

tached to the double bond there is a larger number of possible mesomeric forms. Resonance of this type apparently brings about an increased electron mobility and causes shifts in the absorption to the red. Fluorine appears also to participate in this type of resonance, though not to the same extent because of its strong inductive effect. A comparison of the effects of H and F in shifting the spectra is interesting.

It may be seen from Table II that when H is replaced by F in an ethylenic compound, the absorption shifts to the red. The displacement is about 2.5 kcal. for each H-atom. This is in marked contrast to the situation which obtains for the methanes; there the inductive effect of the fluorine atom when it replaces a hydrogen atom brings about a shift of 2.2 kcal. to shorter wave lengths. Apparently resonance involving fluorine and the double bond is more effective in increasing the mobility of the electrons than the opposing inductive effect.

### Summary

By the use of carefully purified vapor samples, the long wave length ultraviolet absorption spectra of the following compounds have been measured:  $\text{CCl}_4$ ,  $\text{CFCl}_3$ ,  $\text{CHCl}_3$ ,  $\text{CF}_2\text{Cl}_2$ ,  $\text{CHFCI}_2$ ,  $\text{CH}_2\text{Cl}_2$ ,  $\text{CCl}_2=\text{CCl}_2$ ,  $\text{CFCl}=\text{CCl}_2$ ,  $\text{CHCl}=\text{CCl}_2$ ,  $\text{CFCl}=\text{CFCl}$  (*cis-trans*),  $\text{CF}_2=\text{CCl}_2$ ,  $\text{CH}_2=\text{CCl}_2$ ,  $\text{CHCl}=\text{CHCl}$  (*trans*),  $\text{CHCl}=\text{CHCl}$  (*cis*),  $\text{CF}_2=\text{CFCl}$ ,  $\text{CF}_2=\text{CHCl}$ ,  $\text{CF}_2=\text{CF}_2$  and  $\text{CH}_2=\text{CHCl}$ . The spectra appear to be continuous and obey Beer's law. Whenever a H-atom is replaced by F in a halomethane, the absorption shifts to shorter wave lengths because of the inductive effect of the F. In an ethylenic compound, however, the absorption shifts to longer wave lengths when H is replaced by F. This is interpreted to mean that F undergoes resonance with the double bond and that this mesomeric effect outweighs the inductive effect.

BOULDER, COLO.

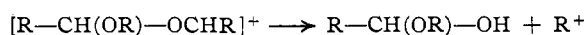
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[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 1326]

## Hydrolysis of the Acetal of D-(+)-2-Octanol

BY JOHN MICHAEL O'GORMAN<sup>1</sup> AND H. J. LUCAS

The first step in the hydrolysis of an acetal is generally assumed to be the formation of the hemiacetal which, according to Hammett,<sup>2</sup> probably is the rate determining step. The relative rates of hydrolysis in water at 25°, for some formals are<sup>3</sup>: methanol, 1; ethanol, 8.5; 2-propanol, 47.1; 1-propanol, 9.4; 2-methyl-1-propanol, 13.0; 1-butanol, 9.3. In order to account for these relative rates, Hammett has suggested for the reaction, which is known to exhibit specific oxonium ion catalysis,<sup>4</sup> a mechanism involving the formation of an intermediate carbonium ion.



The order of rates possesses some of the characteristics of electrophilic displacement on oxygen. A test of this mechanism can be made by studying the hydrolysis of an acetal of an optically active alcohol. More or less extensive racemization of the alcohol would be expected if hydrolysis proceeded in the manner indicated.<sup>5</sup>

Hydrolysis of active di-*s*-butyl acetal was carried out in dilute aqueous phosphoric acid at 100°. The observed rotation of the alcohol re-

covered,  $\alpha^{24.5\text{D}} + 7.91^\circ$ , was essentially identical with that of the starting alcohol,  $\alpha^{24\text{D}} + 7.93^\circ$ . It is concluded, therefore, that hydrolysis of the acetal does not proceed via the intermediate of a carbonium ion which involves the alkyl carbon atom.

This steric result is in agreement with earlier work on the hydrolysis of ketals<sup>6</sup> and with more recent work on the hydrolysis of the formal and acetal of D(-)-2,3-butanediol,<sup>7</sup> which gives the original glycol in excellent yield and with essentially unchanged rotation.

It is evident from the results of rate studies<sup>2,8</sup> that the effect of change in structure operates on the aldehyde carbon, rather than on the alkyl carbon atom, since changes in the nature of the aldehyde part of the molecule exert much more profound effects than changes in the alcohol part. The hydrolysis moreover may be considered to be a typical  $\text{S}_{\text{N}}1$  reaction. In the mechanism proposed the aldehyde carbon atom,

(6) J. Boeseken and H. G. Derx, *Rec. trav. chim. Pay-Bas*, **40**, 519 (1921), found that hydrolysis of the acetone ketal of *cis*-tetrahydronaphthalene-1,2-diol gave the original *cis*-diol and P. H. Hermans, *Ber.*, **57B**, 824 (1924), found the same to be true of *cis*-hydrindene-1,2-diol and of *cis*-tetrahydronaphthalene-2,3-diol. However, Hermans observed that a small amount of the corresponding *trans* isomer is present in each product.

(7) H. K. Garner and H. J. Lucas, *THIS JOURNAL*, **73**, 5497 (1950).

(8) A. Skrabal and M. Zlatewa, *Z. physik. Chem.*, **119**, 305 (1926), have shown that the hydrolysis rates of acetals of pentaerythritol increase very rapidly in the order:  $\text{H}_2\text{CO}$ ,  $\text{MeCHO}$ ,  $\text{EtCHO}$ , *i*- $\text{PrCHO}$ ,  $\text{Me}_2\text{CO}$ .

(1) Present address University of California, Santa Barbara, Calif.

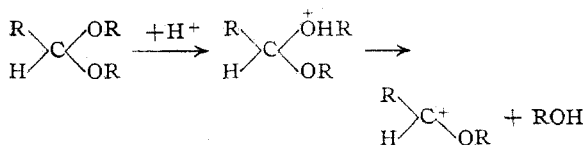
(2) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Company, New York, N. Y., 1940, p. 304.

(3) A. Skrabal and H. H. Eger, *Z. physik. Chem.*, **123**, 349 (1926).

(4) J. N. Brønsted and W. F. K. Wynne-Jones, *Trans. Faraday Soc.*, **25**, 59 (1929).

(5) Two other methods of testing the mechanism are: (1) hydrolysis with water made with  $\text{O}^{18}$ , for the carbonium ion mechanism predicts that heavy oxygen should appear in the alcohol formed; and (2) methanolysis with methyl alcohol, to produce methyl ether.

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.<sup>9</sup> 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,<sup>10</sup> 1 drop of concentrated hydrochloric acid, and 6 g. of anhydrous calcium chloride. After standing

(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.

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,  $\alpha^{25}_D + 18.5^\circ$ .

**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  $\alpha^{24}_D + 7.91^\circ$ . 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.

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## 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*-<sup>1</sup> and D(-)-2,3-butanediol<sup>2</sup> are known, and perhaps the lower boiling formal of Senkus<sup>3</sup> 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)<sup>3</sup> and the butyrals of 2-nitro-2-ethyl-1,3-propanediol.<sup>4</sup> The latter, as well as the six-membered glycerol acetals, have a different ring system, namely, the six-membered 1,3-dioxane ring.<sup>4</sup>

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, be-

cause 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.<sup>2b</sup> 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<sup>5</sup>

**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

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

(2) (a) A. C. Neish and F. J. MacDonald, *Can. J. Research*, **B25**, 79 (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.