The **semicarbazone** was prepared in aqueous ethanol and then recrystallized from methanol; m.p. 214.9–215.9° (cor.).

Anal. Calcd. for $C_{15}H_{21}N_3O_3$: C, 61.83; H, 7.27; N, 14.45. Found: C, 62.01; H, 7.43; N, 14.45.

The eluate fractions contained 35 to 65% benzene, were concentrated individually to give oily material, which were bulked, dissolved in ethanol and treated with 12 g. of semicarbazide hydrochloride and 18 g. of sodium acetate. Water was added until practically no solid remained and the solution was then heated at gentle reflux for two hours. At the end of the heating period crystals began to appear. The solution was cooled and filtered. The dried substance weighed 8.01 g. and melted at 178–184°. After recrystallization from methanol there was obtained 6.29 g. of white crystals, m.p. 185–186.4° (cor.). This was the **semicarbazone of 1,4-dimethoxy-5-methyl-6-tetralone**.

Anal. Calcd. for $C_{14}H_{19}N_3O_3$: C, 60.63; H, 6.91; N, 15.15. Found: C, 60.79; H, 7.01; N, 15.27.

A mixture of the semicarbazones of the monomethyl- and dimethyltetralones melted at 172–180°.

1,4-Dimethoxy-5-methyl-6-tetralone from the corresponding Semicarbazone.—The above semicarbazone (6.25 g.) was gently warmed with 15 ml. of acetic acid until solution was complete. The solution was diluted with 10 ml. of water and 3 g. of redistilled pyruvic acid in 5 ml. of water was added. The whole was refluxed one-half hour and then was diluted with 15 ml. of water. An oil separated and when the mixture was cooled a crystalline solid, presumably pyruvic acid semicarbazone, separated also. The mixture was extracted twice with ether and the combined oil layers were washed with sodium bicarbonate solution and then with water. The ether solution was dried and distilled. After removal of the volatile solvent the residue boiled at 128–130° (0.3 mm.). The 1,4-dimethoxy-5-methyltetralone could not be induced to crystallize.

Anal. Calcd. for $C_{13}H_{16}O_3$: C, 70.89; H, 7.32. Found: C, 70.80; H, 7.38.

RENSSELAER, N. Y.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Ring-Chain Tautomerism of Hydroxy Aldehydes

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A study of the ultraviolet absorption spectra of some simple ω-hydroxy aldehydes has disclosed that in aqueous dioxane 4-hydroxybutanal and 5-hydroxypentanal exist predominantly as the cyclic hemiacetals, containing an estimated 11.4 and 6.1%, respectively, of free aldehyde at 25°. The higher members studied exist as 80–90% free aldehyde. These values were obtained by comparing the extinction coefficients at the carbonyl maximum with those of the corresponding ω-methoxy aldehydes. A number of hydroxy and methoxy aldehydes not previously reported in the literature were prepared, some of these by a new synthetic procedure involving a cyclic acyloin as the starting material.

The position of equilibrium of acyclic ⇄ cyclic forms of hydroxy aldehydes has been qualitatively known to be essentially at the acyclic stage for β-hydroxy aldehydes[1] (aldols) and at the cyclic stage for γ- and δ-hydroxy aldehydes. The latter includes aldoses[2] as well as simple hydroxy aldehydes.[3] There is evidence for cyclization also with 9-hydroxynonanal and 4-methyl-6-hydroxyhexanal.[4]

Quantitative approaches to this problem have been surprisingly few. These include "instantaneous" combination with hydrogen cyanide,[5] reduction of the acyclic form at the dropping mercury electrode,[6] and absorption spectra. Solutions of glucose do not show a maximum in the carbonyl band region of the ultraviolet[7] except under strongly acid conditions, presumably because of the very small quantity of free aldehyde present. 5-Hydroxypentanal,[8] however, shows a maximum at 290 mμ and from the intensity of this band it was estimated that the equilibrium mixture contained about 5% of free aldehyde.

It seemed reasonable to suppose that this approach would be capable of further refinement and extension to other simple hydroxy aldehydes. With this in mind, a study of the ultraviolet absorption of a number of simple ω-hydroxy aldehydes was undertaken. The corresponding ω-methoxy aldehydes were chosen as standards, it being assumed that they would show essentially the same carbonyl absorption as would the hydroxy aldehydes if they were entirely in the open-chain form. The ω-hydroxy and ω-methoxy aldehydes prepared were those having 4, 5, 6, 8, 9 and 10 carbon atoms between the carbonyl oxygen and the hydroxy (or methoxy) group. Of these, 4-hydroxybutanal, 5-hydroxypentanal, 9-hydroxynonanal, 4-methoxybutanal and 5-methoxypentanal were compounds known prior to this investigation.

