−6.9°. This is only about 13% of the rotation of the optically pure formal. Brucine does not seem to be a satisfactory alkaloid for the resolution.[15]

Summary

A number of glycols have been shown to react with phosphorus trichloride. The products are highly reactive chlorophosphite esters. From these, by reaction with alcohols, are formed mixed glycol alkyl phosphites, which undergo hydrolysis slowly. Addition of brucine to the resulting solutions yields brucine salts. These have some promise as a means of resolving DL-glycols.

Propylene formal is useful in recovering 1,2-propanediol from dilute aqueous solution.

PASADENA 4, CALIF. RECEIVED AUGUST 30, 1949

[15] It is planned to continue this investigation with other alkaloids.

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 1329]

Preparation and Hydrolysis of Some Acetals and Esters of D(—)-2,3-Butanediol

BY H. K. GARNER* AND H. J. LUCAS

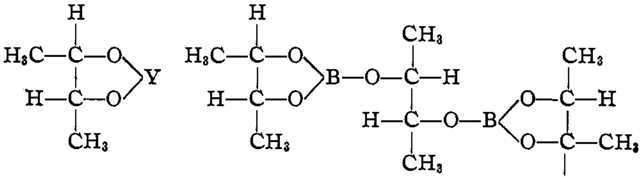
The value of formals in the recovery of the lower glycols from dilute aqueous solutions[1] and the possibility that phosphite esters may serve as intermediates in resolving glycols[2] makes desirable a study of the stereochemistry of formation and hydrolysis of cyclic acetals and cyclic esters of glycols. D(−)-2,3-Butanediol was used since it is the most readily available active glycol.[3] The structures, configurations and names of the compounds studied are shown in Fig. 1.

Nomenclature.—The names shown in Fig. 1 are based on the parent ring systems of the Ring Index.[4] Thus I, II and III are derivatives of 1,3-dioxalane, and IV and V of 1,3,2-dioxathiolane, but the ring systems of VI to X are not found in the Index. The nomenclature of compounds VI to IX as derivatives of 1,3,2-dioxaphospholane follows that of *Chemical Abstracts*.[5] The system of X is more complex. It seems better to use only the common name.

In Table I, in which are listed properties and the analytical data, are given also the common names, which indicate better the chemical nature of the acetal or ester.

Hydrolysis.—In Table II are shown the conditions for hydrolysis of the compounds of Table I and the properties of the resulting glycol, in the case of the formal, or of the resulting formal, in all the other cases. In the first case the glycol recovered had $\alpha^{25}D$ −12.96°. Since the initial glycol had $\alpha^{25}D$ −13.00° it is evident that during the changes glycol → formal → glycol the maximum loss of optical activity is only 0.3%. Thus the method of converting the glycol to the formal, for the purpose of removing it from a dilute aqueous solution, followed by hydrolysis of the formal to the glycol, does not cause any appreciable change in configuration at either asymmetric carbon atom, for the over-all change. In other cases, therefore, it was necessary only to recover the formal from reaction mixtures and to determine its physical properties. By comparison of the resulting data with the properties of the active formal or with those of the *meso* formal, the properties of which are known,[1] conclusions could be drawn as to configurational changes. Hydrolysis of acetal, carbonate, sulfite and chlorophosphite yield formal of high rotation, thus showing that formation and hydrolysis of these compounds does not involve any significant change in configuration.

The results with the formal and acetal indicate



I to IX X

Y		Name
I	CH_2	D(−)-4,5-Dimethyl-1,3-dioxolane
II	$CH—CH_3$	D(−)-2,4,5-Trimethyl-1,3-dioxolane
III	$C=O$	D(+)-2-Oxo-4,5-dimethyl-1,3-dioxolane
IV	$S=O$	D(+)-2-Oxo-4,5-dimethyl-1,3,2-dioxathiolane
V	SO_2	D(+)-2,2-Dioxo-4,5-dimethyl-1,3,2-dioxathiolane
VI	P—Cl	D(+)-2-Chloro-4,5-dimethyl-1,3,2-dioxaphospholane
VII	P—OMe	D(+)-2-Methoxy-4,5-dimethyl-1,3,2-dioxaphospholane
VIII	P—OEt	D(+)-2-Ethoxy-4,5-dimethyl-1,3,2-dioxaphospholane
IX	$P—NEt_2$	D(−)-2-Diethylamino-4,5-dimethyl-1,3,2-dioxaphospholane
X		Neutral borate of D(−)-2,3-butanediol

Fig. 1.—Configurations and names of some cyclic acetals and esters of D(−)-2,3-butanediol.

