

acids, the value for the second hydrogen of sulfuric acid being 3×10^{-2} ; for the first constant of oxalic acid, 3.8×10^{-2} .⁶ The very sharp break occurring at the end-point of the curve of the free acid (Fig. 3) lends itself well to the quantitative estimation of the acid.

Summary

1. 2-Hydroxynaphthalene-6-sulfonic acid has been purified by recrystallization of the acid from aqueous solutions by means of the addition of hydrogen chloride. The identity of a monohydrate and a dihydrate has been established. Melting points for these three compounds have been determined.

2. The 2-hydroxynaphthalene sulfonic acids have been studied electrometrically and values determined for their acid dissociation constants. The nature of the curve obtained for the 2-hydroxynaphthalene-6-sulfonic acid shows that the quantitative estimation of the acid or of its salts might be possible in the presence of the isomeric 2-hydroxynaphthalene-1-sulfonic acid, or of neutral salts.

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RESEARCHES ON CYCLIC ACETALS. I. FORMATION OF CYCLIC ACETALS OF 4,5-DIHYDROXY-2,6-OCTADIENE¹

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The tendencies toward formation of cyclic acetals have been investigated by Hibbert and co-workers.² In the majority of these investigations both the aldehyde and the glycol used were of the saturated type. More recently³ work has been published on the tendencies of unsaturated glycols. The present investigation deals with a saturated glycol to form acetals with both the saturated and unsaturated type of aldehyde.

Experiments were carried out on the condensation of 4,5-dihydroxy-2,6-octadiene (dipropenyl glycol), $\text{CH}_3\text{CH}=\text{CHCHOHCHOHCH}=\text{CHCH}_3$, with acetaldehyde, paraldehyde, propionaldehyde, butyraldehyde, heptaldehyde, acetone, benzaldehyde, crotonaldehyde, cinnamaldehyde and chloral, using sulfuric acid as a catalyst. The yields of cyclic acetals obtained were taken as a basis of comparison for the tendencies of the aldehydes toward cyclic acetal formation.

¹ This paper is constructed from a dissertation submitted in partial fulfillment of the requirements for the degree of Master of Arts at Smith College.

² Hibbert and co-workers, *J. Ind. Eng. Chem.*, **13**, 256, 334 (1921); *THIS JOURNAL*, **45**, 734, 2433, 3108, 3117, 3124 (1923); **46**, 1283 (1924); **50**, 1411, 2235, 2242 (1928).

³ Hibbert, Houghton and Taylor, *ibid.*, **51**, 611 (1929).

The saturated carbonyl derivatives, acetaldehyde, paraldehyde, acetone, propionaldehyde, butyraldehyde and heptaldehyde all readily formed acetals of dipropenyl glycol with yields of 90, 83, 71, 90, 92 and 85%, respectively, acetaldehyde and paraldehyde forming the same acetal. Hibbert⁴ has shown that acetaldehyde, butyraldehyde and heptaldehyde form acetals of ethylene glycol with yields of 87, 50 and 50%, respectively. It can, therefore, be concluded that unsaturation of the type in dipropenyl glycol does not decrease the tendency toward cyclic acetal formation, but instead seems to increase such a tendency. In attempting to condense chloral with dipropenyl glycol, a mixture of products was obtained but none could be identified as the acetal. It should not be concluded, however, that a cyclic acetal of chloral cannot be formed. Reaction apparently took place in all cases, but resulted in the original or resinous substances when attempts were made to isolate the products.

According to Hibbert,³ substitution of hydrogen by chlorine atoms in the aldehyde residue of saturated aldehydes results in the formation of acetals of ethylene glycol in two cases. β -Phenyl- α,β -dichloropropylidene ethylene glycol was formed with a yield of 37%, and dichlorobutylidene ethylene glycol was formed with a yield of 50%. Experiments are now in progress on the condensation of several other saturated chloroaldehydes with dipropenyl glycol.

Negative results were also obtained when benzaldehyde was used with dipropenyl glycol. It has been shown that benzaldehyde with ethylene glycol⁴ gives a yield of 80–85% of the acetal. The tendency of dipropenyl glycol to form an acetal with benzaldehyde is, therefore, much less than in the case of ethylene glycol.

The unsaturated aldehydes, crotonaldehyde and cinnamaldehyde, also showed little tendency to form the acetals of dipropenyl glycol; this is in agreement with the results of Hibbert,³ who showed that the amount of reaction of ethylene glycol with these aldehydes was negligible.

Experimental Part

In all cases one part of dipropenyl glycol and about twice the calculated quantity of the aldehyde or ketone were heated in a bath at about 70° for four hours with a few drops (4–6) of 40% sulfuric acid for each tenth mole of the glycol used. At the end of the reacting period an equal volume of ether and sufficient 5% sodium carbonate solution for neutralization were added. The ether solution was washed, dried and distilled. Acetals were obtained as slightly yellow oils in high yield (71–92%) from acetaldehyde, paraldehyde, propionaldehyde, butyraldehyde, heptaldehyde and acetone, as shown in the table, while no product could be obtained when using crotonaldehyde, cinnamaldehyde, chloral and benzaldehyde.

⁴ Hibbert, *THIS JOURNAL*, **46**, 1286 (1924).

TABLE OF RESULTS
CONDENSATION PRODUCTS OF DIPROPENYL GLYCOL WITH VARIOUS HYDROCARBON
CARBONYL DERIVATIVES

	Carbonyl deriv.	B. p., °C.	Acetal, -dipropenyl glycol	B. p., °C.	Press., mm.
1	Acetaldehyde	21	Ethylidene	88-89	20
2	Paraldehyde	124	Same results as with acetaldehyde		
3	Propionaldehyde	48.8	Propylidene	99-100.5	21
4	Butyraldehyde	73-74	Butylidene	104-105	15
5	Heptaldehyde	153-155	Heptylidene	129-131	4
6	Acetone	56.5	Acetone	72-75	8

No.	Calcd.		Analysis, %	
	C	H	C	H
1	71.37	9.59	70.97, 71.20	10.16, 10.31
2
3	72.47	9.96	72.02, 72.07	10.58, 10.51
4	73.41	10.27	73.10, 72.75	11.08, 10.92
5	75.56	11.00	75.29, 75.67	11.09, 11.40
6	72.47	9.96	72.57, 72.37	10.25, 9.97

Summary

1. A comparison has been made of the tendency of saturated, chloro-saturated and unsaturated aldehydes to form acetals of dipropenyl glycol.

2. The saturated aliphatic carbonyl derivatives, acetaldehyde, paraldehyde, propionaldehyde, butyraldehyde, heptaldehyde and acetone showed a marked tendency to form acetals with yields of 90, 83, 90, 92, 85 and 71%, respectively, indicating that the length of the hydrocarbon chain of the carbonyl compound has practically no effect on the yield. The saturated chloro derivative, chloral, does not give an acetal as a product. The acetal of benzaldehyde was not formed under the conditions used.

3. The unsaturated aldehydes, cinnamaldehyde and crotonaldehyde show practically no tendency to form acetals.

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