was added to 500 ml. of a solution either of sodium chloride which was *ca.* 4×10^{-3} *N* in sulfuric acid, or of hydrochloric acid, allowed to decompose for at least ten half-lives,[19] and then cooled. For the reactions at 100° part of the chloride solution was kept cold, and some used to dissolve the diazonium salt. The solution was poured through the reflux condenser into the reaction vessel which was just below the boiling point. The remainder of the cold solution was added as a rinse and boiling recommenced. In this way the diazonium salt was never in contact with a solution more dilute than that in the reaction vessel, although the temperature was uncertain. After cooling, the solution was made strongly basic with sodium hydroxide and again cooled. A convenient amount (*ca.* 50 ml.) of 20–40° petroleum ether was added and a sample, accurately measured with a micropipet, of ethylbenzene approximately equal to the expected yield of chlorobenzene was added, then the mixture was well shaken. Vapor phase chromatography of the petroleum ether solution, both before and after evaporation of the main body of the petroleum ether gave the ratio of chlorobenzene to ethylbenzene from a calibration curve of peak height ratio *vs.* mole ratio, and hence the yield of chlorobenzene. In the range of mole ratios and sample sizes used the peak height ratio and the mole ratio were nearly linearly related and the calibration was insensitive to sample size; although neither of these were true with excessive samples. The separation was distinct but incomplete on a 2-meter column with a nonyl phthalate stationary phase.

Phenol analyses on two runs were done by Mr. J. Cooper by the standard bromination procedure.

Reaction in the Presence of Sulfate.—Two runs were made in 1.5 *M* Na_2SO_4 containing 0.15 *M* H_2SO_4 at 70°. Because of the perceptible weakness of HSO_4^- the *p*H of this solution is about 2.7. The analysis of phenyl sulfate depended on the fact that at 288 mμ the extinction coefficient[20] of the phenoxide ion is about 20 times that of the phenyl sulfate ion, and that the latter ion is stable in basic solution and at the *p*H necessary for diazonium salt decomposition, but is rapidly hydrolyzed in strongly acid solution.[21] A solution of benzenediazonium fluoroborate was kept at 70° in the sodium sulfate solution for ten half-lives,[19] then a sample was made basic and the absorbance at 288 mμ was measured.

Another sample was acidified and heated long enough to complete the hydrolysis of the phenyl sulfate ion, then again made basic and the absorbance again measured. A blank, identical except for the absence of sodium sulfate, was carried through the same procedure to eliminate uncertainties attributable to pipet errors, uncertainties in the extinction coefficient and impurity of the starting material. Absorption measurements were also made at 380 mμ, where *p*-hydroxyazobenzene absorbs strongly (not the maximum), showing that the yield under these conditions (ArN_2BF_4 = 5×10^{-3} *M*, $H^+ = 2 \times 10^{-3}$ *M*) of this azo compound is not more than 2% and is very likely less. Measurements at the phenoxide minimum wave length, 260 mμ, showed that small quantities of other absorbing substances were present, one of which was in the sodium hydroxide. This error contributes to an unknown extent to the absorbance at 288 mμ and is a serious source of error. The yield of phenyl sulfate was calculated from the expression

$$Y_{ArOSO_3^-} = \frac{A_B - A_S + A_{SH} - A_{BH}}{A_{BH}} \times 100$$

where A_B and A_S are the absorbances of the blank and the sulfate containing sample before hydrolysis, and A_{BH} and A_{SH} are the samples of blank and sample after hydrolysis. The yields in the experiments were 4.1 and 3.5%. The large uncertainty arises from the non-identity of A_B, A_{SH} and A_{BH}, and the estimated error given is the range derived from the use of alternative methods of calculating the yield from the somewhat unsatisfactory data. The less accurately determined phenol yield varied from 100 to 109% among several blank runs, and the two measurements of A_{SH}. The large yield may in part represent contamination of the starting material with phenol, and in part the unidentified absorbing species; the competition factors are not significantly affected by phenol contamination.

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(19) Calculated from the Arrhenius parameters given by D. F. DeTar and A. R. Ballentine, THIS JOURNAL, **78**, 3916 (1956).

