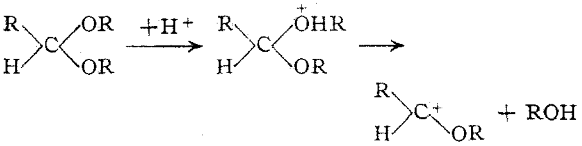
not the alkyl carbon atom, forms the carbonium ion.



Experimental

D(+)-**2-Octanol.**—2-Octanol, Eastman Kodak Co. White Label, was resolved by the method of Kenyon.[9] The *dextro* alcohol, b. p. 73° at 10 mm., had an observed rotation, $\alpha^{24}D$ + 7.93.

Active *s*-Octyl Acetal.—To 0.31 mole (40 g.) of D(+)-2-octanol was added 0.2 mole (12 ml.) of freshly prepared acetaldehyde,[10] 1 drop of concentrated hydrochloric acid, and 6 g. of anhydrous calcium chloride. After standing for two days the solid, which had become mushy, was removed by suction filtration and some drierite was added, with resultant heating. After filtering again the liquid was fractionally distilled at reduced pressure, yielding 16 g. (36%) of acetal, b. p. 115° (1.5 mm.), observed rotation in 1-dm. tube, $\alpha^{25}D$ + 18.5°.

Hydrolysis of Acetal.—A mixture of 8 g. of active *s*-octyl acetal and 20 g. of 5% aqueous phosphoric acid was heated at refluxing temperature for one hour. The organic phase was separated, dried with magnesium sulfate and distilled. The entire product distilled in the range 72–73° at 10 mm., and had an observed rotation $\alpha^{24.5}D$ + 7.91°. This shows complete retention of configuration of the alcohol during both formation and hydrolysis of the acetal.

Summary

When active *s*-octyl acetal is hydrolyzed by dilute aqueous phosphoric acid, the D(+)-*s*-octyl alcohol formed has the same rotation as the original alcohol. The reaction does not proceed via an alkyl carbonium ion.

PASADENA, CALIF.

RECEIVED AUGUST 30, 1949

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[9] J. Kenyon, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, New York, N. Y., second ed., 1941, p. 418.

[10] Lucas and Pressman, "Principles and Practice in Organic Chemistry," John Wiley and Sons, New York, N. Y., 1949, p. 287.

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 1327]

Geometrical Isomerism of Propylene Acetals

BY H. J. LUCAS AND M. S. GUTHRIE

The simplest cyclic acetals which can exist in *cis* and *trans* forms are the dimethyl-1,3-dioxolanes. These are 2,4-dimethyl-1,3-dioxolanes (propylene acetals) and 4,5-dimethyl-1,3-dioxolanes (2,3-butanediol formals). There are seven possible stereoisomers, four of the former and three of the latter, excluding DL-forms. Of the formals, those of *meso*-[1] and D(−)-2,3-butanediol[2] are known, and perhaps the lower boiling formal of Senkus[1] is the DL-formal, but no rotation is given. Other similar examples of *cis–trans* isomerism are derivatives of cyclic acetals from *p*-nitrobenzaldehyde and glycerol (both 5-membered and 6-membered ring systems)[3] and the butyrals of 2-nitro-2-ethyl-1,3-propanediol.[4] The latter, as well as the six-membered glycerol acetals, have a different ring system, namely, the six-membered 1,3-dioxane ring.[4]

The four stereoisomeric forms of propylene acetal constitute two pairs of enantiomorphs which are inactive *cis* and *trans* isomers. These were prepared in good yield in an exchange reaction of propylene glycol with *n*-amyl acetal, by heating the reactants with an acid catalyst and distilling out the most volatile component, which is the desired acetal. This operation can be carried out under anhydrous conditions. It is especially useful with ethylene and propylene glycols, because the high mutual solubilities of these glycols with water, and the good solubilities of the resulting acetals in water, make it desirable to work in a completely anhydrous system. The method also works well with 2,3-butanediol.[2b] Moreover, the possibility of being able to find isomeric forms was believed to depend upon driving them out of the reaction mixture as soon as formed rather than let them remain in contact with the catalyst, which would promote isomerization, with the possibility of changing one form into the other, more or less completely.