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[1] M. Senkus, *Ind. Eng. Chem.*, **38**, 913 (1946).

[2] H. J. Lucas, F. W. Mitchell, Jr., and C. N. Scully, THIS JOURNAL, **72**, 5491 (1950).

[3] About the time these investigations were started, publications began to appear by Neish and co-workers in the *Canadian Journal of Research* on various derivatives of this glycol, including cyclic acetals and esters. Pertinent work of theirs is referred to later.

[4] A. M. Patterson and L. T. Capell, "The Ring Index," Reinhold Publishing Corp., New York, N. Y., 1940.

[5] *C. A.* Decennial Index, 1937-1946, pp. 3553, 5463.

TABLE I

PROPERTIES OF SOME CYCLIC ACETALS AND ESTERS OF D(−)-2,3-BUTANEDIOL

		B. p., °C. (Cor.)	Mm.	$n^{25}D$	d^{25}_4	$\alpha^{25}D$	$[\alpha]^{25}D$	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Phosphorus, % Calcd.	Phosphorus, % Found	Sulfur, % Calcd.	Sulfur, % Found	Molecular weight Calcd.	Molecular weight Found (Rast)
I	Formal[a]	95.6–95.9	746	1.3959	0.9346	−23.38°	−25.01°										
II	Acetal[b]	102.6–103.1	746	1.3920	0.8915	− 9.63°	−10.80°	62.03	61.92	10.42	10.11						
III	Carbonate[c]	104.8–104.9	10	1.4160	1.1122	+36.39°	+32.72°	51.72	51.79	6.94	6.94					116	125
IV	Sulfite[d]	60.5–60.7	10	1.4300	1.1942	+24.29°	+20.32°	35.29	35.14	5.89	5.94			23.55	24.00	136	134
V	Sulfate[e]	123.8–124.0	10	1.4159	1.2898	+ 2.26°	+ 1.75°	31.57	32.02	5.30	5.33			21.07	20.51	152	152
VI	Chlorophosphite	49.1–49.2	10	1.4604	1.2038	+116.91°	+97.12°	31.09	31.36	5.22	5.56	20.05	20.08	22.95[g]	22.94[g]		
VII	Methoxyphosphite	46.0–46.2	10	1.4318	1.0830	+58.08°	+53.63°	40.00	40.70	7.39	7.25	20.64	20.66				
VIII	Ethoxyphosphite	54.3	10	1.4297	1.0408	+51.99°	+49.95°	43.90	44.18	7.98	8.54	18.87	18.97				
IX	Diethylamino-phosphite	85.1–85.2	10	1.4549	0.9922	−11.09°	−11.18°	50.25	51.07	9.49	9.75	16.20	15.96	7.33[h]	7.34[h]	286	167
X	Borate (neutral)[f]	138.0–138.5	6	1.4252	1.0383	− 2.58°	− 2.49°	50.40	50.72	8.46	8.63						
		105.3–105.7	0.6														

[a] Previous values[17] b. p. 97°; $n^{25}D$ 1.3960; d^{25}_4 0.9346; $[\alpha]^{25}D$ −24.9°. [b] Previous values[17,18] b. p. 103°; $n^{25}D$ 1.3924; d^{25}_4 0.8914; $[\alpha]^{25}D$ −10.8°. [c] M. p., °C. (cor.), 21.2–21.5. [d] Previous values[21] b. p. 177–178°; $n^{25}D$ 1.4296; d^{25}_4 1.192; $[\alpha]^{25}D$ +19.92°. [e] M. p., °C. (cor.) 6.1–6.4; b. p. at 2 mm. 92.9–93.1°. [f] Neutral equiv.: calcd., 143; found, 139. [g] % chlorine. [h] % nitrogen.