(20) G. Kortüm, *Z. physik. Chem.*, **B42**, 39 (1939), gives log ϵ_{max} 3.34 at 289 mμ, for the phenoxide ion; a new determination in which precautions to ensure complete ionization were taken gave log ϵ_{max} 3.43 at 288 mμ.

(21) G. N. Burkhardt, W. G. K. Ford and E. Singleton, *J. Chem. Soc.*, 17 (1936).

[CONTRIBUTION FROM INSTITUTE OF PHARMACY, MEDICAL FACULTY, THE UNIVERSITY OF TOKYO]

Organic Phosphates. V. Hydrobenzoin Cyclic Phosphate, a New Phosphorylation Reagent

BY TYUNOSIN UKITA, KINZO NAGASAWA AND MASACHIKA IRIE

RECEIVED SEPTEMBER 3, 1957

Hydrobenzoin cyclic phosphate (I) has been synthesized from hydrobenzoin and phosphorus oxychloride. Treatment of the sodium salt of I with various alcohols in the presence of trifluoroacetic acid gave alkyl 1,2-diphenyl-2-hydroxyethyl-1-phosphates which yielded monoalkyl phosphates on catalytic hydrogenolysis. In contrast to trifluoroacetic acid, similar alcoholyses with hydrogen chloride gave the monoalkyl phosphates. These reactions demonstrate the usefulness of I as a phosphorylation reagent.

Tener and Korana[1] have reported that several 2′,3′-cyclic nucleotides, treated with alcohols in hydrogen chloride–dioxane, gave both alkyl 2′- and 3′-nucleotides.

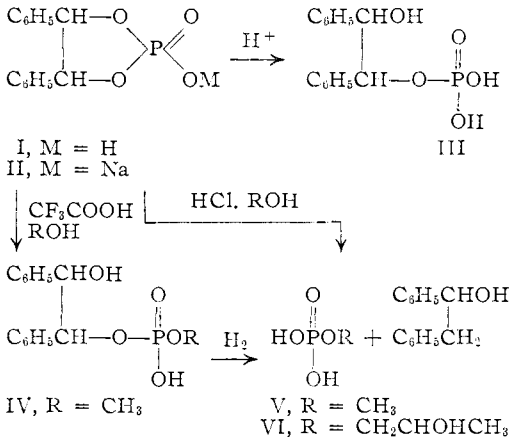
We found that the cyclic phosphates of aliphatic diols are alcoholyzed easily by mono- or 1,2-dihydroxy compounds with trifluoroacetic acid or hydrogen chloride as catalyst to give the corresponding alkyl or hydroxyalkyl 1,2-diol phosphodiesters,[2] *e.g.*, propane-1,2-diol cyclic phosphate treated with methanol gave methyl 2-hydroxypropyl-1-phosphate.

In subsequent experiments which were designed to reveal whether a 1,2-diol cyclic phosphate could serve as a phosphorylation reagent, we found that hydrobenzoin cyclic phosphate (I) fulfils this requirement, as the alcoholysis products of I readily lose their 1,2-diphenyl-2-hydroxyethyl moieties

(1) G. H. Tener and H. G. Khorana, THIS JOURNAL, **77**, 5349 (1955).

(2) T. Ukita, K. Nagasawa and M. Irie, *Pharm. Bull.*, **5**, 208 (1957).

upon hydrogenolysis. In this work we synthesized I from hydrobenzoin and phosphorus oxychloride, and studied its alcoholysis reactions with trifluoroacetic acid or hydrogen chloride as catalyst.



Compound I is unstable in acid; by treatment of its aqueous solution with Amberlite IR-120-H^+, it is hydrolyzed to 1,2-diphenyl-2-hydroxyethyl-1-phosphate (III), which can be isolated as the crystalline cyclohexylammonium salt.

Sodium hydrobenzoin cyclic phosphate (II) was treated with various alcohols in the presence of trifluoroacetic acid; the results are summarized in Table I. The phosphorus compounds in the reaction mixtures were separated by paper chromatography.

