ (yield, 68%) (Chart 2).

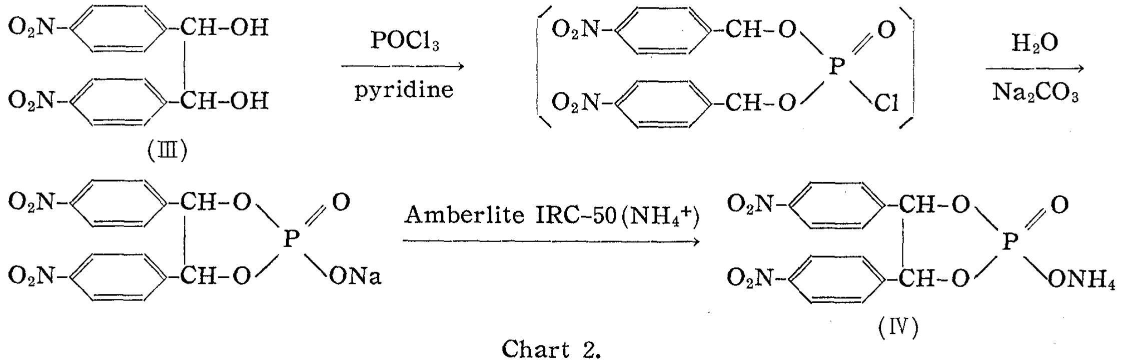

Chart 2.

The cyclic phosphate thus obtained was readily hydrolyzed in acid and alkaline solutions, as well as in pyridine. By paper chromatography run with two different solvent systems, the hydrolysis product in each case was identified as 4,4′-dinitrohydrobenzoin phosphate, obtained as the crystalline cyclohexylammonium salt (VI), $C_{20}H_{25}O_9N_3P \cdot H_2O$.

The ammonium salt of (IV) was incubated with various hydroxylic compounds in the presence of trifluoroacetic acid or dry hydrogen chloride-dioxane[2]; the phosphorus compounds produced were separated and detected by paper chromatography. The Rf$_1$ and the yield of the phosphorus products are summarized in Table I. Table I shows that

Table I. Trifluoroacetic Acid-catalyzed Alcoholysis of 4,4′-Dinitrohydrobenzoin Cyclic Phosphate

Alcohol	Product of Alcoholysis Phosphodiester of the Alcohol used		Product of Hydrolysis (VI)	
	Rf$_1$	(Yield %)	Rf$_1$	(Yield %)
Methanol	0.90	(100)	0.68	(0)
Ethanol	0.91	(80)	0.68	(20)
Isopropanol	0.92	(50)	0.68	(50)
Butanol	0.94	(63)	0.68	(37)
tert-Butanol	——		0.68	(100)
Benzyl alcohol	0.93	(50)	0.68	(50)

---

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

except in the case of *tert*-butanol new spots were detected having larger Rf_1 values than that of the starting material (IV). These new spots were attributed to the alcoholysis products of (IV) having *p*-nitrophenyl moiety because their Rf_1 values were different for various hydroxylic compounds used and because they showed ultraviolet absorption caused by the nitrophenyl group.

The weak spot with an Rf_1 value of 0.68 commonly observed for each incubation was identified as 4,4′-dinitrohydrobenzoin phosphate (VI) prepared by treating the cyclic phosphate (IV) with Amberlite IR-120 (H^+).

The yield of the alcoholysis product of (IV) in the case of isopropanol was larger than that in the case of a similar reaction for hydrobenzoin cyclic phosphate¹⁾ (VII).

When ammonium 4,4′-dinitrohydrobenzoin cyclic phosphate (IV) was submitted to alcoholysis with various monofunctional hydroxylic compounds, ethanol, isopropanol, and butanol in pyridine at 80°, each reaction mixture, on paper chromatography, gave a phosphorus spot with Rf_1 value corresponding to respective alcoholysis product obtained by acid-hydrolysis of the starting compound (IV).