Ozonolysis of 4-penten-1-ol and 9-octadecen-1-ol according to the directions of Helferich and Schäfer[4] yielded 4-hydroxybutanal and 9-hydroxynonanal, respectively. Methylation, then ozonolysis of the resulting unsaturated ethers gave rise to 4-methoxybutanal and 9-methoxynonanal. The same approach was used in the preparation of 10-hydroxy- and 10-methoxydecanal, 10-undecen-1-ol being the starting material.

5-Hydroxypentanal was synthesized from dihydropyran.[8] A synthesis of 5-methoxypentanal was devised to replace the previous method, ozonolysis of the difficulty obtainable 6-methoxy-1-hexene.[9] Mercaptalation[10] of 5-hydroxypentanal to

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(1) C. D. Hurd and J. L. Abernethy, THIS JOURNAL, **63**, 1966 (1941).

(2) W. W. Pigman and R. M. Goepp. "Chemistry of the Carbohydrates," Academic Press, Inc., New York, N. Y., 1940, Chapter II.

(3) B. Helferich and co-workers, *Ber.*, **52**, 1123, 1800 (1919); **54**, 930, 2640 (1921); **55**, 702 (1922); **56**, 2088 (1923).

(4) B. Helferich and W. Schäfer, *ibid.*, **57**, 1911 (1924); B. Helferich and G. Sparmberg, *ibid.*, **64**, 104 (1931).

(5) F. Lippich, *Biochem. Z.*, **248**, 280 (1932).

(6) S. M. Cantor and Q. P. Peniston, THIS JOURNAL, **62**, 2113 (1940); P. Delahay and J. E. Strassner, *ibid.*, **74**, 893 (1952).

(7) E. Pacsu and L. A. Hiller, *ibid.*, **70**, 523 (1948).

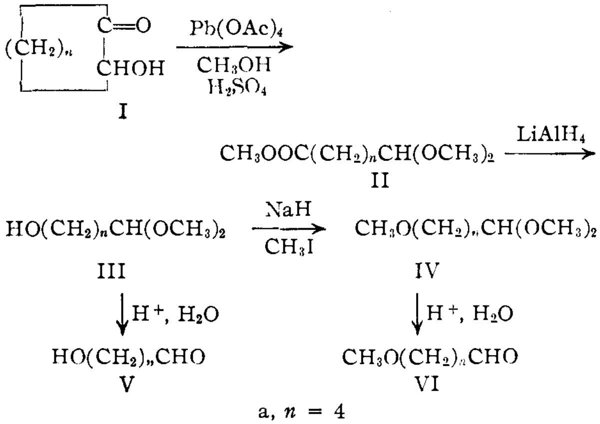
(8) L. E. Schniepp and H. H. Geller, *ibid.*, **68**, 1646 (1946).

(9) R. Pummerer and M. Schonamsgruber, *Ber.*, **72**, 1834 (1939).

(10) This sequence of reactions was adapted from procedures for the preparation of open-chain aldose derivatives. See E. Fischer, *ibid.*, **27**, 647 (1894); P. A. Levene and G. M. Meyer, *J. Biol. Chem.*, **69**, 175 (1926); M. L. Wolfrom, THIS JOURNAL, **51**, 2188 (1929).

5-hydroxyvaleraldehyde ethyl mercaptal, then methylation, yielded 5-methoxyvaleraldehyde ethyl mercaptal which was converted readily to 5-methoxypentanal.

The remaining two pairs of the series were prepared by a new synthesis starting with the cyclic acyloin possessing the same number of carbon atoms as the desired product. The cyclic acyloin Ia (adipoin) was obtained by hydrolysis of 2-chlorocyclohexanone[11] while suberoin, Ib, was produced by the action of metallic sodium on methyl suberate in boiling xylene according to the general procedure of Prelog.[12] The acetal-esters IIa and IIb were obtained by treating methanolic solutions of the acyloins with lead tetraacetate[13] followed by addition of sulfuric acid to catalyze the reaction of the aldehydic acids with methanol. IIb was contaminated with a yellow liquid, presumably 1,2-cyclooöctanedione carried over from the impure Ib. The reduction and methylation steps proceeded smoothly but some difficulty was encountered in the acid hydrolysis of the hydroxy acetals IIIa and IIIb, since the acid promoted formation of condensation products by the hydroxy aldehydes Va and Vb. Even under the very mild conditions of treatment with cold saturated tartaric acid solution,[14] IIIb gave only a 37% yield of Vb along with a higher-boiling residue. This tendency to form condensation products was much less troublesome in the preparation of the methoxy aldehydes VIa and VIb.



a, $n = 4$
b, $n = 6$

The hydroxy aldehydes of six carbons and more were waxy solids insoluble in all common solvents in the cold but soluble in many on heating. Their dual nature is reflected in rather indefinite and variable melting points. The most striking example is 6-hydroxyhexanal, whose melting point ranged from 57 to 86° and varied with the age of the sample and the rate of heating.