Table I shows that except for the case of *t*-butyl alcohol, the reaction mixtures contained no starting material. In the other cases new spots were detected having R_{f_1} values which differed according to the alcohol used and which were attributed to the alcoholyses products. A weak spot with an R_{f_1} value of 0.64 frequently was observed; this product was identified as 1,2-diphenyl-2-hydroxyethyl-1-phosphate by comparison with III prepared by the hydrolysis of hydrobenzoin cyclic phosphate.

As the product of methanolysis (R_{f_1} 0.83) could not be distinguished chromatographically from the starting material (R_{f_1} 0.84), it was isolated as the sodium salt, sodium methyl 1,2-diphenyl-2-hydroxyethyl-1-phosphate (IV), from which the ammonium salt was prepared.

Unlike the starting cyclic phosphate, at least 50% of which was converted to III (R_{f_1} 0.64) by treatment at room temperature for 10 minutes with Amberlite IR-120-H^+, this methanolysis product (IV) was stable under these conditions. At 85° for 30 minutes, Amberlite IR-120-H^+ decomposed 100% of I to III, while IV was hydrolyzed to monomethyl phosphate (R_{f_1} 0.15).

When methyl 1,2-diphenyl-2-hydroxyethyl-1-phosphate (IV) was hydrogenolyzed, the reaction mixture gave a single phosphate spot corresponding to that of monomethyl phosphate (R_{f_1} 0.15). Phenylbenzylcarbinol and monomethyl phosphate (as the barium salt) were isolated from the hydrogenolysis mixture. The carbinol was identified by a mixed melting point determination, and the phosphate was identified chromatographically.

Thus, in the presence of trifluoroacetic acid, hydrobenzoin cyclic phosphate is alcoholyzed to alkyl 1,2-diphenyl-2-hydroxyethyl-1-phosphate.

The results of the hydrogen chloride-catalyzed alcoholyses of II are summarized in Table II.

TABLE I

TRIFLUOROACETIC ACID-CATALYZED ALCOHOLYSIS OF SODIUM HYDROBENZOIN CYCLIC PHOSPHATE[a]

Alcohol	Products R_{f_1} (yield, %)	Hydrobenzoin cyclic phosphate, R_{f_1}	1,2-Diphenyl-2-hydroxyethyl-1-phosphate, R_{f_1} (yield, %)
Methanol	0.83(100)	..	.....
Ethanol	.87(77)	..	0.64(23)
Isopropyl alc.	.88(35)	..	.64(65)
1-Butanol	.93(70)	..	.64(30)
t-Butyl alc.	.....	0.84	.....
Benzyl alc.	0.90(52)	..	0.64(48)

[a] 24 hours incubation period.

TABLE II

HYDROGEN CHLORIDE-CATALYZED ALCOHOLYSIS OF SODIUM HYDROBENZOIN CYCLIC PHOSPHATE (II)[a]

Alcohol	Products with large R_f values, R_{f_1}	Hydrobenzoin cyclic phosphate, R_{f_1}	1,2-Diphenyl-2-hydroxyethyl-1-phosphate, R_{f_1}	Products with small R_f values, R_{f_1} (yield, %)[a]	Inorganic phosphate, R_{f_1} (yield, %)[a]
Methanol	.....	....	0.64(trace)[b]	0.15(69)	0.10(31)
Ethanol	0.86(trace)[b]	....	.64(trace)[b]	.18(77)	.10(23)
Isopropyl alc.	.87(trace)[b]	....	.64(trace)[b]	.22(55.3)	.10(33.6)
1-Butanol	.97(trace)[b]	....	.64(trace)[b]	.37(66.5)	.10(33.5)
t-Butyl alc.	.....	....	.64	.. (..)	.. (..)
Benzyl alcohol	.....	....	.64[b]	0.33(23.8)	0.10(76.2)
1,2-Propanediol	.....	....	.....	0.27(87)	0.10(13)

[a] The yields were determined on paper chromatograms after 72 hours incubation. [b] The incubation period was 24 hours; after 72 hours of incubation these spots had disappeared.