The product of methanolysis of (IV) catalyzed by trifluoroacetic acid, methyl 4,4′-dinitrohydrobenzoin phosphate (V), was isolated as the ammonium salt, $C_{15}H_{15}O_9N_2P \cdot 2H_2O$, m.p. 198.5°. On acid and alkaline hydrolysis, the methanolysis product (V) revealed an interesting result in the mode of the reaction. On incubation in 1*N* hydrochloric acid at 100° for 30 minutes, (V) was completely converted into 4,4′-dinitrohydrobenzoin phosphate (VI), while by treatment with 1*N* sodium hydroxide for 5 minutes at 100°, (V) was hydrolyzed completely to monomethyl phosphate which was isolated as its barium salt.

These modes of hydrolysis reaction of (V) in acid and alkaline environments are just the reverse of those for methyl hydrobenzoin phosphate¹⁾ (VIII), which gave monomethyl phosphate and hydrobenzoin phosphate on respective hydrolysis with 1*N* hydrochloric acid and 1*N* sodium hydroxide. When methyl 4,4′-dinitrohydrobenzoin phosphate (V) was catalytically hydrogenolyzed with palladium-charcoal, the reaction mixture gave a single phosphorus spot identified with that of monomethyl phosphate and which was isolated as its barium salt (Chart 3).

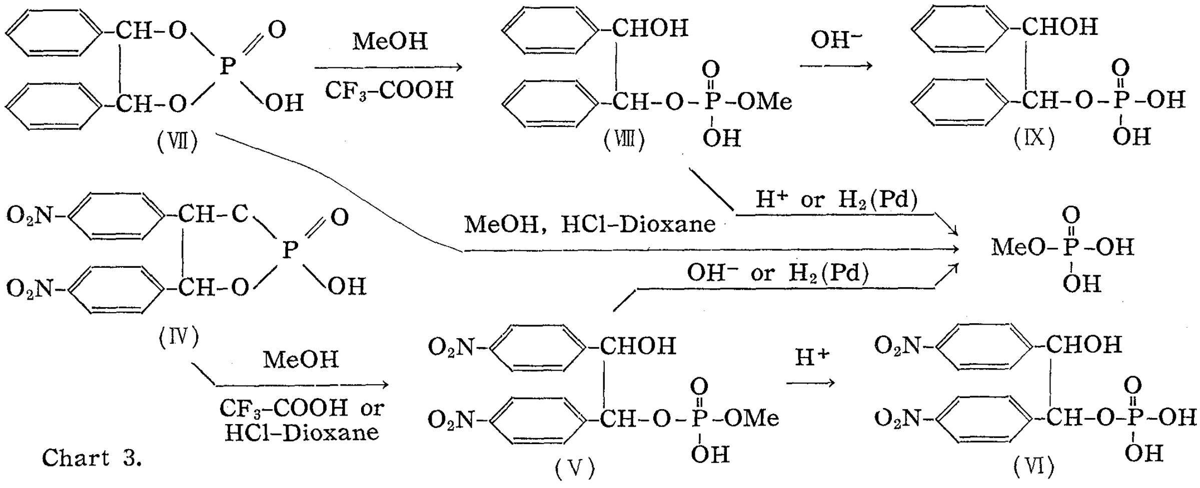

Chart 3.

In order to see the behavior of 4,4′-dinitrohydrobenzoin cyclic phosphate (IV) to alcoholysis with several polyols in acid media, (IV) was incubated with 1,2-propanediol in the presence of trifluoroacetic acid or dry hydrogen chloride-dioxane,²⁾ and with DL-erythritol or D-mannitol in N,N-dimethylformamide in the presence of dry hydrogen chloride, and the reaction mixtures were submitted to paper chromatography.

These reaction mixtures revealed one respective phosphorus spot for each of the three polyol with larger Rf_1 value (0.90, 0.79, and 0.71) than that of (VI). The larger

Rf_1 value and intensive ultraviolet absorption of these spots, together with positive reaction to periodate-Schiff reagent, gave the evidence that the spots were of phosphodiester type compounds produced by alcoholysis of (IV) with polyols.