In choosing a solvent for the spectrophotometric measurements on the hydroxy aldehydes, it was hoped that an inert solvent could be used so that there would be no uncertainties in results due to interaction of compound and solvent. Dioxane was the first tried, but a satisfactory equilibrium could not be established in this medium. The solvents finally chosen were 95% ethanol and a 3:1 mixture of dioxane and water, in both of which satisfactory equilibration occurred within a few days. The methoxy aldehydes underwent extensive interaction with the former, presumably hemiacetal formation,[15] so that no comparison could be made in alcohol. In the dioxane–water mixture such interactions appeared to be quite small and a comparison could be made. The failure to attain equilibrium in inert solvents is probably associated with the necessity of having some medium which will effect the transfer of a proton from the hydroxyl group to the carbonyl oxygen in the ring closure and effect the reverse process in the ring opening.[16]

Solutions of the hydroxy and methoxy aldehydes were measured in 75% dioxane, the measurements on the hydroxy aldehydes being made at 25 and 35°. From the extinction coefficients the percentage of free aldehyde was estimated as in the following example: 4-methoxybutanal had ϵ 17.4 and 4-hydroxybutanal had ϵ 1.99 at 25°, from which the percentage of free aldehyde at 25° is 11.4 (1.99/17.4 × 100). These results are recorded in Table I, the extinction coefficients of the hydroxy aldehydes in both 75% dioxane and in 95% ethanol being included for convenient comparison. No suitable solvent could be found for measurements on 10-hydroxydecanal. The diffuse and irreproducible maxima shown by this compound in various solvents suggest that it tends to exist as a colloid rather than as a true solution.

For an equilibrium between cyclic and acyclic structures, one would expect the two main factors influencing the position of the equilibrium to be the probability of ring formation and the amount of strain in the resulting ring.[17] The greater stability of the six-membered ring as compared to the five-membered ring is as expected, since the former is highly stable in the preferred chair form, while the latter is under considerable strain arising from hydrogen–hydrogen repulsions.[18] This order is also in accord with the observation that the pyranose structure is almost invariably favored in simple sugars.[2] There is much evidence that strain is also present in the medium-size rings, such strain being ascribed chiefly to hydrogen–hydrogen repulsions in the unfavorable constellations required by the geometry of these rings.[18,19] Since both the ring strain and probability factors favor the open-chain form beyond the six-membered ring, a large increase in free aldehyde from 5-hydroxypentanal

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(11) A. Kötz, K. Blendermann, R. Rosenbusch and E. Sirringhaus, *Ann.*, **400**, 62 (1913).

(12) V. Prelog, L. Frenkiel, M. Kobelt and P. Barman, *Helv. Chim. Acta*, **30**, 1741 (1947).

(13) E. Baer, THIS JOURNAL, **64**, 1416 (1942), has reported the cleavage of some cyclic acyloins, including Ia, with lead tetraacetate in acetic acid.

(14) O. Fischer and K. Löwenberg, *Ann.*, **494**, 272 (1932).

(15) A. M. Buswell, E. C. Dunlop, W. H. Rodebush and J. B. Swartz, THIS JOURNAL, **62**, 325 (1940).

(16) E. R. Alexander, "Principles of Ionic Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1950, pp. 159–160.

(17) L. Ruzicka, W. Brugger, M. Pfeiffer, H. Schinz and M. Stoll, *Helv. Chim. Acta*, **9**, 499 (1926), postulate these same factors to explain the variation in yields of cyclic ketones from the pyrolysis of salts of dicarboxylic acids.

(18) H. C. Brown, R. S. Fletcher and R. Johannesen, THIS JOURNAL, **73**, 212 (1951). See also K. Pitzer, *Science*, **101**, 672 (1945).

(19) V. Prelog, *J. Chem. Soc.*, 424 (1950); Abstracts of Papers presented at American Chemical Society Meeting, New York, N. Y., September, 1951.