that the reaction of hydrolysis of an acetal does not proceed via a carbonium ion mechanism involving the butane carbon chain as has been postulated[6] for acetals of monohydric alcohols, otherwise there would be considerable racemization. The result here is a confirmation of the results obtained in the hydrolysis of the acetal of *s*-octyl-alcohol[7] where no racemization could be detected. The absence of any configurational change in the case of the cyclic carbonate, sulfite and chlorophosphite, under either acidic or basic conditions, shows that these esters hydrolyze much as do carboxylate esters.[8]

The cyclic sulfate of D(−)-2,3-butanediol differs from the other esters in that a configurational change accompanies hydrolysis. Moreover, the results are different in acid and basic solutions. Acid hydrolysis gives the *meso* glycol but basic hydrolysis gives mainly DL-glycol with about 15% *meso* and about 2% D-glycol. The *meso*-isomer in acid hydrolysis results from a Walden inversion at one carbon atom and zero or an even number of inversions at the other. The formation of the DL isomer under basic conditions can be accounted for if the *cis*-oxide is an intermediate,[9] for hydration of the oxide would take place later, and would be complete in dilute acid solution to give the DL-glycol.[10,11] It is of interest to note that active *s*-butyl acid sulfate also hydrolyzes differently in acid and base.[12] However the results are quite unlike those obtained here. In the case of *s*-butyl sulfate, extensive racemization accompanies hydrolysis under acid conditions while essentially complete inversion of configuration occurs under basic conditions.

Molecular Refractions.—These are shown in Table III. The observed values of formal, acetal, carbonate and borate agree well with calculated values. For the sulfite and sulfate, values were obtained for *M*D of SO_3 and SO_4, respectively, namely, 10.98 and 11.13. From known refractive indices of some alkyl sulfates,[13] four values of *M*D for SO_4 are calculated, *viz.*, 11.29, 11.38, 11.71 and 11.78, mean 11.54. The value for the cyclic sulfate is lower than this figure by 0.4 unit.

The values found for the atomic refraction of phosphorus in the cyclic phosphite esters are in good agreement with those listed for esters of

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[6] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Company, Inc., New York, N. Y., 1940, p. 304.

[7] J. M. O'Gorman and H. J. Lucas, THIS JOURNAL, **72**, 5489 (1950). The possibility that the formal and acetal of D(−)-2,3-butanediol may have the L configuration should not be overlooked. It is planned to investigate this.

[8] L. P. Hammett, ref. 6, p. 356.

[9] This oxide results from the action of base on active *threo*-3-chloro-2 butanol; H. J. Lucas and C. W. Gould, Jr., THIS JOURNAL, **63**, 2548 (1941).

[10] C. E. Wilson and H. J. Lucas, *ibid.*, **58**, 2396 (1936).

[11] It is planned to investigate this reaction in more detail.

[12] R. L. Burwell, Jr., and H. E. Holmquist, THIS JOURNAL, **70**, 878 (1948).

[13] C. M. Suter, "The Organic Chemistry of Sulfur," John Wiley and Sons, Inc., New York, N. Y., 1944, p. 73.

TABLE II

HYDROLYSIS OF CYCLIC ACETALS AND ESTERS

		Acid hydrolysis						Basic hydrolysis					
		Reaction temp., °C.	Properties of formal			Recov., %	Active isomer, %	React. temp., °C.	Properties of formal			Recov., %	Active isomer, %
			B. p., °C. (cor.)	$n^{25}\text{D}$	$\alpha^{25}\text{D}$				B. p., °C. (cor.)	$n^{25}\text{D}$	$\alpha^{25}\text{D}$		
I	Formal	80-90					100						
II	Acetal	80-90	95.4-96.8	1.3959	−23.39°		100						
III	Carbonate	80-90	93.5-96.3	1.3959	−23.54°	85	100	30	95.8-96.3	1.3959	−23.63°	86	100
IV	Sulfite	100	95.5-95.7	1.3962	−23.37°	90	100	100	95.3-96.3	1.3960	−23.61°	94	100
V	Sulfate[a]	100	100.4-102.4	1.4041	000°	95	0	100	94-98	1.3972	−0.46°	83	2
VI	Chlorophosphite	25	95.3-96.3	1.3956	−23.42°	93	100	25	94.8-96.3	1.3956	−23.34°	94	99.8
X	Borate	25	95.4-95.9	1.3959	−23.39°	97	100						

[a] Formal of *meso*-2,3-butanediol[1]: b. p. 101.5°; $n^{20}\text{D}$ 1.4055; d^{20}_{20} 0.9601.

ethylene glycol and propylene glycol,[2] where the values lie in the range 6.7 to 7.0.