Table II. Hydrogen Chloride-catalyzed Alcoholysis of 4,4′-Dinitrohydrobenzoin Cyclic Phosphate with Polyols

Reaction time (hr.)	Polyol	Product of Alcoholysis: Phosphodiester of the Alcohol used Rf_1	(Yield %)	Product of Alcoholysis: Phosphomonoester of the Alcohol used Rf_1	(Yield %)	Product of Hydrolysis (VI) Rf_1	(Yield %)
3	1,2-Propanediol	0.90					
24	1,2-Propanediol	0.90	(46)	0.27	(40)	0.68	(14)
1	DL-Erythritol	0.79				0.68	
3	DL-Erythritol	0.79	(28)	0.20	(10)	0.68	(10)
1	D-Mannitol	0.71				0.68	
3	D-Mannitol	0.71	(25)	0.18	(11)	0.68	(64)

In the case of DL-erythritol and D-mannitol, after 3 hours' incubation another respective phosphorus spot with smaller Rf_1 value (0.20 and 0.18) than that of (VI) was observed and they gave positive reaction to periodate-Schiff reagent but no ultraviolet absorption. These two spots were identified by paper chromatography with the authentic samples of DL-erythritol 1-phosphate (XI) and D-mannitol 1-phosphate (XII), respectively (Table II). Furthermore, the amount of these polyol monophosphates was found to be increased by prolonged incubation of the reaction mixture with simultaneous decrease in the corresponding diesters produced.

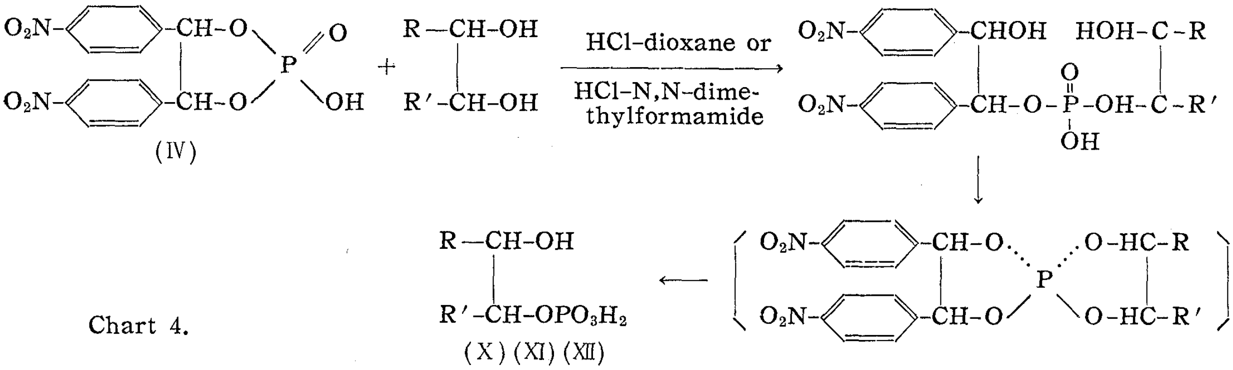

Chart 4.

(X) 1,2-propanediol $R=CH_3$, $R'=H$
(XI) DL-erythritol $R=CH_2OH\text{-}(CHOH)_2$, $R'=H$
(XII) D-mannitol $R=CH_2OH\text{-}(CHOH)_3$, $R'=H$

Thus, in the cases of the reaction with polyhydroxy alcohols, in contrast to that of monofunctional alcohols, the phosphodiester-type compounds initially produced were further decomposed by prolonged incubation to the phosphomonoester of the polyol used by cleavage of the 4,4′-dinitrohydrobenzoin moiety (Chart 4). However, for the isolation of the phosphomonoesters (X, XI, and XII) of the polyols, direct catalytic hydrogenation of the reaction mixture, after removal of chloride ion, was found more effective than hydrolysis of the diesters by prolonged incubation.