TABLE I

$$HO(CH_2)_nCHO \rightleftharpoons \overline{O(CH_2)_nC}HOH$$

	Free aldehyde^a (in 75% dioxane), %		Extinction coefficients^a In 75% dioxane				In 95% ethanol			
n	At 25°	At 35°	Concn.^{b}	mμ	$\epsilon_{25°}$	$\epsilon_{35°}$	Concn.^{b}	mμ	$\epsilon_{25°}$	$\epsilon_{35°}$
3	11.4	13.4	0.141	286	1.99	2.34	0.203	286	1.00	1.24
4	6.1	6.8	.222	287	1.17	1.30	.415	285	0.42	0.57
5	85	89	.0308	288	16.6	17.2	.0404	286	3.44	4.43
7	80	^{c}	.0140	289	16.1	^{c}	.0191	287	4.08	5.08
8	91	^{c}	.0178	288	19.1	^{c}	.0175	284	6.52	7.20^d
			$CH_3O(CH_2)_nCHO$							
3			0.0367	286	17.4^e					
4			.0383	288	19.2					
5			.0257	289	19.4					
7			.0209	289	20.1					
8			.0361	287	21.1					
9			.0208	290	21.6					

[a] Though most values are given to three significant figures, the actual precision is in most observations ±2 to 3%. [b] In moles per liter. [c] No appreciable temperature effect. [d] Measurement at 30°. [e] Measurements made on freshly distilled samples because of sensitivity to oxidation by air. No temperature control was used, since the absorption was found to be quite insensitive to temperature.

to 6-hydroxyhexanal is to be anticipated, though the great magnitude of the change is somewhat surprising. The reversal of the order between 6-hydroxyhexanal and 8-hydroxyoctanal in 75% dioxane would not be predicted, and may be caused by an error or failure to attain true equilibrium, although repeated runs yielded essentially the same results. It will be noted that the expected order is observed in 95% ethanol. The more gradual increase in free aldehyde with chain length (as measured by the extinction coefficients) observed in 95% ethanol probably is the result of a greater variation in solvent interaction with the aldehydic form rather than any large solvent effect on the equilibrium itself.

It might be pointed out that this method is less capable of giving good results on the higher members, since the values are much more closely spaced and hence the same relative error could cause a more significant variation in percentage of free aldehyde. Uncertainties as to the solvent interactions preclude any detailed thermodynamic analysis of the results of these studies, since more than one equilibrium is involved. The possibility of some intermolecular hemiacetal formation by the hydroxy aldehyde should also be mentioned. However, the fact that measurements were made in rather dilute solutions in hydroxylic media makes it probable that this reaction is negligible, particularly in comparison with the reaction between aldehyde and solvent. In spite of these difficulties, this approach still seems capable of yielding valuable semi-quantitative information where relatively large differences are involved and the percentage of free aldehyde is neither very small nor very large.

Experimental

5-Hydroxypentanal was prepared according to the directions of Schniepp and Geller.[8] From 50 g. of dihydropyran there was obtained 29 g. (48%) of 5-hydroxypentanal, b.p. 83–88° (15 mm.). Redistillation yielded a sample of b.p. 81° (12 mm.), $n^{20}D$ 1.4530 (lit. $n^{25}D$ 1.4514).[8]

5-Hydroxyvaleraldehyde Ethyl Mercaptal.—To a solution of 10.2 g. (0.1 mole) of 5-hydroxypentanal in 20 ml. of 8 *N* hydrochloric acid was added, while shaking and cooling the flask, 13.6 g. (0.22 mole) of ethyl mercaptan. The flask was stoppered and shaken at intervals for one hour. The mixture was then extracted with three 15-ml. portions of ether, the extracts washed successively with 20 ml. of 5% sodium hydroxide and 20 ml. of saturated sodium chloride, and dried over sodium sulfate. Removal of the ether and vacuum distillation of the residue yielded 18.8 g. (90%) of the desired mercaptal, b.p. 153–158° (8 mm.). An analytical sample had b.p. 110° (0.5 mm.), $n^{20}D$ 1.5177.

Anal. Calcd. for $C_9H_{20}OS_2$: C, 51.87; H, 9.67. Found: C, 51.59; H, 9.65.

5-Methoxypentanal.—A solution of 9.0 g. of 5-methoxyvaleraldehyde ethyl mercaptal in a mixture of 10 cc. of water and 40 cc. of acetone was placed in a 200-cc., 3-neck, r.b. flask fitted with sealed stirrer, reflux condenser and dropping funnel. There was added 20 g. of cadmium carbonate and through the dropping funnel, with stirring, was added a solution of 27 g. of mercuric chloride in 30 cc. of acetone during 15 minutes. After 24 hours of stirring, the solid matter was separated and washed thrice with acetone. The filtrate and washings were combined and heated under reduced pressure at 40–50° to remove most of the acetone. The resulting water solution of the product was extracted with four 30-cc. portions of ether, some separation of solid occurring during this process. After drying over sodium sulfate, the product was distilled under reduced pressure. The material darkened as the distillation proceeded, but the product came over clear and colorless.