TABLE III

MOLAR REFRACTIONS OF CYCLIC ACETALS AND ESTERS OF D(−)-2,3-BUTANEDIOL

		Obs.	$M\text{D}$ calcd.	
I	Formal	26.26	26.38	
II	Acetal	31.03	30.98	
III	Carbonate	26.20	26.39	
IV	Sulfite	29.45	18.47[a]	
V	Sulfite	29.60	18.47[b]	
X	Borate	70.69[c]	70.70	P
VI	Chlorophosphite	35.185	27.725[d]	7.460
VII	Methoxyphosphite	35.937	29.119[d]	6.818
VIII	Ethoxyphosphite	40.715	33.737[d]	6.978
IX	Diethylaminophosphite	52.274	45.270[d]	7.004

[a] Without SO_3, for which $M\text{D} = 10.98$. [b] Without SO_4, for which $M\text{D} = 11.13$. [c] Using the value 7.64 for the BO_3 group. This was calculated from the refractive indices and densities of the isobutyl and isoamyl esters of boric acid. N. A. Lange, "Handbook of Chemistry," Handbook Publishers, Sandusky, Ohio, 1944, pp. 938, 939. [d] Without P.

Comments on Preparations.—Yields of formal, acetal, carbonate, sulfite and chlorophosphite were all good. The respective reactants were: paraformaldehyde, paraldehyde (or *n*-amyl acetal), phosgene, thionyl chloride and phosphorus trichloride. The surprising result obtained with boric acid, where one might well expect to obtain a complex mixture of reaction products, may be due to disproportionation during distillation and removal of the most volatile product, which would be the smallest molecule not containing any free hydroxyl group. This seems reasonable in view of the great reactivity of borate esters.

The preparation of the cyclic sulfate by oxidation of the cyclic sulfite with calcium permanganate is of interest since the preparation of glycol sulfites can be accomplished with good yields. Substitution of calcium permanganate for potassium permanganate in the procedure of Evans[14] allows the reaction to be carried out at a lower temperature and with a much smaller volume of solvent. The assumption that the sulfate has the D configuration is justified on the basis that the C–to–O bond is not altered.

Experimental[15]

D(—)-**2,3-Butanediol.**—This was a gift of the Northern Regional Research Laboratory at Peoria, Ill., and for this the authors acknowledge their indebtedness to the laboratory, and to Dr. A. F. Langlykke. The glycol, produced by the fermentation of starch with *Bacillus polymyxa*, had an observed rotation $\alpha^{25}\text{D}$ −12.4°, which after one distillation at reduced pressure gave $\alpha^{25}\text{D}$ −13.00°, $[\alpha]^{25}\text{D}$ −13.17°.

D(−)-**4,5-Dimethyl-1,3-dioxolane, I.**—This was prepared according to the method of Senkus[1] by distilling the formal through a fractionating column from a mixture of 0.10 mole of the glycol, 0.15 mole of formaldehyde (4.5 g. of paraformaldehyde) and 50 ml. of 0.5 *f* sulfuric acid. The 2-phase azeotropic distillate was saturated with potassium carbonate, the aqueous phase drawn off and the formal dried with anhydrous potassium carbonate, crude yield 10.0 g. (98%). The product was subjected to two fractional distillations.[16] The yield is higher than in the method of Neish and MacDonald.[17] Physical constants checked well with previous values.[17,18]

D(—)-**2,4,5-Trimethyl-1,3-dioxolane, II. Method A.**—By the method of Lucas and Guthrie,[19] 0.25 mole (22.5 g.) of active glycol, 0.30 mole (60.6 g.) of diamyl acetal and 1 g. of *p*-toluenesulfonic acid, when distilled through a fractionating column, gave 27.2 g. (94%) of crude distillate at 101–105°. After standing overnight with metallic sodium to remove amyl alcohol and after fractionally distilling twice with no change in the refractive index the last time, there was obtained 19.09 g. (66%) of acetal, b. p. 102.5–103.1° (cor.) 746 mm.; $n^{25}\text{D}$ 1.3920; $\alpha^{25}\text{D}$ −9.63°; $[\alpha]^{25}\text{D}$ −10.80°.