Experimental

Di-O-acetyl-4,4′-dinitrohydrobenzoin (II)——To 30 cc. of fuming nitric acid (sp. gr. 1.50), 5.0 g. of di-O-acetylhydrobenzoin (I) was slowly added with stirring and chilling to below −10° in a freezing mixture. The stirring was continued for additional 30 min. during which the color of the solution turned from reddish brown to yellow. The reaction mixture was poured on 100 g. of crushed ice and allowed to stand overnight. The pasty mass that appeared was collected and recrystallized from pyridine to white to pale yellow crystals which melted at 232°. Yield, 71%. *Anal.* Calcd. for $C_{18}H_{16}O_8N_2$: C, 55.67; H, 4.15; N. 7.12. Found : C, 55.42; H, 3.81; N, 7.51.

Hydrolysis of (II) to 4,4′-Dinitrohydrobenzoin (III)——5.0 g. of (II) obtained as above was hydrolyzed by refluxing with EtOH containing 20% of H_2SO_4. On pouring the reaction mixture into ice-water, a soft and waxy product precipitated which was recrystallized from pyridine to white crystalline 4,4′-dinitrohydrobenzoin (III) melting at 231°(decomp.). Yield, 88%. *Anal.* Calcd. for $C_{14}H_{12}O_6N_2$: C, 55.26; H, 3.97; N, 9.20. Found : C, 55.72; H, 3.73; N, 9.12.

In order to ascertain the position of nitro group substituted in hydrobenzoin, 100 mg. of (III) was added to 10 cc. of $(AcO)_4Pb$ dissolved in Ac_2O and the mixture was refluxed for 30 min. The reaction mixture was poured into ice-water and the precipitate formed was recrystallized from hydr. EtOH to slightly yellow crystalline *p*-nitrobenzaldehyde, m.p. 106°, in a good yield. *Anal.* Calcd. for $C_7H_5O_3N$: C, 55.63; H, 3.33; N, 9.26. Found : C, 55.93; H, 3.25; N, 9.15.

The *p*-nitrophenylhydrazone of this product melted at 249° and showed no depression by mixed fusion with authentic specimen.

Paper Chromatography——The following solvent systems were used for paper chromatography: (1) iso-PrOH-conc. NH_4OH-H_2O(7:1:2), (2) PrOH-conc. NH_4OH-H_2O(6:3:1).³⁾ The Rf values found with these solvent systems are designated as Rf_1 and Rf_2, respectively. The product was chromatographed as follows :

A sample containing 10～40 γ of P was applied to Toyo Roshi No. 53 filter paper and run ascendingly for 15 hr. For the detection of spots, Bandurski-Axelrod method⁴⁾ for phosphate, periodate-Schiff reagent⁵⁾,⁶⁾ for 1,2-glycol group, and UV absorption*5 for nitrophenyl group were employed.

Synthesis of Ammonium 4,4′-Dinitrohydrobenzoin Cyclic Phosphate (IV)——According to the method similar to that used in the synthesis of hydrobenzoin cyclic phosphate,¹⁾ 4,4′-dinitrohydrobenzoin (meso-form) and $POCl_3$ were reacted in pyridine. After removal of the solvent *in vacuo*, the residue was dissolved in 10 cc. of cooled distilled water and the aqueous layer, after being adjusted to pH 8.0 with solid Na_2CO_3, was shaken twice with 20 cc. each of Et_2O. From the pyridine layer, which was salted out, pyridine was evaporated *in vacuo* and the residue was combined with the above aqueous alkaline layer. This aqueous solution was again saturated with Na_2CO_3 and extracted three times with 10 cc. each of AcOEt. To the AcOEt solution, Et_2O was added and the mixture was allowed to stand overnight at room temperature. The precipitate that appeared was dissolved in a small volume of EtOH (filtered when insoluble substance was observed) and precipitated with Et_2O. The precipitate thus obtained was applied to paper chromatography to find a small amount of contaminant by-product of 4,4′-dinitrohydrobenzoin phosphate (VI).

The cyclic phosphate (IV) was dissolved in 20 cc. of distilled water and passed through a column of Amberlite IRC-50(NH_4^+) to convert it into the ammonium salt. On lyophilization of the effluent and washings, a white powder was obtained, which was dissolved in a minimum volume of Me_2CO to form white crystals. The crystals were dissolved in a minimum volume of EtOH and recrystallized by addition of Et_2O. Long needles thus obtained were dried over P_2O_5 at 110° to a constant weight, m.p. 225°(decomp.), Rf_1 0.87. *Anal.* Calcd. for $C_{14}H_{14}O_8N_3P$(Ammonium salt) : C, 43.83; H, 3.66; N, 10.95; P, 8.09. Found : C, 43.58; H, 3.89; N, 11.04; P, 8.31.