There was obtained 2.5 g. (53%) of material boiling at 81–83° (40 mm.). Redistillation yielded a center cut of b.p. 67° (20 mm.), $n^{20}D$ 1.4159 (lit.[9] b.p. 59° (14.5 mm.), $n^{20}D$ 1.4162).

2-Hydroxycyclohexanone (Adipoin).—This was obtained in 48% yield by hydrolysis of 2-chlorocyclohexanone[20] as directed by Kötz, *et al.*[11] The colorless crude product was used without further purification.

Methyl 6,6-Dimethoxyhexanoate.—To a solution of 20 g. of 2-hydroxycyclohexanone in 200 cc. of methanol there was added, with shaking and cooling, small portions of lead tetraacetate until a slight molar excess persisted for ten minutes, as shown by starch–iodide paper. This required about 80 g. of the tetraacetate. The excess was then destroyed by the addition of a few drops of glycerol and a solution of 32 g. of concd. sulfuric acid in 80 cc. of methanol was added.

After the mixture had stood in a stoppered flask for two days, lead sulfate was removed by suction filtration through celite and washed with three 25-cc. portions of methanol. The filtrate and washings were combined and poured, with vigorous stirring, into 300 cc. of 30% sodium carbonate solution. Some solid separated which was separated. The clear solution was extracted with four 200-cc. portions of ether and the combined extracts washed with 100 cc. of water. After drying over sodium sulfate, the ether and re-

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(20) M. S. Newman, M. D. Farbman and H. Hipsher, *Org. Syntheses*, **25**, 22 (1945).

TABLE II

RESULTS OF METHYLATION REACTIONS

Name	Yield, %	B.p., °C.	Mm.	n^{20}D	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
5-Methoxy-1-pentene[a]	71	96	750	1.4027	...	...	...	...
5-Methoxyvaleraldehyde ethyl mercaptal	73	140–145	10	....				
		89	0.6	1.4959	54.00	54.00	9.97	10.04
1,1,6-Trimethoxyhexane	73	101–104	19	....				
		96	13	1.4189	61.33	61.39	11.44	11.14
1,1,8-Trimethoxyoctane	89	95–98	3.6	1.4258[b]	64.66	64.83	11.84	11.66
1-Methoxy-9-octadecene	80	135–145	0.8	....	...	[c]	...	
11-Methoxy-1-undecene	78	115–120	18	....				
		89	2.8	1.4342	78.19	77.91	13.13	13.30

[a] Lit.[3] gives b.p. 96–98°, n^{17}D 1.4032. [b] At 21.5°. [c] Unsatisfactory analysis even after redistillation, but ozonolysis of this material was satisfactory.

maining methanol were distilled off. A small amount of water always separated at this point and had to be removed and extracted once or twice with ether. The ether extracts were again dried and the ether removed.

Vacuum distillation of the residue yielded 21.7 g. (65%) of a colorless liquid of b.p. 79–83° (1.8 mm.). A portion of this was redistilled through a 7-cm. vacuum-jacketed Vigreux column to yield a liquid of b.p. 83° (2.2 mm.), n^{20}D 1.4262.

Anal. Calcd. for $C_9H_{18}O_4$: C, 56.84; H, 9.54. Found: C, 56.93; H, 9.36.

6,6-Dimethoxy-1-hexanol.—A solution of 21.3 g. of methyl 6,6-dimethoxyhexanoate in 30 ml. of dry ether was added with stirring over 1.5 hours to 3.0 g. of lithium aluminum hydride in 100 ml. of dry ether, taking the usual precautions for exclusion of moisture. The processing followed the procedure of Amundsen and Nelson.[21] A yield of 16.5 g. (91%) of 6,6-dimethoxy-1-hexanol, b.p. 83–88° (0.9 mm.), was obtained. Redistillation gave an analytical sample of b.p. 84° (1.0 mm.), n^{20}D 1.4358.

Anal. Calcd. for $C_8H_{18}O_3$: C, 59.24; H, 11.18. Found: C, 59.33; H, 11.14.