Method B.—In a method based upon that of Neish and MacDonald[17] but differing in that sodium bisulfate was added later, 0.25 mole (22.5 g.) of active glycol, 0.17 mole (22 g.) of paraldehyde and 2 g. of *p*-toluenesulfonic acid were allowed to stand for 1 day. There were 2 liquid phases, the lower about one-third of the total. Then 5 g. of sodium bisulfate was added, and after standing for 3 more days there were three liquid phases: bottom 5.5 ml.; middle, 4 ml.; top, 43 ml. Only the top phase was not miscible with water. This was separated, washed with concentrated aqueous potassium carbonate to remove acid, dried with anhydrous potassium carbonate and distilled, giving 23.0 g. (79%) at 102-105° and 4.0 g. (14%) at 105-110°. Two refractionations gave 14.5 g. (50%) of pure acetal.[16]

Method B can be made to give nearly as good yields as method A, but the final purification of the product is more difficult, because a small amount of amyl alcohol can be conveniently removed from the acetal with metallic sodium in method A, whereas careful fractional distillation is necessary to remove paraldehyde in method B. The yield

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(14) Evans, Ph.D. Thesis, Northwestern University, 1935; see C. M. Suter, "The Organic Chemistry of Sulfur," John Wiley and Sons, Inc., New York, N. Y., 1944, p. 68.

(15) Microanalyses by G. Oppenheimer, G. A. Swinehart and A. Elek.

(16) Physical constants are given in Table I.

(17) A. C. Neish and F. J. MacDonald, *Can. Jour. Research*, **B25**, 70 (1947).

(18) F. M. Robertson and A. C. Neish, *ibid.*, **B26**, 737 (1948).

(19) H. J. Lucas and M. S. Guthrie, THIS JOURNAL, **72**, 5490 (1950).

by method B is somewhat better than that reported by Neish and MacDonald.[17]

D(+)-2-Oxo-4,5-dimethyl-1,3-dioxolane, III.—This was prepared by running a solution of 0.30 mole (30 g.) of phosgene in 200 ml. of toluene slowly into a solution of 0.25 mole (22.5 g.) of the active glycol in 100 ml. of toluene, letting stand for about 1 hour, removing hydrogen chloride, excess phosgene and most of the toluene by distillation at atmospheric pressure and collecting the product by fractionally distilling at reduced pressure. The carbonate weighed 22.0 g. (76%), b. p., 104.7-104.9° (cor.) (10 mm.); $n^{25}\text{D}$ 1.4160; $\alpha^{25}\text{D}$ +35.96°. There were no higher boiling residues. Part, after three crystallizations from ethyl ether and two more distillations, had the properties shown in Table II, essentially those given above.

The carbonate described by Kolfenbach, Fulmer and Underkofler[20] was prepared by passing phosgene over 2,3-butanediol at 150°, without a solvent. The higher physical constants shown for their product, $\alpha^{26}\text{D}$ 1.4226 and $d^{26}{}_4$ 1.129, indicate that they were working either with the *meso* glycol or with a mixture.

D(+)-2-Oxo-4,5-dimethyl-1,3,2-dioxathiolane, IV.—This was prepared from 0.25 mole (22.5 g.) of D(−)-2,3-butanediol in 100 ml. of methylene chloride by slowly adding, while stirring, 0.30 mole (37.5 g.) of thionyl chloride during one-half hour. At first some heating was observed, but later as hydrogen chloride was evolved the temperature dropped to 0°. After heating at refluxing temperature for ten minutes, water was added to decompose excess thionyl chloride, the organic phase was washed with aqueous potassium carbonate, then with water and dried with anhydrous potassium carbonate. After removal of solvent at atmospheric pressure the product was distilled at 10 mm. to give 31.0 g. (91%)[16] of the sulfite.