Hydrolysis Product (VI) of 4,4′-Dinitrohydrobenzoin Cyclic Phosphate (IV)——To a solution of 0.2 g. of ammonium salt of (IV) in 10 cc. of distilled H_2O, 2 cc. of freshly prepared Amberlite IR-120 (H^+) was added. The mixture was warmed at 80～85° for 10 min. and filtered. After addition of cyclohexylamine to the filtrate to render it slightly alkaline, the solution was concentrated *in vacuo* and the residue was recrystallized from iso-PrOH, m.p. 206°(decomp.). The crystals were dried over P_2O_5, Rf_1 0.68. *Anal.* Calcd. for $C_{20}H_{25}O_9N_3P\cdot H_2O$ (Mono-cyclohexylammonium salt) : C, 52.16; H, 6.56; N, 9.36; P, 5.96. Found : C, 51.73; H, 6.52; N, 8.95; P, 6.07.

Isolation of Hydrolysis Product (VI) of (IV) in Pyridine——To 5 cc. of dehyd. pyridine, 200 mg. of ammonium salt of (IV) was added and the mixture was warmed at 80～85° for 6 hr. The crystals that appeared were collected, washed with a small volume of EtOH, and recrystallized from EtOH m.p. 174°(decomp.). The product was dried over P_2O_5. *Anal.* Calcd. for $C_{24}H_{23}O_9N_4P\cdot H_2O$ (Di-pyridinium salt) : C, 52.94; H, 4.59; N, 10.29; P, 5.53. Found : C, 52.88; H, 4.62; N, 10.30; P, 5.59.

Alcoholysis Reaction of 4,4′-Dinitrohydrobenzoin Cyclic Phosphate (IV) with Various Monofunctional Hydroxylic Compounds——To a series of tubes containing 2 mg. of ammonium salt of (IV), each dissolved in 0.2 cc. of monofunctional hydroxylic compounds, 0.05 cc. of CF_3COOH or 0.2 cc. of

---

*5 Manaslu-light (type UV-S1) was used.

3) C.S. Hanes, F.A. Isherwood : Nature, **164**, 1107 (1949).

4) R.S. Bandurski, B. Axelrod : J. Biol. Chem., **193**, 405 (1951).

5) J.G. Buchanan, C.A. Dekker, A.G. Long : J. Chem. Soc., **1950**, 3162.

6) J. Baddiley, J.G. Buchanan, R.E. Handschumacher, J.E. Prescott : *Ibid.*, **1956**, 2818.

dioxane saturated with dry HCl[2)] was added and the mixture was incubated at 37° for 24 hr. Each 0.02 cc. of reaction mixtures which contained 30~40 γ of P was applied to the filter paper and chromatographed ascendingly with the solvent system 1. From the chromatogram, the spots showing ultraviolet absorption were cut out, the cuttings were boiled with $HClO_4$, and submitted to the determination of phosphorus by the Allen method.[7)] Untreated pieces of the filter paper of the same size as the cuttings surved as blanks. The results are given in Table I.

Isolation of the Methanolysis Product of (IV); Methyl 4,4′-Dinitrohydrobenzoin Phosphate (V)——To a solution of 1.0 g. of the ammonium salt of (IV) dissolved in 10 cc. of MeOH, 1.5 cc. of CF_3COOH was added. After the reaction mixture was kept at room temperature for 6 hr. in a sealed tube, MeOH was removed by distillation. The residue was washed with a small volume of H_2O and recrystallized from hot H_2O. The crystals obtained were further dissolved in a minimum volume of MeOH and recrystallized by addition of Et_2O to form white crystals which melted at 198.5°. For analysis, the product was dried over P_2O_5 to a constant weight. *Anal.* Calcd. for $C_{15}H_{15}O_9N_2P \cdot 2H_2O$ (Ammonium salt) : C, 39.90; H, 4.91; N, 9.31; P, 7.24. Found : C, 40.13; H, 4.84; N, 9.18; P, 7.50.