6-Hydroxyhexanal.—Ten grams of 6,6-dimethoxy-1-hexanol and 15 ml. of 1:10 hydrochloric acid were mixed and warmed gently on the steam-bath for ten minutes. The solution was made weakly alkaline (*p*H 7–8) by the addition of solid potassium carbonate, saturated with sodium chloride and extracted with five 10-ml. portions of ether. The ether solution was dried over magnesium sulfate, the ether removed and the residue distilled *in vacuo* to yield 3.7 g. (52%) of 6-hydroxyhexanal, b.p. 72–77° (0.9 mm.). A center cut of b.p. 73° (0.9 mm.) was analyzed. Both fractions solidified on standing.

Anal. Calcd. for $C_6H_{12}O_2$: C, 62.03; H, 10.42. Found: C, 61.65; H, 10.39.

Melting points of the solidified product ranged from 57–86° for different runs, increasing with the age of the sample, and generally covered about a 10° range unless the temperature was raised very slowly. The solid was insoluble in all common solvents at room temperature. Although it dissolved in a variety of solvents on heating, it separated with reluctance on cooling and no suitable medium for recrystallization could be found. A Rast molecular weight determination in camphor gave values of 115 and 119, as compared to 116 calculated for $C_6H_{12}O_2$.

6-Methoxyhexanal.—The same hydrolytic and processing procedures were applied as for 6-hydroxyhexanal, starting with 1,1,6-trimethoxyhexane. The yield of 6-methoxyhexanal, b.p. 82–85° (19 mm.) was 70%. An analytical sample had b.p. 82° (18 mm.), n^{22}D 1.4205.

Anal. Calcd. for $C_7H_{14}O_2$: C, 64.58; H, 10.84. Found: C, 64.07; H, 10.91.

Preparation of Aldehydes by Ozonolysis.—Helferich's directions[3,4] were followed for ozonizing 4-penten-1-ol[22] and 9-octadecen-1-ol. The 4-hydroxybutanal obtained had these constants: b.p. 57.5–58° (9 mm.), n^{20}D 1.4450. Helferich reported no b.p. but did give n^{18}D 1.4291. Paul[23] obtained the compound by periodate cleavage and by lead tetraacetate cleavage of 1,2,5-pentanetriol and reported b.p. 59–60° (8 mm.), n^{20}D 1.4403. In the present work difficulty was encountered in purification when any unreacted 4-penten-1-ol remained in the reaction mixture.

The 9-hydroxynonanal obtained melted at 58–59° (lit.[4] 58°) after several recrystallizations from xylene–ligroin. On standing, the m.p. increased to 62–64°.

4-Methoxybutanal.—To ozonize 5-methoxy-1-pentene, 5.2 g. of it in 20 ml. of methylene chloride was chilled to −78° and subjected to a stream of ozonized oxygen for three hours. It was then added to a mixture of 10 ml. of glacial acetic acid, 20 ml. of ether and 1 g. of water. Four grams of zinc dust was added in small portions. Decomposition of the ozonide was completed by refluxing for 1.5 hours. The mixture was filtered, the residue washed thrice with ether, and the combined filtrate and washings washed with concentrated potassium carbonate solution. After drying with magnesium sulfate, the solvent was removed and the residue distilled under reduced pressure. The yield of 4-methoxybutanal, b.p. 56–61° (40 mm.), was 2.2 g. or 42%. On redistillation there was obtained a sample of b.p. 66° (50 mm.), n^{20}D 1.4101 (lit. b.p. 138–140°, n^{20}D 1.4073[22]).

9-Methoxynonanal.—An ozone stream was passed through a solution of 11.6 g. of crude 1-methoxy-9-octadecene in 15 g. of glacial acetic acid. After processing with zinc dust, washing, etc., distillation gave a forerun of pelargonaldehyde, followed by 2.7 g. (38%) of 9-methoxynonanal, b.p. 100–110° (4 mm.). Redistillation yielded an analytical sample of b.p. 91° (1.7 mm.), $n^{21.5}$D 1.4326.

Anal. Calcd. for $C_{10}H_{20}O_2$: C, 69.70; H, 11.70. Found: C, 70.00; H, 12.04.

10-Hydroxydecanal.—A solution of 6 g. of 10-undecen-1-ol in 12 ml. of glacial acetic acid was ozonized similarly. From the products was obtained 5.7 g. of a viscous oil which on cooling turned to a waxy solid. The crude product was recrystallized five times from a xylene–ligroin mixture to yield a powdery solid of m.p. 68–70°. This value increased to 71–73° on standing for several weeks.

Anal. Calcd. for $C_{10}H_{20}O_2$: C, 69.70; H, 11.70. Found: C, 69.71; H, 11.97.