The addition of methylene chloride is advantageous in giving a better yield, for Robertson and Neish[21] report a 70% yield without a solvent. The constants of the products check well.

D(+)-2,2-Dioxo-4,5-dimethyl-1,3,2-dioxathiolane, V.—This was prepared from IV by permanganate oxidation following the procedure of Evans,[14] but modified by using the more soluble calcium permanganate. To a cold (10°) solution of 0.20 mole (27.2 g.) of IV in 100 ml. of glacial acetic acid was added slowly, with mechanical stirring, a filtered solution of 0.150 mole (50 g.) of impure calcium permanganate tetrahydrate (the only material available then) in 50 ml. of water. Actually, the theoretical amount of permanganate ion (0.067 mole) appeared to be sufficient for the oxidation. The temperature was kept below 15°. The rapid, strongly exothermic reaction was accompanied by an immediate formation of colloidal manganese dioxide. When additional permanganate caused no rise in temperature and the pink color of permanganate ion could be detected in the solution, the mixture was poured into 150 g. of sodium carbonate and ice water. Sodium bisulfite was added to destroy excess permanganate and the entire mixture was extracted with six 100-ml. portions of ethyl ether. After drying over calcium chloride, ether was removed at room temperature with an aspirator and the product was fractionally distilled at reduced pressure to give 13.6 g. (45%)[16] of the sulfate.

D(+)-2-Chloro-4,5-dimethyl-1,3,2-dioxaphospholane, VI.—This was prepared by the inclined tube method described elsewhere for the preparation of the chlorophosphite ester of propylene glycol.[2] The reacting solutions were 0.50 mole (45 g.) of active glycol in 150 ml. of recently distilled chloroform and 0.50 mole (69 g.) of phosphorus trichloride in 150 ml. of chloroform. The reaction time was forty minutes. The same phenomena of slight warming near point of contact of the two solutions and cooling in the flask were observed. After removal of the chloroform by distillation at atmospheric pressure the product was fractionally distilled at 10 mm., yielding 51 g. (66%)[16] of the chlorophosphite.

D(+)-2-Methoxy-4,5-dimethyl-1,3,2-dioxaphospholane, VII.—With careful exclusion of moisture throughout, 0.05 mole (1.6 g.) of methanol in 10 ml. of 30-60° petroleum ether was added dropwise to a solution of 0.05 mole (7.7 g.) of VI and 0.075 mole (8.6 g.) of N-ethylmorpholine in 15 ml. of 30-60° petroleum ether. The reaction took place rapidly with a hissing sound, and a precipitate of ethylmorpholine hydrochloride formed immediately. The solution was separated from the solid by suction filtration, the solid was washed with three 25-ml. portions of 30-60° petroleum ether, the combined filtrate and washings heated carefully to remove most of the solvent at atmospheric pressure and the product was obtained by fractional distillation at 10 mm.; yield, 3.6 g. (47%).[16]

D(+)-2-Ethoxy-4,5-dimethyl-1,3,2-dioxaphospholane, VIII.—This was prepared in 52% yield by the procedure described for VII, but using ethanol in place of methanol.[16]

D(−)-2-Diethylamino-4,5-dimethyl-1,3,2-dioxaphospholane, IX.—This was prepared in 61% yield by the procedure described for VII but using diethylamine in place of methanol.[16]

The liquid diethylaminophosphite slowly changed to a crystalline, hygroscopic solid within a few hours when allowed to stand exposed to laboratory air. This solid behaved as a salt, giving an immediate strong odor of diethylamine with aqueous base. It seemed to be the diethylamine salt of the monoacid phosphite of D(−)-2,3-butanediol, $\text{HO-C}_4\text{H}_8\text{-O-P(OH)-}\overset{-}{\text{O}}.(\text{C}_2\text{H}_5)_2\overset{+}{\text{N}}\text{H}_2$. It was crystallized four times from dioxane: m. p., 82-83°; $[\alpha]^{25}\text{D}$ −10.5° (0.0934 g. in 2.00 ml. CHCl_3 solution).