Alcoholysis Reaction of 4,4′-Dinitrohydrobenzoin Cyclic Phosphate by Various Monofunctional Hydroxylic Compounds in Pyridine——To a series of tubes containing 2 mg. of (IV) dissolved in 0.1 cc. each of monofunctional hydroxylic compounds to be tested 0.1 cc. of pyridine was added. The mixture was heated at 80° and the aliquots of reaction mixtures were applied to paper chromatography at intervals.

Hydrolysis of Methyl 4,4′-Dinitrohydrobezoin Phosphate (V)——Two tubes each containing 5 mg. of (V) dissolved in 0.5 cc. of 1*N* HCl or 1*N* NaOH were warmed in a boiling water bath. From each tube, 0.02 cc. of the mixture was taken out at intervals and applied to paper chromatography. The results are given in Chart 3.

Isolation of Alkaline Hydrolysis Product of Methyl 4,4′-Dinitrohydrobenzoin Phosphate (V)——A solution of 400 mg. of (V) in 50 cc. of 1*N* NaOH was warmed in a boiling water bath for 10 min. The crystals that appeared were collected and recrystallized successively from pyridine and EtOH to show the melting point of 231° and the product was identified with an authentic specimen of (III) by mixed fusion. The filtrate obtained from the reaction mixture was concentrated *in vacuo* to 20 cc. and immediately decationized with Amberlite IR-120(H^+). The acidic aqueous layer, obtained after extraction with two 10-cc. portions of Et_2O, was adjusted to pH 8.0 with saturated $Ba(OH)_2$ solution and the solution was saturated with CO_2 to remove the excess of Ba ion. After removal of $BaCO_3$ by centrifugation, the supernatant was lyophilized to leave a white powder which was recrystallized from hot H_2O and dried over P_2O_5. This product was identified with authentic monomethyl phosphate by paper chromatography. *Anal.* Calcd. for $CH_3O_4BaP \cdot H_2O$ (Barium salt) : C, 4.52; H, 1.89; P, 11.67. Found : C, 4.02; H, 1.89; P, 11.82.

Hydrogenolysis of Methyl 4,4′-Dinitrohydrobenzoin Phosphate (V)——A mixture containing 500 mg. of Pd-C (10% Pd) and 500 mg. of (V) dissolved in 20 cc. of MeOH was shaken in H_2 atmosphere at room temperature. The reaction mixture was treated similarly as in the case of isolation of monomethyl phosphate from methyl 4,4′-dinitrohydrobenzoin phosphate.[1)] The barium salt of the phosphate was recrystallized from hot H_2O dried over P_2O_5 to a constant weight. *Anal.* Calcd. for $CH_3O_4BaP \cdot H_2O$ (Barium salt) : C, 4.52; H, 1.89; P, 11.67. Found : C, 4,24; H, 1.53; P, 11.83. This product was identified with monomethyl phosphate by paper chromatography.

Alcoholysis Reaction of 4,4′-Dinitrohydrobenzoin Cyclic Phosphate (IV) with Various Polyfunctional Hydroxylic Compounds——To a mixture of 0.2 cc. of 1,2-propanediol and 2 mg. of (IV), 0,05 cc. of CF_3COOH was added. In the case of DL-erythritol and D-mannitol, 10 mg. of each was dissolved in 0.2 cc. of N,N-dimethylformamide and, after addition of 2 mg. of (IV), the mixture was saturated with dry HCl. All the mixtures were incubated at 37° and aliquots were withdrawn from the reaction mixture at intervals for paper chromatography.

In one run of the chromatography, the chromatogram was sprayed with the periodate-Schiff reagent to detect the products which contain polyol moiety. In another chromatogram obtained in second run, both spots with positive periodate-Schiff reaction and positive in ultraviolet absorption were cut out and the cuttings were applied for P determination by the method described above. The results are given in Table II.