The product was separated by fractional distillation into two main fractions, which after heating with metallic sodium to remove any water and *n*-amyl alcohol, distilled at 90.1° and 93.0°, respectively. The preponderance of the lower boiling isomer seems to indicate that the method of preparation favors this form, even though there was little fractionation. Senkus observed that the amount of the higher boiling isomer of the two butyrals of 2-nitro-2-ethyl-1,3-propanediol was almost 7 times that of the lower. He carried out the reaction at 15°.

Experimental[5]

Di-*n*-amyl Acetal.—Hydrogen chloride was passed into a mixture of 161.5 g. (1.83 mole) of anhydrous freshly distilled *n*-amyl alcohol, b. p. 134° (747 mm.), and 60 g. (0.45 mole) of paraldehyde, b. p. 119° (747 mm.), until a cloudiness developed. The mixture was allowed to stand until the aqueous phase no longer increased in volume. After separation of the phases, the organic phase

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

[2] (a) A. C. Neish and F. J. MacDonald, *Can. J. Research*, **B25**, 70 (1947); (b) H. K. Garner and H. J. Lucas, THIS JOURNAL, **72**, 5497 (1950).

[3] H. Hibbert and N. M. Carter, *ibid.*, **50**, 3376 (1928).

[4] M. Senkus, *ibid.*, **65**, 1656 (1943).

[5] Analyses by G. Oppenheimer and G. A. Swinehart.

was subjected to distillation at 30 mm. In this way any remaining paraldehyde was depolymerized to aldehyde and removed at a relatively low temperature, with minimum loss of acetal. The main fraction distilled at 98–110°, weight 140 g., yield 75%. The product was washed with saturated aqueous potassium carbonate until neutral to litmus, then dried over anhydrous potassium carbonate. It was used without further purification, since any contamination by *n*-amyl alcohol is not important in the subsequent exchange reaction in which this alcohol is one of the reaction products. However, it is important to remove hydrogen chloride, even though an acid is needed in the exchange reaction, because any volatile acid in the mixture of *cis–trans* isomers probably would cause isomerization during distillation with resultant complete disappearance of the more volatile isomer. The boiling point of *n*-amyl acetal,[6] 225°, is so high that it can be easily removed from propylene acetal.

2,4-Dimethyl-1,3-dioxolane.—To a mixture of 110 g. (0.54 mole) of *n*-amyl acetal and 47.0 g. (0.62 mole) of propylene glycol (b. p., 85.5° at 10 mm.)[7] in a modified Claisen flask having a 7-cm. packing of glass rings[8] was added about 0.5 g. of *p*-toluenesulfonic acid. After standing for some time (one day) or upon being heated to about 40°, the original two-phase system became a single phase. Product was then taken off as quickly as possible, the flame being adjusted to keep the reflux ratio low so as to minimize refluxing of the propylene acetal and at the same time reflux back *n*-amyl acetal. It is desirable to distil out the propylene acetal as formed, otherwise a considerable amount of the higher boiling isomer might be converted into the lower boiling one.

The material distilling at 80–102° was collected as the product; weight, 49.5 g. (89%). At least 90% of this is the acetal for when redistilled, 46.5 g. came over without the temperature rising above 92.8°, where the distillation stopped. The rest was holdup.

Two fractional distillations, in the presence of potassium hydroxide pellets, through a fractionating column rated at 25 theoretical plates and designed to have a small holdup[9] gave two main fractions: I (about 60%), b. p. 90.0–90.2° (745 mm.); n^{25}_D 1.3923; II (about 10%) b. p. 92.8–92.9° (745 mm.) n^{25}_D 1.3939. These were purified by heating with metallic sodium to remove water and *n*-amyl alcohol. The constants, as shown in Table I, were essentially unchanged. These compounds represent *cis* and *trans* forms, but no decision in regard to further identity can be made without additional data.