Table II reveals that after 72 hours incubation, the reaction mixtures, except for that containing *t*-butyl alcohol, gave spots the R_{f_1} values of which varied with the alcohol used; see column 5. The R_{f_1} values of these spots are much smaller than those observed for the alkyl 1,2-diphenyl-2-hydroxyethyl-1-phosphates obtained by the trifluoroacetic acid-catalyzed alcoholyses of II (Table I). After 24 hours incubation, however, the reaction mixtures for some of the alcohols (ethanol, isopropyl alcohol and 1-butanol) gave faint spots with large R_{f_1} values (0.86–0.97) which are comparable to those obtained for the alkyl 1,2-diphenyl-2-hydroxyethyl-1-phosphates (Table I); they had disappeared after 72 hours of incubation.

The R_{f_1} values of the products of alcoholysis by methanol and by 1,2-propanediol (R_{f_1} 0.15 and

0.27, respectively) corresponded with the R_{f_1} values previously reported for methyl- and 2-hydroxypropyl-1-phosphate.[3]

The product of methanolysis (V) (R_{f_1} 0.15) was identified as monomethyl phosphate. This product monomethyl phosphate, and the product obtained by the decomposition of methyl 1,2-diphenyl-2-hydroxyethyl-1-phosphate (IV) by hydrogen chloride–dioxane gave paper chromatograms with spots of identical R_f value; see Table III.

TABLE III

IDENTIFICATION OF HCl-DIOXANE-METHANOLYSIS PRODUCT (I) AND HCl-DIOXANE HYDROLYSIS PRODUCT OF METHYL 1,2-DIPHENYL-2-HYDROXYETHYL-1-PHOSPHATE WITH MONOMETHYL PHOSPHATE

	Methanolysis product of II	Decompn. prod. of IV with HCl–dioxane	Monomethyl phosphate
R_{f_1}	0.15	0.15	0.15
R_{f_2}	.52	.52	.52
R_{f_3}	.88	.88	.88

It is interesting that hydrogen chloride–dioxane, in contrast to trifluoroacetic acid, caused complete hydrolysis of the alkyl 1,2-diphenyl-2-hydroxyethyl-1-phosphates (the alcoholysis product of hydrobenzoin cyclic phosphate) to the monoalkyl esters of phosphoric acid.

The product of the alcoholysis of II by 1,2-propanediol with hydrogen chloride was isolated as the barium salt, which was converted to the cyclohexylammonium salt. The latter was identified by a mixed melting point determination with cyclohexylammonium 2-hydroxypropyl-1-phosphate reported previously[3] and by paper chromatography as

Cyclohexylammonium compd.	R_{f_1}	R_{f_2}	R_{f_3}
Salt obtained from reacn. mixt.	0.27	0.58	0.83
2-Hydroxypropyl-1-phosphate	0.27	0.58	0.83

The phosphorylation of more complicated hydroxy compounds, such as the carbohydrates, by this type of reaction is under investigation.

Acknowledgment.—The authors are indebted to Mr. B. Kurihara and Miss R. Ohta for the microanalyses.

Experimental

The following solvent systems were used for paper chromatography: (1) isopropyl alcohol-5 *N* ammonium hydroxide (2:1): (2) isopropyl alcohol-*t*-butyl alcohol-concentrated ammonium hydroxide-water (40:20:1:39); (3) *t*-butyl alcohol-water-picric acid (80 ml.:20 ml.:4 g.). The R_f values found with these solvent systems are designated as R_{f_1}, R_{f_2} and R_{f_3}, respectively.

Synthesis of Sodium Hydrobenzoin Cyclic Phosphate (II).—To an ice-cooled solution of 3.6 g. of phosphorus oxychloride in 15 ml. of dry pyridine was added 3 g. of hydrobenzoin (m.p. 137°, *meso*-form) dissolved in 70 ml. of dry pyridine with vigorous stirring over a period of 1 hour. Stirring was continued for an additional 30 minutes at room temperature and the pyridine was removed *in vacuo*. The residue, dissolved in 50 ml. of cooled distilled water, was shaken twice with 25-ml. portions of ether. The *p*H of the aqueous layer was adjusted to 8.0 with solid sodium carbonate. The pyridine was removed under vacuum from the pyridine layer and the residue was combined with the alkaline aqueous solution. This solution was saturated with solid sodium carbonate and extracted exhaustively with ethyl acetate.

