TABLE III

ANALYSES FOR CARBON AND HYDROGEN

Name	Molecular formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
1,5-Dioxaoctahydroindene	$C_7H_{12}O_2$	65.59	65.54	9.44	9.60
α-*n*-Propyltetrahydrofuran	$C_7H_{14}O$	73.63	72.70	12.36	12.41
Tetrahydrofurfural diacetate	$C_9H_{14}O_5$	53.46	53.28	6.98	6.92
1-Tetrahydrofuryl-3-phenylpropane	$C_{13}H_{18}O$	82.15	82.15	9.48	9.37
1-Tetrahydrofuryl-3-cyclohexylpropane	$C_{13}H_{24}O$	79.63	79.45	12.26	12.28

Summary

The conversion of various furan derivatives by hydrogen over nickel or copper chromium oxide to a variety of products has been described. Especially noteworthy was the cyclization of β-furylacrolein or β-furylpropionaldehyde to 1,5-dioxaoctahydroindene.

MADISON, WIS. RECEIVED SEPTEMBER 25, 1933

[A COMMUNICATION FROM THE LABORATORY OF ORGANIC CHEMISTRY, UNIVERSITY OF WISCONSIN]

Structure of Reactants and Extent of Acetal Formation. II[1]

BY RALPH E. DUNBAR AND HOMER ADKINS

Originally it was planned to study the effect of modifications in the structure of aldehydes and alcohols upon acetal formation by determining the concentration of an aldehyde at equilibrium with "representative" alcohols, or of alcohols with "representative" aldehydes. The necessity for such a limitation upon the number of reaction mixtures to be studied is obvious when it is noted that 680 acetals might be prepared from the 34 alcohols and 20 aldehydes that so far have been investigated for acetal formation in this Laboratory. Actually 108 of these reactions have been followed and it is not yet certain which are the "representative" aldehydes and alcohols that will best serve as standards for comparison. However, it appears that for present purposes the extent of reaction of the straight chain unsubstituted aldehydes and alcohols with each other may be regarded as the standard; *e. g.*, the average percentage conversion in eight cases of 5 moles of ethyl, propyl, butyl, pentyl or heptyl alcohol with 1 mole of acetaldehyde, propionaldehyde, butyraldehyde or heptaldehyde was 80%. Similarly, for 8 acetals formed from the secondary alcohols propanol-2, butanol-2, pentanol-2 and octanol-2 the percentage conversion at equilibrium was 46%.

The experimental results summarized in Table I are concerned primarily with the behavior of hexahydrobenzaldehyde, cyclopentylaldehyde and trimethylacetaldehyde. Attention was directed

TABLE I

EXTENT OF REACTION OF VARIOUS ALCOHOLS AND ALDEHYDES

Alcohol	(11 alc. to 1 ald.) % conv.	(11 alc. to 1 ald.) *K*	(5 alc. to 1 ald.) % conv.	(5 alc. to 1 ald.) *K*
Hexahydrobenzaldehyde				
Methanol	98	6.48	93	6.35
Tetrahydrofurfuryl	..	...	92	5.38
3-Tetrahydrofurylpropanol-1	..	...	91	4.63
Isoamyl	..	...	88	3.15
Cyclohexylcarbinol	..	...	87	2.75
Butanol-1	..	...	80[a]	1.44
Ethanol	91	1.21	78[a]	1.22
Cyclohexanol	88	0.84	75	0.96
Octanol-2	..	...	74	.88
Cyclopentanol	60	.107	44	.101
Propanol-2	43	.037	29	.035
Benzaldehyde				
Cyclohexylcarbinol	..	...	35	.059
Cyclohexanol	35	.021	23	.019
Trimethylacetaldehyde				
Ethanol	73	.25	56[b]	...
Cyclohexylcarbinol	58	.095	42[b]	...
Octanol-2	38	.026	26[b]	...
Cyclohexanol	24	.007	16[b]	...
Propanol-2	21	.006	11[b]	...
Cyclopentylaldehyde				
Octanol-2	..	...	50	.168
Ethanol	61	.114	45	.122
Cyclohexylcarbinol	..	...	41	.092
Cyclohexanol	..	...	35	.056
Propanol-2	19	.005	13[b]	...

[a] This value was duplicated by the hydrolysis of the acetal. [b] This value was calculated from the value of *K* obtained from the percentage conversion at the 11 to 1 ratio of reactants.