Anal. Calcd. for $\text{C}_8\text{H}_{22}\text{O}_4\text{NP}$: C, 42.28; H, 9.76; N, 6.17; P, 13.63. Found: C, 42.25; H, 9.75; N, 6.12; P, 13.65.

D(−)-2,3-Butanediol Borate (Neutral) X.—In a 100-ml. flask provided with a fractionating column was heated 0.25 mole (22.5 g.) of D(−)2,3-butanediol, 0.167 mole (10.3 g.) of boric acid and 25 ml. of benzene. By azeotropic distillation and recycling the benzene 8.8 ml. of water was removed in 2 hours (theory, 9.0 ml.). After removal of benzene by distillation at atmospheric pressure the product was distilled at 6 mm., giving 21.3 g. (90%), b. p. 138.0-138.5°; $n^{25}\text{D}$ 1.4252. It was redistilled twice.[16]

Molecular weight by the Rast camphor method was 167, theoretical 286. The ester is very hygroscopic and undergoes hydrolysis rapidly. The water absorbed during the weighing process probably accounts for the low result.

The borate of *meso*-2,3-butanediol was prepared by Morell and Lathrop[22] in an analogous fashion, b. p. 290-292° (uncor.).

Hydrolysis of Acetals: Formal, I.—In a flask attached to a fractionating column was heated 0.05 mole (5 g.) of I, 2 ml. of water, 0.1 ml. of concentrated hydrochloric acid and 10 ml. of methanol. The methylol was taken off intermittently at 41.5° as it accumulated at the column head, about ten hours being required. Finally, the excess methanol was distilled over, the residue was neutralized with solid potassium carbonate (0.2 g.) and the glycol was distilled at 10 mm., b. p. 77.3-77.4° (cor.); m. p. 18.3-19.0° (cor.); $\alpha^{25}\text{D}$ −12.96°. The value of the rotation was only 0.04° less than that of the original glycol. Therefore there was essentially complete retention of configuration in the over-all change, glycol to formal to glycol.

Acetal, II.—In a flask attached to a fractionating column, 0.10 mole (11.6 g.) of II was heated with 50 ml. of 1*f* sulfuric acid until acetaldehyde was no longer evolved. Part of the water was distilled so as to remove the last traces of acetal and acetaldehyde. Then 4.5 g. of paraformaldehyde was added to the boiler and the formal was distilled over as the azeotrope with water. After drying the crude product, 9.5 g. (93%), was distilled.[23] Here also there was complete retention of configuration for the over-all change, glycol to acetal to glycol.

Hydrolysis of the Cyclic Esters, General Procedure: Acid Hydrolysis.—The ester, usually 0.05 mole, was

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[20] J. J. Kolfenbach, F. I. Fulmer and L. A. Underkofler, THIS JOURNAL, **67**, 502 (1945).

[21] F. M. Robertson and A. C. Neish, *Can. Jour. Research*, **B25**, 491 (1947).

[22] S. A. Morell and E. C. Lathrop, THIS JOURNAL, **67**, 879 (1945).

[23] The data are shown in Table II.

heated with 50 ml. of 1 *f* sulfuric acid under a reflux condenser until it dissolved. Then the liquid was cooled to room temperature, 3.0 g. of paraformaldehyde was added and the formal was removed as the azeotrope with water by distillation through a fractionating column. The formal was dried and distilled.[23]

Basic Hydrolysis.—This was similar to acid hydrolysis except that the reagent was 2 *f* potassium hydroxide, which was neutralized, using some excess of sulfuric acid, before conversion to the formal.[23]

It is noted from Table II that hydrolysis of carbonate, sulfite, chlorophosphite, methoxyphosphite, ethoxyphosphite, and diethylaminophosphite gave active formal of high optical purity. Therefore, hydrolysis under either acidic or basic conditions gives the original glycol without any change in configuration. In some cases the rotation actually was improved, which may indicate that in the preparation of the ester some purification was effected.