The crystals which separated from the ethyl acetate solution (yield 92–96%) were recrystallized as follows: 0.5 g. of the product was dissolved in 3 ml. of methanol and filtered. To the filtrate was added 3 ml. of ethyl acetate and the solution was covered with 3 ml. of ether. Long needles of II which separated from the methanol-ethyl acetate layer were dried over P_2O_5 at 110° to constant weight; m.p. 262° dec., R_{f_1} 0.88. The electrometric titration showed no secondary phosphate dissociation. *Anal.* Calcd. for $C_{14}H_{12}O_4PNa$: C, 56.37; H, 4.02; P, 10.38, mol. wt., 298. Found: C, 56.11; H, 4.32; P, 9.76, mol. wt., 307.7.

The product was chromatographed as follows: a sample containing 10–40 γ of phosphorus was applied to Toyo Roshi no. 53 filter paper and run ascendingly for 15 hours with solvent 1. Phosphorus was detected by the method of Bandurski and Axelrod.[4]

Hydrolysis of Hydrobenzoin Cyclic Phosphate.—To a solution of 0.2 g. of II in 10 ml. of water was added 5 ml. of freshly prepared Amberlite IR-120-H^+. The mixture was warmed at 80–85° for 15 minutes and filtered. The filtrate was passed through a column of Amberlite IRC-50-cyclohexylamine to convert the product to the cyclohexylammonium salt; the *p*H of the effluent was 8.0. On lyophilization of the effluent a white powder was obtained which was dissolved in the minimum volume of water–isopropyl alcohol (1:2) and filtered. Upon the addition of an equal volume of acetone to the filtrate, a white precipitate appeared which was filtered. The filtrate was stored in a refrigerator; the crystals which separated were centrifuged, washed with acetone and dried over P_2O_5; m.p. 190–192° dec. *Anal.* Calcd. for $C_{26}H_{41}O_5PN_2 \cdot H_2O$: C, 61.18; H, 8.43; N, 5.49. Found: C, 61.61; H, 8.53; N, 5.56; R_{f_1}, 0.64.

Alcoholysis of II with Trifluoroacetic Acid as the Catalyst.—To a series of tubes containing 2 mg. of II dissolved in 0.2 ml. of the alcohol was added 0.05 ml. of trifluoroacetic acid. The mixtures were incubated for 24 hours at 37°. Chromatography was carried out as follows: two samples of each reaction mixture (0.02 ml.). containing 30–40 γ of phosphorus, were applied to the filter paper and run ascendingly with solvent 1. Each paper was cut vertically to the starting line to separate two chromatograms. In order to obtain the R_{f_1} values of the phosphorus compounds, one of the chromatograms was developed with Hanes-Isherwood reagent. From the other chromatogram the corresponding parts containing the phosphorus compounds were cut out and the cuttings boiled with perchloric acid; phosphorus was determined by Allen's method.[5] Untreated pieces of filter paper of the same size as the cuttings served as blanks.

Isolation of the Methanolysis Product (Methyl 1,2-Diphenyl-2-hydroxyethyl-1-phosphate)(IV).—To a solution of 1.25 g. of II dissolved in 30 ml. of methanol was added 2 ml. of trifluoroacetic acid. The mixture was kept at room temperature for 24 hours in a sealed tube. From the reaction mixture, which showed a single spot (R_{f_1} 0.83), methanol was removed by distillation. The residue dissolved in the minimum amount of water was crystallized with isopropyl alcohol. It was recrystallized from methanolic solution with ether and then from aqueous solution with isopropyl alcohol (yield 80%). The sample for analysis was dried at 110° over P_2O_5 to constant weight. *Anal.* Calcd. for $C_{15}H_{16}O_5PNa$: C, 54.54; H, 4.84; P, 9.39. Found: C, 54.06; H, 4.80; P, 9.55.