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(1) The previous paper of the same title [Minné and Adkins, THIS JOURNAL, **55**, 299 (1933)] gives leading references to earlier papers.

particularly to the behavior of these aldehydes with ethanol, cyclohexylcarbinol, cyclohexanol, propanol-2 and octanol-2. Ethanol and propanol-2 were selected for this purpose because with the simple aldehydes they have been found to be representative of a considerable number of alcohols. The other alcohols were chosen because they have sometimes given anomalous results. In order to bring out the similarities and differences of these five alcohols in their reaction with eight aldehydes there are presented in Table II figures which indicate the divergence, if any, between the observed percentage conversion to acetals and the percentage which would be expected if the alcohols and aldehydes were straight chain compounds.

TABLE II

COMPARISONS IN ACETAL FORMATION[a]

The * figures are from data previously published

Aldehyde	Ethanol	Cyclohexyl carbinol	Cyclohexanol	Propanol-2	Octanol-2
Acet-	− 2*	−24*	+10*	− 3*	0*
Dimethylacet-	− 9*	−38*	..	−23*	..
Trimethylacet-	−24	−38	−30	−35	−20
Cyclopentyl-	−35	−39	−11	−33	+ 4
Benz-	−41*	−45	−23	−32*	+ 3*
Hexahydrobenz-	− 2	+ 7	+29	−17	+28
Furfur-	−49*	..	..	−29*	−35*
Tetrahydrofurfur-	− 1*	..	+42*	+ 3*	+44*

[a] The figures given in the table are obtained by subtracting 80 (primary alcohols) or 46 (secondary alcohols) from the percentage conversion to the acetal of 5 moles of alcohol and 1 mole of aldehyde.

The figures for acetaldehyde, dimethylacetaldehyde and trimethylacetaldehyde show a progressive lowering of the extent of conversion to acetals. There is thus evident the marked effect of branching, or carbon substitution on the α carbon atom, upon lowering affinity for acetal formation.[2]

Cyclopentylaldehyde is rather similar to trimethylacetaldehyde in its affinity for acetal formation despite the fact that with respect to carbon substitution on the α carbon atom of the aldehyde it is structurally similar to dimethylacetaldehyde. It is even more nearly like benzaldehyde in acetal formation despite the difference in degree of saturation.

The relationship of hexahydrobenzaldehyde to benzaldehyde in acetal formation is very much the same as that found by Minné for tetrahydrofurfural and furfural, *i. e.*, the saturated compounds have a much higher affinity for acetal formation than the unsaturated and in fact are similar to the straight chain compounds of similar carbon content.

The fact emerges then that the two multiplanar cyclic aldehydes, tetrahydrofurfural and hexahydrobenzaldehyde, despite branching at the α carbon atom, have a high affinity for acetal formation, while the monoplanar cyclopentylaldehyde has a low affinity value which is similar to two unsaturated monoplanar cyclic aldehydes furfural and benzaldehyde and to the highly branched trimethylacetaldehyde.

In connection with the alcohols the most striking "abnormality" is the high affinity (actual or relative) which the two secondary alcohols, cyclohexanol and octanol-2, show with the cyclic aldehydes. This is to be contrasted with the fact that cyclopentanol behaved toward hexahydrobenzaldehyde as would a simple secondary alcohol. Thus there appears to be a fundamental difference between the influence of the cyclopentyl and the cyclohexyl group upon acetal formation irrespective of whether the cycle is in the aldehyde or the alcohol.[3]

Hexahydrobenzaldehyde, cyclopentylaldehyde and trimethylacetaldehyde were prepared by the dehydrogenation of the corresponding carbinols over copper–chromium oxide.[4] Cyclohexyl and *tert*-butylcarbinols were made by the hydrogenation of ethyl hexahydrobenzoate or ethyl trimethylacetate[5] and also by the Grignard reaction from cyclohexyl or *tert*-butylmagnesium bromide and formaldehyde.[6] Cyclopentylcarbinol was made by the series of transformations: cyclohexanol ⟶ adipic acid ⟶ cyclopentanone ⟶ cyclopentanol ⟶ cyclopentyl chloride ⟶ cyclopentylmagnesium chloride ⟶ cyclopentylcarbinol. We are indebted to Dr. D. W. MacCorquodale for carrying out the synthesis as far

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(2) As has been noted,[1] cyclohexylcarbinol and cyclohexanol are abnormal with acetaldehyde; *i. e.*, the former gives a lower and the latter alcohol a higher value than would be expected of a primary and secondary alcohol, respectively.

(3) It is perhaps obvious that one method of rationalizing the high affinity of octanol-2 and cyclohexanol with the cyclic aldehydes is to assume that steric hindrance slows down the rate of hydrolysis more than it does the rate of synthesis. The concentrations at equilibrium are determined by the concentration of reactants at which the two rates are equal, so that slowing down the rate of hydrolysis would raise the percentage conversion at equilibrium. A similar "explanation" could be made for the variation in affinity for acetal formation, manifested by stereoisomeric methylcyclohexanols.