10-Methoxydecanal.—11-Methoxy-1-undecene (in acetic acid) was ozonized similarly. From 6.5 g. there was obtained 4.5 g. (69%) of 10-methoxydecanal, b.p. 75–80° (0.5 mm.). Redistillation gave a center cut of b.p. 78° (0.5 mm.), n^{21}D 1.4357.

Anal. Calcd. for $C_{11}H_{22}O_2$: C, 70.92; H, 11.91. Found: C, 71.44; H, 12.12.

Methylations.—In a 3-neck, r.b. flask fitted with a sealed stirrer, reflux condenser and dropping funnel was placed 0.1 mole of sodium hydride and 50 cc. of dry ether. Then, with stirring, 0.1 mole of the alcohol (4-penten-1-ol, 5-hydroxyvaleraldehyde ethyl mercaptal, 6,6-dimethoxy-1-hexanol, 8,8-dimethoxy-1-octanol, 9-octadecen-1-ol, 10-undecen-1-ol) was added at such a rate as to keep the evolution of hydrogen under control. After 24 hours the ether was removed and to the gray-brown paste was added 0.12–0.2 mole of methyl iodide. Heat of reaction caused gentle refluxing. Stirring was continued for 1.5 hours or longer, then 30 cc. of dry ether was added. After filtration and rinsing of the precipitate with ether the filtrate was distilled. Results are collected in Table II.

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[21] L. H. Amundsen and L. S. Nelson, THIS JOURNAL, **73**, 242 (1951).

[22] Obtained as in *Org. Syntheses*, **25**, 84 (1945).

[23] R. Paul, *Compt. rend.*, **215**, 303 (1942); R. Paul and S. Tchelitcheff, *Bull. soc. chim.*, [5] **15**, 197 (1948).

High Dilution Reflux Cycle.—This apparatus was prepared for use in the next synthesis. A 2-liter, 3-neck, r.b. flask was fitted with a sealed Hershberg stirrer, a gas inlet tube through which a slow stream of dry, pure[24] nitrogen was admitted and a high dilution reflux cycle. The last consisted of three parts: (1) a side-arm tube about 30 × 150 mm.; (2) above this and fitted to it, a reflux condenser; (3) attached at the top of the latter, a dropping funnel and gas vent.

The side arm was equipped with a stopcock at the bottom for convenience in draining, and with a 24/40 female joint at the top to accommodate the condenser. The side-arm, near the top of the tube, was of 12 mm. diameter, and was bent to fit into one neck of the flask. The tube contained a funnel to force the condensed vapor to flow to the bottom of the tube before returning to the flask.

The gas vent was simply a tube which conveyed the escaping gas through a layer of xylene in a test-tube, thus forming a seal. The reflux cycle is sketched in Fig. 1.

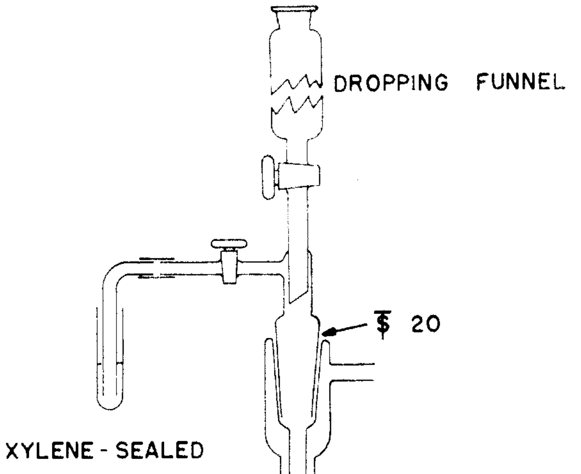

Fig. 1.—Reflux cycle.

2-Hydroxycyclooöctanone (Suberoin).—Except for the design of the dilution cycle, the procedure essentially followed the general directions of Prelog and collaborators.[12] The flask was charged with 800 ml. of dry xylene and a little was distilled off to remove any moisture. There was added 37 g. (1.6 moles) of clear sodium and the sodium dispersed by rapid stirring in the refluxing (135–137°) xylene. A solution of 76 g. (0.38 mole) of methyl suberate in 70 ml. of dry xylene was added through the dilution cycle over seven hours. After it had been stirred with refluxing for two more hours the mixture was cooled and processed.[12] The xylene was removed from the dried solution through a Vigreux column under reduced pressure and the residue distilled *in vacuo*. There was obtained 25.4 g. (47%) of a pale yellow semi-solid, b.p. 90–100° (5 mm.). Attempts at further purification by distillation and recrystallization failed. On standing the product decomposed slowly to suberic acid, identified by m.p. and mixed m.p.