A part of the expenses for this work was supported by the Grant-in-Aid for Scientific Research provided by the Ministry of Education to which the authors' thanks are due. Thanks are also due to Mr. D. Ohata, Iatrochemical Institute of Pharmacological Research Foundation, and Miss M. Iwanaga and S. Ohno, Institute for Infectious Diseases, University of Tokyo, for the microanalyses.

---

7) R. J. Allen : Biochem. J., **34**, 858 (1940).

Summary

4,4′-Dinitrohydrobenzoin cyclic phosphate was synthesized. Alcoholysis reaction of this compound with various hydroxylic compounds in acid or alkaline medium was found to occur to a greater extent than a similar reaction for non-substituted hydrobenzoin cyclic phosphates. Thus, the new cyclic phosphate was alcoholyzed with polyols such as DL-erythritol and D-mannitol, which were found to be inert to the non-substituted hydrobenzoin cyclic phosphate. The mode of the hydrolysis reaction of methyl 4,4′-dinitrohydrobenzoin phosphate, an intermediate product of methanolysis of 4,4′-dinitrohydrobenzoin cyclic phosphate, in acid and alkaline media was found to be different from that of methyl hydrobenzoin phosphate.

(Received October 21, 1960)

UDC 547.677.5′118.5.07

98. **Tyunosin Ukita**[*1] **and Ryuzo Takeshita**[*2] : Organic Phosphates. XVI.[*3] Synthesis and Alcoholysis Reaction of 9,10-Dihydro-9,10-phenanthrenediol Cyclic Phosphate.[*4]

(*Faculty of Pharmaceutical Sciences, University of Tokyo*[*1])

The usefulness of hydrobenzoin cyclic phosphate as a phosphorylating agent for hydroxylic compounds has been reported by one of the present authors in a previous paper1) of this series and in a further study,[*3] the enhanced reactivity of a substituted hydrobenzoin cyclic phosphate, 4,4′-dinitrohydrobenzoin cyclic phosphate, in the similar type of alcoholysis reaction and some different mode in hydrolysis reaction of its alcoholysis product, alkyl 4,4′-dinitrohydrobenzoin phosphate, from that of alkyl hydrobenzoin phosphate were also reported.

As a structurally further modified cyclic phosphate, 9,10-dihydro-9,10-phenanthrenediol cyclic phosphate, was synthesized and its behavior in the alcoholysis reaction was investigated, the results of which are described in this paper.

9,10-Dihydro-9,10-phenanthrenediol (trans type) (II), obtained by the reduction of phenanthraquinone (I) with lithium aluminum hydride,2) was reacted with phosphoryl chloride

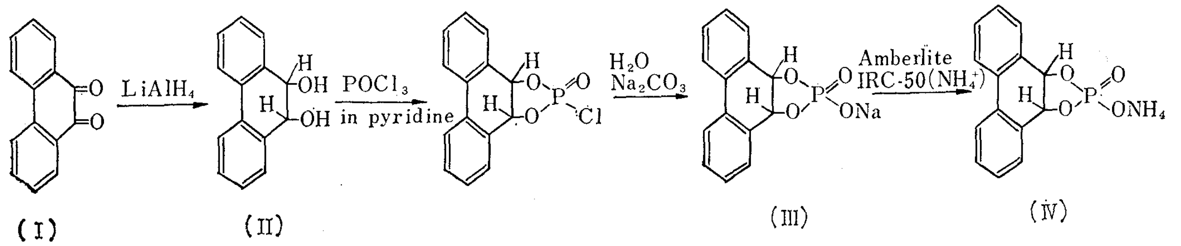

Chart 1.

[*1] Hongo, Tokyo (浮田忠之進).

[*2] Present Adress : Institute of Public Health, Shirokane-Daimachi, Minato-ku, Tokyo (竹下隆三).

[*3] Part XV : This Bulletin, 9, 600 (1961).

[*4] From the thesis of Ryuzo Takeshita for the degree of Doctor of Pharmaceutical Sciences, University of Tokyo, 1959.

1) T. Ukita, K. Nagasawa, M. Irie : J. Am. Chem. Soc., **80**, 1373 (1958).