An aqueous solution of the sodium salt obtained above was treated with Amberlite IR-120-H^+ to give a solution of free methyl hydrobenzoin phosphate. This solution was adjusted to *p*H 9.0 with ammonia and lyophilized. The ammonium salt was recrystallized from isopropyl alcohol; m.p. 168–169°. The sample for analysis was dried at room temperature over P_2O_5 for 3 hours. *Anal.* Calcd. for $C_{15}H_{20}O_5PN \cdot H_2O$: C, 52.47; H, 6.42; N, 4.08; P, 9.03. Found: C, 52.36; H, 6.64; N, 4.50; P, 8.82.

Hydrogenolysis of Methyl 1,2-Diphenyl-2-hydroxyethyl-1-phosphate (IV).—A mixture containing 250 mg. of palladium–charcoal (10% Pd) and 260 mg. of the ammonium salt of methyl 1,2-diphenyl-2-hydroxyethyl-1-phosphate, dissolved in 14 ml. of methanol, was shaken in an hydrogen atmosphere at room temperature. The reaction was complete

(3) T. Ukita, K. Nagasawa and M. Irie, *Pharm., Bull.*, **5**, 121 (1957).

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

(5) G. W. Kenner and J. Mater, *J. Chem. Soc.*, 3524 (1956).

in 2 hours with the consumption of 1.2 moles of hydrogen. The reaction mixture gave an intense spot of methyl phosphate (R_{f_1} 0.15) and a faint spot of inorganic phosphate. The catalyst was filtered and washed with methanol; the washings and filtrate were combined. Water (20 ml.) was added, the mixture was extracted with ether and the extract dried. On removal of the solvent, 100 mg. of white needles was obtained which were recrystallized from aqueous ethanol; m.p. 64–65.5°. A mixture of this product and an authentic sample of phenylbenzylcarbinol[6] showed no depression of the melting point.

The aqueous layer, obtained above after extraction with ether, was adjusted to *p*H 8.0 with a barium hydroxide solution. Barium phosphate was removed by centrifugation and the supernate was decationized with Amberlite IR-120-H$^+$. The resulting acidic solution was again adjusted to *p*H 8.0 with a saturated barium hydroxide solution. After removal of excess barium ion with carbon dioxide, the solution was concentrated to 10 ml. and poured into acetone. The resulting precipitate was dried over P_2O_5 at 130°. *Anal.* Calcd. for CH_3O_4PBa: C, 4.85; H, 1.21; P, 12.53. Found: C, 5.12; H, 1.29; P, 12.50.

Alcoholysis of II with Hydrogen Chloride–Dioxane as the Catalyst.—To tubes containing a solution of II (2 mg.) in 0.2 ml. of the alcohol was added 0.2 ml. of hydrogen chloride-saturated dioxane. One series was incubated at 37° for 24 hours and the other for 72 hours. The reaction mixtures were chromatographed as described for the trifluoroacetic acid-catalyzed alcoholysis reactions.

Preparation of 1,2-Propanediol-1-phosphate (VI) by Phosphorylation of Propanediol with II.—To 2.0 g. of II was added 15 ml. of dry 1,2-propanediol. The mixture was saturated with dry hydrogen chloride gas. After 24 hours incubation at 37°, the salt disappeared with the simultaneous separation of sodium chloride. The excess hydrochloric acid was removed by aeration and the inorganic salt was centrifuged.

Water (60 ml.) and an excess of silver carbonate were added to the supernate, and the mixture was kept at room temperature overnight. After removal of the insoluble silver salt by centrifugation, the supernate was extracted exhaustively with ether, and the aqueous layer which contained silver ion was treated with hydrogen sulfide. From the silver ion-free solution the excess of hydrogen sulfide was removed by aeration and the solution was lyophilized. The residue which contained a small amount of propanediol was again dissolved in 100 ml. of water. This solution was adjusted to *p*H 8.0 with barium hydroxide solution, kept overnight at room temperature, treated with carbon dioxide and filtered. The filtrate was lyophilized to give a white powdery barium salt contaminated with propanediol, the latter was removed by washing the salt twice with acetone. The salt, dissolved in 20 ml. of water, was kept overnight in a refrigerator, and a small amount of material which separated was filtered. The filtrate was added to 40 ml. of acetone, and the resulting precipitate was centrifuged and dried over P_2O_5, yield 0.8 g.

