2. A satisfactory method for control of the nitration of ortho and para cyclohexylphenol, whereby one or two nitro groups may be introduced into the phenolic nucleus, has been developed. Acetyl derivatives of the reduction products of a number of the nitrocyclohexylphenols have been obtained.

3. In the preparation of the ethyl and methyl ethers of dinitro-*p*-cyclohexylphenol it is probable that aci-ethers are formed which subsequently rearrange to give the true ethers. Undoubtedly some hydrolysis of these aci-ethers also takes place during the reaction with liberation of the free dinitro-*p*-cyclohexylphenol.

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Researches in Cyclic Acetals. II. Formation of Cyclic Acetals of 4,5-Dihydroxy-2,6-octadiene

BY C. PAULINE BURT, D. R. CORCORAN AND I. V. KOERBER

In an earlier paper the tendencies of certain aldehydes to form cyclic acetals with 4,5-dihydroxy-2,6-octadiene (dipropenyl glycol), $CH_3CH{=}CH CHOHCHOHCH{=}CHCH_3$ were reported.[1] It was shown that the saturated unsubstituted aliphatic aldehydes showed a marked tendency to form cyclic acetals while certain unsaturated aldehydes, halogen substituted aldehydes and benzaldehyde did not show such a tendency. These observations were in accordance with those of Hibbert and coworkers,[2] who found that unsaturation in the aldehyde residue lowered the tendency of formation of cyclic acetals of ethylene glycol.

This present investigation is an extension of the work by Burt and Howland using longer chain aldehydes, aldehydes with benzene nuclei and ketones. The saturated aliphatic aldehydes such as isobutyraldehyde, valerylaldehyde, and isovalerylaldehyde formed acetals with yields of 86, 65 and 77%, respectively. The saturated ketones did not all form ketals as readily, for while acetone had given the ketal in 71% yield and diethyl ketone gave a yield of 55%, neither[1] the methyl hexyl ketone nor pinacoline gave ketal products. Unsaturated aldehydes and ketones in both the aliphatic and aromatic series did not form acetals or ketals. No products could be isolated when methylheptenone, citral, benzylidene-acetophenone, benzylidene-acetone, acetophenone, benzophenone, *p*-tolylbenzophenone, *o*-chlorobenzaldehyde, *o*-nitrobenzaldehyde, salicylaldehyde or anisaldehyde were used. When, however, β-phenylpropionaldehyde (hydrocinnamaldehyde) was used, the acetal was formed with a 79% yield. In

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[1] Burt and Howland, THIS JOURNAL, **52**, 217 (1930).

[2] Hibbert, Houghton and Taylor, *ibid.*, **51**, 611 (1929).

this case the phenyl group was not directly attached to the reacting carbonyl group. It therefore may be said that saturated aldehydes and ketones tend to form cyclic acetals of dipropenyl glycol but that the presence of unsaturated groups or phenyl groups in the aldehyde or ketone seem to inhibit this tendency. The exception to this observation was in the case of the hydrocinnamaldehyde where the phenyl group being in the beta position had apparently lost its inhibiting effect. The densities, molecular weights (determined by the freezing point method using benzene) and the indices of refraction for all of the acetals of dipropenyl glycol which have been made were determined. In all cases the compounds were found to be monomolecular.

Experimental Part

One part of dipropenyl glycol and twice the calculated quantity of the aldehyde or ketone were heated in a wax-bath at about 70° for four hours with 4 to 6 drops of 40% sulfuric acid for each tenth mole of the glycol used. The product obtained was extracted with ether and the acid neutralized with 5% sodium carbonate solution. The product after washing and drying was distilled under reduced pressure. In the cases where the

TABLE OF RESULTS

CONDENSATION PRODUCTS OF DIPROPENYL GLYCOL WITH VARIOUS HYDROCARBON CARBONYL DERIVATIVES

	Carbonyl deriv.	Yield, %	Product B. p., °C.	Press., mm.
1	Isobutyraldehyde	86	101	14
2	Valerylaldehyde	65	110–111	5
3	Isovalerylaldehyde	77	106	4
4	Hydrocinnamaldehyde	79	160–161	4
5	Diethyl ketone	57	100–101	4.5