Hydrolysis of the sulfate under acid conditions gave a formal which, from boiling point and refractive index, was largely *meso* formal. Had the amount of D- or DL-formal been significant it would have been detected during distillation. The refractive index of 1.4041 at 25° probably corresponds closely to 1.4055 at 20° for d*n*/d*t* usually is about − 0.0004 per degree.[2]

Basic hydrolysis of the sulfate gave largely DL-glycol, with about 15% *meso*, calculated from the refractive index, and 2% of D-glycol, calculated from the rotation of the formal. The range of boiling point also indicates a mixture, largely DL.

Summary

A number of cyclic acetals and esters of D(−)-2,3-butanediol have been prepared and a study has been made of the steric changes on hydrolysis. The cyclic sulfate was the only one to show abnormal behavior. In acid solution it gives *meso* glycol almost exclusively and in basic solution, DL-glycol mainly, with some *meso* and a very little D(−)-glycol.

Calcium permanganate is an excellent reagent for oxidizing the glycol sulfite to the glycol sulfate.

Molecular refractivities, *M*D have been obtained for the following: SO_4, 11.13; SO_3, 10.98; P, 6.8 to 7.4.

PASADENA 4, CALIFORNIA RECEIVED AUGUST 30, 1949

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMICAL ENGINEERING OF ILLINOIS INSTITUTE OF TECHNOLOGY]

Reactions of Paraffin Hydrocarbons in the Presence of Sulfuric Acid

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The use of sulfuric acid as an isomerization catalyst for certain paraffin hydrocarbons has been reported in the literature.[2-6]

This article presents the results of the reactions of *n*-octane, 2,4-dimethylpentane, 2,2,4-trimethylbutane (triptane) and 2,2-dimethylbutane (neohexane) in the presence of 96 and 98% sulfuric acid as catalyst at the boiling point temperatures of the respective hydrocarbons.

Experimental

Materials.—Baker and Adams C. P. grade sulfuric acid was used. Its concentration was varied from 96–100%. The paraffins, with the exception of triptane, were obtained from the Phillips Petroleum Company. They were pure grade with a guaranteed purity of 99 mole per cent. The triptane was obtained from the Ethyl Corporation with a purity of 97%. Each of these paraffins was redistilled in a Podbielniak column. The physical constants are as follows: *n*-octane, b. p. 125.6°, $n^{25}D$ 1.3952; 2,4-dimethylpentane, b. p. 80.5°, $n^{25}D$ 1.3789; 2,2-dimethylbutane, b. p. 49.6°, $n^{25}D$ 1.3660; 2,2,3-trimethylbutane, b. p. 80.7°, $n^{25}D$ 1.3869.

Apparatus and Procedure.—The experiments were performed in a standard closed system apparatus with a Dry Ice trap for condensable gases and a gas collecting bottle. A wide-blade stirrer maintained at seven hundred r. p. m. violently agitated the contents of the creased reaction flask. Upon completion of the reaction the hydrocarbon layer was separated, stabilized, washed and dried. It was the distilled over metallic sodium in a one hundred theoretical plate Podbielniak column. The compositions of the fractions were determined by physical constants and infrared spectra. The infrared absorption spectra

TABLE I

2,4-DIMETHYLPENTANE

Temperature, °C.	25	80
Time, hr.	10	
Sulfuric acid concn., %	96%	98%
Materials charged (g.)		
Sulfuric acid	175.0	181.0
Hydrocarbon	87.5	90.5
Products obtained (g.)		
Acid layer	174.0	181.0
Hydrocarbon layer	86.5	86.0
Gas	...	2.0
Composition of hydrocarbon layer (wt. %)		
Lower boiling compounds	...	0.5
Unreacted 2,4-dimethylpentane	87.6	51.3
Isomers	11.7	47.4
Higher boiling compounds	0.6	0.8

Composition and constants of the hydrocarbon layer from 98% acid experiment

Boiling range, °C.	Weight, %	$n^{25}D$	Composition
35–80	0.5	1.3706	...
80–81	51.3	1.3790	2,4-Dimethylpentane
89–90.5	47.4	1.3880	2,3-Dimethylpentane 2-Methylhexane (minor) 3-Methylhexane (minor)
Above 90.5	0.8	1.4095	...

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