An aqueous solution of 0.2 g. of this powder was treated with Amberlite IR-120-H$^+$. An equivalent amount of cyclohexylamine was added to the acidic solution. On lyophilization, 0.32 g. of residue was obtained which was dissolved in a small quantity of water and filtered. On addition of acetone, the filtrate gave white needles which were dried over P_2O_5 at room temperature; m.p. 168–169° dec. *Anal.* Calcd. for $C_{15}H_{35}O_5N_2P\cdot{}^1/_2H_2O$: C, 49.59; H, 9.92. Found: C, 49.26; H, 10.30.

(6) H. Limpricht and H. Schwanert, *Ann.*, **155**, 63 (1870).

HONGO, TOKYO, JAPAN

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF BOSTON UNIVERSITY AND THE DANIEL SIEFF RESEARCH INSTITUTE WEIZMANN INSTITUTE OF SCIENCE]

Acetylene–Allene Isomerization of Nonadiyne-1,4[1]

BY WALTER J. GENSLER AND JOSEPH CASELLA, JR.

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Alkali at room temperature isomerizes nonadiyne-1,4 to nonadien-1,2-yne-4, and then to nonadiyne-2,4. The preparation and properties of the three hydrocarbons are described.

Nonadiyne-1,4 (I) with alkaline mercuric iodide furnishes a crystalline mercuric acetylide derivative in high yield.[2] The observation that exposure of nonadiyne-1,4 to alkali before forming the mercury compound decreases the yield indicated that alkali acts to change the hydrocarbon in some way. The present paper reports the results of a study of this action.

Isomerization of Nonadiyne-1,4.—It was found that nonadiyne-1,4 (I) in contact with alkali

$$\underset{\text{I}}{C_4H_9C{\equiv}CCH_2C{\equiv}CH} \longrightarrow \underset{\text{II}}{C_4H_9C{\equiv}CCH{=}C{=}CH_2} \longrightarrow \underset{\text{III}}{C_4H_9C{\equiv}CC{\equiv}CCH_3}$$

isomerizes readily and cleanly to the allenic compound, nonadien-1,2-yne-4 (II); and that allene II under the same conditions isomerizes further to the conjugated diacetylene, nonadiyne-2,4 (III). Under the proper conditions, the latter two compounds could be isolated from the reaction mixture in acceptable yields. The isomerization could be followed conveniently by observing the change in intensity of the 220.5 mμ absorption of allene II, or by noting the intensities of the absorptions at 3.03 μ, which is the acetylenic hydrogen stretching vibration for nonadiyne-1,4; at 5.15 μ, the allenic stretching vibration for compound II; and at 4.91 μ, an unassigned vibration characteristic of the conjugated diyne III.

The changes in compound I are analogous to those observed in other terminal acetylenes,[3,4] and follow the generalization that in the compounds $RCH_2C{\equiv}CH$, $RCH{=}C{=}CH_2$ and $RC{\equiv}CCH_3$ the thermodynamic stability is least in the terminal acetylene and greatest in the methylacetylene. In addition to the factors pointed out before in interpreting this order of stability[5,6] the presence of conjugation in compounds II and III and the absence of conjugation in I should favor compounds II and III over I.

(1) This is Paper VI in a series on skipped unsaturation.

(2) W. J. Gensler, A. P. Mahadevan and J. Casella, Jr., THIS JOURNAL, **78**, 163 (1956).

(3) T. L. Jacobs, R. Akawie and R. G. Cooper, *ibid.*, **73**, 1273 (1951).

(4) T. L. Jacobs in R. Adams, "Organic Reactions," Vol. V, John Wiley and Sons, Inc., New York, N. Y., 1949, p. 13.

(5) R. A. Raphael, "Acetylenic Compounds in Organic Synthesis," Academic Press, Inc., New York, N. Y., 1955, p. 134.

(6) E. R. H. Jones, G. H. Whitham and M. C. Whiting, *J. Chem. Soc.*, 3201 (1954).