Table I

Constants of Isomeric 2,4-Dimethyl-1,3-Dioxolanes

		I	II
B. p., °C. (747 mm.)		90.1	93.0
n^{25}_D		1.3922	1.3938
d^{25}_4		0.9204	0.9269
M_D obs.		26.436	26.345
M_D calcd.		26.376	26.376
Carbon, %	Calcd.	58.80	58.80
	Found	58.90	58.66
Hydrogen, %	Calcd.	9.87	9.87
	Found	9.86	9.96

Summary

2,4-Dimethyl-1,3-dioxolane (propylene acetal) has been prepared by an exchange reaction between propylene glycol and *n*-amyl acetal. It has been separated into *cis* and *trans* forms by fractional distillation.

Pasadena, California

Received August 30, 1949

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[6] J. Béduivé, *Bull. Soc. Chim. Belg.*, **34**, 53 (1925).

[7] Kindly supplied by F. W. Mitchell, Jr.

[8] Lucas and Pressman, "Principles and Practice of Organic Chemistry," John Wiley and Sons, New York, N. Y., 1949, Figure 9-4G, page 287,

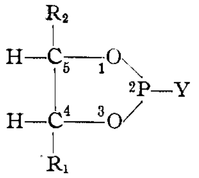
[9] F. W. Mitchell, Jr., and J. M. O'Gorman, *Anal. Chem.*, **20**, 315 (1948).

[Contribution No. 1328 from the Gates and Crellin Laboratories of Chemistry, California Institute of Technology]

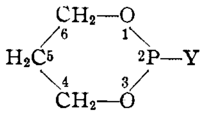
Cyclic Phosphites of Some Aliphatic Glycols

By H. J. Lucas, F. W. Mitchell, Jr., and C. N. Scully

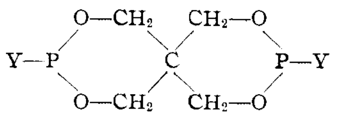
The possibility that phosphites of glycols might serve as a means of resolving DL-glycols led to an investigation of cyclic phosphites of some of the lower glycols. The compounds described are principally those related to ethanediol (I, R_1 and R_2 = H), 1,2-propanediol (I, $R_1 = CH_3$, R_2 = H), 1,3-propanediol (II) and 2,3-butanediol (I, R_1 and $R_2 = CH_3$), and are glycol chlorophosphites (Y = Cl), glycol hydrogen phosphites (Y = OH), glycol (alkylene) alkyl phosphites (Y = OR), and glycol amidophosphites (Y = NR_2). Also, a few derivatives, III, of pentaerythritol are mentioned.



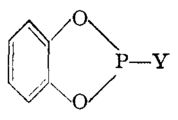
I



II



III



IV

At the time this investigation was started the only previously described phosphites of dihydroxy compounds were compounds from pyrocatechol, IV (Y = Cl and others),[1] a dimeric product from ethylene glycol,[2] and the chlorophosphite ester of *meso*-2,3-butanediol, on which preliminary studies only had been made.[3] After the work had well

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[1] W. Knauer, *Ber.*, **27**, 2565 (1894). The structure of IV (Y = Cl) was first elucidated by L. Anschutz and W. Broeker, *ibid.*, **61**, 1264 (1928), and later prepared in good yield by A. E. Arbuzov and F. G. Valitova, *Trans. Kirov Inst. Chem. Tech. Kazan*, No. 8, 12 (1940); *cf. C. A.*, **35**, 2485 (1941).

[2] P. Carre, *Compt. rend.*, **136**, 756 (1903).

[3] E. Patterson, Thesis, California Institute of Technology, 1942.