ANALYSES, %

	Calcd.		Found			
	C	H	C		H	
1	73.42	10.24	72.47	72.47	9.90	9.90
2	74.16	10.54	73.27	73.45	10.51	10.39
3	74.16	10.54	73.94	73.97	10.47	10.57
4	79.01	8.58	78.56	78.55	8.55	8.60
5	74.16	10.54	73.74	73.69	10.36	10.23

PHYSICAL CONSTANTS OF ACETALS AND KETALS OF DIPROPENYL GLYCOL

	Mol. wts. Calcd.	Found		d_4^{20}	n_D^{20}
Acetaldehyde	168	162	168	0.9352	1.4564
Acetone	182	189	185	.9543	1.4492
Propionaldehyde	182	176	179	.9304	1.4558
Butyraldehyde	196	193	193	.9304	1.4555
Isobutyraldehyde	196	189	189	.9409	1.4538
Valerylaldehyde	210	207	206	.9228	1.4570
Isovalerylaldehyde	210	212	217	.9218	1.4529
Heptaldehyde	238	236	233	.9078	1.4592
Hydrocinnamaldehyde	258	251	249	.9996	1.5132
Diethyl ketone	210	209	211	.9237	1.4573
Methyl ethyl ketone	196	198	191	.9270	1.4551

yield was low or acetals did not form, zinc chloride and anhydrous copper sulfate were used as condensing agents instead of sulfuric acid. Neither of these gave products where sulfuric acid had failed.

Summary

1. It has been shown that carbonyl compounds such as isobutyraldehyde, valerylaldehyde, isovalerylaldehyde, hydrocinnamaldehyde, diethyl ketone and methyl ethyl ketone will form acetals of dipropenyl glycol in good yield.

2. Carbonyl compounds such as methyl hexyl ketone, pinacoline, acetophenone, benzophenone, methylheptanone, citral, benzylidene-acetone, benzylidene-acetophenone, *o*-chlorobenzaldehyde, *o*-nitrobenzaldehyde, salicylaldehyde and anisaldehyde gave no acetal or ketal products of dipropenyl glycol.

3. The molecular weights, indices of refraction and densities of all the dipropenyl glycol acetals have been determined and listed.

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Reactions of Certain Halogen Substituted Aryl, Alkyl and Di-alkyl Sulfides with Benzylamine. I

BY THOMAS P. DAWSON[1]

Introduction.—This investigation was undertaken with the object of obtaining further information concerning the reactions of certain halogen substituted aryl, alkyl and di-alkyl sulfides with benzylamine. The work entailed, as the first step, the preparation of a series of halogen substituted sulfides, three of which have not previously been described in the literature, and, as a second step, the reaction of twelve of these sulfides with benzylamine.

Historical Part.—The interaction of bis-(β-chloroethyl) sulfide with primary amines to form compounds of the thiazane type was first shown by Clarke.[2] However, the parent substance, 1,4-thiazane, was prepared by Davies[3] by heating bis-(β-chloroethyl) sulfide with an excess of alcoholic ammonia in a sealed tube at 60°. Helfrich and Reid[4] also studied the reaction and found that bis-(β-chloroethyl) sulfide, sulfoxide, and sulfone react with primary aromatic amines to form aryl derivatives of thiazane and sulfonazane.

The condensation of bis-(β-chloroethyl) sulfide with amino bodies has been advanced by Cashmore and McCombie[5] as a possible explanation

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(1) Technical Divisions, Chemical Warfare Service, Edgewood Arsenal, Md.

(2) Clarke, *J. Chem. Soc.*, **101**, 1583 (1912).

(3) Davies, *ibid.*, **117**, 297 (1920).

(4) Helfrich and Reid, THIS JOURNAL, **42**, 1208 (1920).

(5) Cashmore and McCombie, *J. Chem. Soc.*, **123**, 2884 (1923).