(4) Adkins, Kommes, Struss and Dasler, THIS JOURNAL, **55**, 2992 (1933).

(5) Folkers and Adkins, *ibid.*, **54**, 1146 (1932).

(6) Gilman and Catlin, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, New York, 1932, p. 182.

TABLE III

PHYSICAL CONSTANTS AND ANALYTICAL DATA

Compound, acetal of	B. p., °C.	d^{25}_4	n_D	M_D		C, %		H, %	
				Calcd.	Found	Calcd.	Found	Calcd.	Found
Methanol and hexahydrobenzaldehyde	183 (753 mm.), 63 (25 mm.)	0.9363	1.4402	44.79	44.51	68.29	68.33	11.47	11.37
Ethanol and hexahydrobenzaldehyde	115–117 (20 mm.), 94–95 (12 mm.)	.9021	1.4399	54.00	54.38	70.90	70.71	11.91	11.96
n-Butanol and hexahydrobenzaldehyde	149–150 (22 mm.), 134–136 (8 mm.)	.8893	1.4439	72.41	72.34	74.31	74.25	12.48	12.43
Isoamyl alcohol and hexahydrobenzaldehyde	168–169 (8 mm.)	.8781	1.4456	81.62	82.00	75.48	75.36	12.68	12.59
Octanol-2 and hexahydrobenzaldehyde	215–217 (8 mm.)	.8701	1.4475	109.24	108.89	77.89	77.94	13.08	13.18
γ - Tetrahydrofurfurylpropyl alcohol and hexahydrobenzaldehyde	236–238 (10 mm.)	.9821	1.4620	99.19	99.18	71.12	71.02	10.81	10.95
Cyclohexanol and hexahydrobenzaldehyde	202–203 (20 mm.)	.9589	1.4782	86.62	86.88	77.49	77.08	11.63	11.67
Cyclohexylcarbinol and hexahydrobenzaldehyde	234–235 (20 mm.)	.9689	1.4887	95.83	95.95	78.19	78.00	11.88	11.90
Ethanol and trimethylacetaldehyde	146–148 (742 mm.)	.8192	1.3942	46.90	46.88	67.43	67.45	12.59	12.62
Cyclohexylcarbinol and trimethylacetaldehyde	194–195 (22 mm.)	.9235	1.4635	88.72	88.45	76.95	76.78	12.25	12.19
Hexahydrobenzaldehyde[a]	70.5–72 (33 mm.)	.9235	1.4506	32.40	32.65				
Trimethylacetaldehyde[b]	74–75 (740 mm.)								
Cyclopentylaldehyde[c]	62–64 (27 mm.)	.9356	1.4435	27.72	27.79				

[a] M. p. of semicarbazone 166° (uncorr.). [b] M. p. of semicarbazone 189° (uncorr.). Tissier, *Bull. soc. chim.*, [3] **5**, 835 (1891); Bouveault, *ibid.*, [3] **15**, 1020 (1896). [c] M. p. of 2,4-dinitrophenylhydrazine 158.7°; Nametkin and Rushenzowa, *Chem. Zentr.*, **86**, I, 1111 (1915).

as cyclopentanol. The concentration at equilibrium of hexahydrobenzaldehyde and cyclopentylaldehyde was determined by the sodium sulfite method. Trimethylacetaldehyde and benzaldehyde were determined by the hydrogen peroxide method.

All attempts to form an acetal through the reaction of hexahydrobenzaldehyde and *tert*-butyl alcohol in the presence of hydrogen chloride failed because of the polymerization of the aldehyde. The polymer (m. p. 195–196°) had a molecular weight by Rast's method[7] of 219 while that for the dimer is 224. Polymerization also occurred in propanol-2 when the concentration of hydrogen chloride was 0.023 g. per mole of alcohol but with a lower concentration (0.01 g.) the acetal reaction proceeded smoothly without the separation of the very insoluble polymer.

The higher concentration of catalyst (0.023 g.) used in this investigation as compared with that used by Minné (0.0005 g.) is necessary at least with hexahydrobenzaldehyde in order to attain equilibrium conditions within a reasonable time; in fact the lower concentration of catalyst produced no appreciable reaction with hexahydrobenzaldehyde even after many days.

Summary

The concentration of aldehyde at equilibrium in the reaction of various alcohols with trimethyl-, cyclopentyl-, hexahydrobenz- and benzaldehydes has been determined and the data discussed with respect to unsaturation and branched cyclic chains.

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RECEIVED SEPTEMBER 28, 1933

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(7) Emich, "Microchemical Laboratory Manual," John Wiley and Sons, Inc., New York, 1932, p. 138.