The 2,4-dinitrophenylosazone was prepared from 0.4 g. of suberoin and a solution of 0.4 g. of 2,4-dinitrophenylhydrazine in strongly acidic aqueous ethanol.[25] Recrystallization of the product from chloroform–ethanol yielded orange-red needles melting with decomp. at 215–216° (cor.).

Anal. Calcd. for $C_{20}H_{20}N_8O_8$: N, 22.39. Found: N, 22.32.

Methyl 8,8-dimethoxyoctanoate was prepared according to the procedure given for methyl 6,6-dimethoxyhexanoate. From 15 g. of 2-hydroxycyclooöctanone (contaminated with the yellow diketone) in 150 ml. of methanol and 50–55 g. of lead tetraacetate there was obtained 14.9 g. (65%) of a pale yellow oil, b.p. 105–110° (1.7 mm.). Redistillation yielded a colorless center cut, b.p. 81° (0.5 mm.), n^{25}D 1.4321.

Anal. Calcd. for $C_{11}H_{22}O_4$: C, 60.52; H, 10.16. Found: C, 60.20; H, 9.96.

8,8-Dimethoxy-1-octanol.—The reaction of 17 g. of methyl 8,8-dimethoxyoctanoate (pale yellow material obtained in the first distillation) in 20 ml. of dry ether with 2.3 g. of lithium aluminum hydride in 100 ml. of dry ether, followed by the aforementioned processing,[23] yielded 11.3 g. (76%) of 8,8-dimethoxy-1-octanol as a colorless oil, b.p. 105–110° (0.6 mm.). An analytical sample had b.p. 96° (0.4 mm.), n^{20}D 1.4426.

Anal. Calcd. for $C_{10}H_{22}O_3$: C, 63.11; H, 11.66. Found: C, 63.24; H, 11.74.

8-Hydroxyoctanal.—Hydrolysis of 8,8-dimethoxy-1-octanol with dilute hydrochloric acid gave poor yields of the aldehyde (21%), so a modification of the procedure devised by Fischer[14] for the hydrolysis of sensitive acetals was used.

There was mixed 5.0 g. (0.026 mole) of redistilled (b.p. 95–99° at 0.4 mm.) 8,8-dimethoxy-1-octanol and 5 cc. of saturated tartaric acid solution. The mixture was shaken until it became homogeneous (about one minute) and allowed to stand for 15 minutes. On the addition of 10 cc. of saturated sodium chloride solution, the aldehyde separated. It was extracted with three 15-cc. portions of ether and the combined extracts were washed with 10 cc. of 5% potassium carbonate solution. After drying over magnesium sulfate, the mixture was distilled.

There was obtained 1.4 g, (47% of the theoretical) of material boiling 90–100° (0.5 mm.). This was viscous and it slowly turned semi-solid. In addition 0.6 g. came over in the range 100–150° (0.5 mm.). No suitable medium for recrystallization of the first fraction could be found, but purification was accomplished by grinding the 90–100° (0.5 mm.) fraction with dry ether in a mortar, filtering, and washing the residue repeatedly with dry ether. In this manner there was obtained a powdery white solid of m.p. 63–65°. This m.p. decreased after a week to 59–63°. Repeated ether treatment gave a sample melting at 66–68°.

Anal. Calcd. for $C_8H_{16}O_2$: C, 66.62; H, 11.18. Found: C, 66.10; H, 11.47.

8-Methoxyoctanal.—The procedure given for 8-hydroxyoctanal was followed using 7.0 g. of 1,1,8-trimethoxyoctane and 20 ml. of saturated tartaric acid except the heterogeneous mixture was shaken at intervals for one hour and then worked up as described above to yield 3.9 g. (72%) of 8-methoxyoctanal, b.p. 81–86° (3.2 mm.). This product gave a poor analysis, so it was further purified through its bisulfite addition compound, giving a liquid of b.p. 67° (1.2 mm.), n^{24}D 1.4282.

Anal. Calcd. for $C_9H_{18}O_2$: C, 68.32; H, 11.47. Found: C, 68.52; H, 11.58.

2,4-Dinitrophenylhydrazones of all aldehydes not previously reported were prepared. Melting points and analyses are recorded in Table III.

Spectrophotometric measurements were made on a Beckman DU spectrophotometer. For the hydroxy aldehydes the cell compartment was kept at the stated temperature ±0.1°. The 95% ethanol was a commercial grade while

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[24] L. Fieser, This Journal, **46**, 2639 (1924).

[25] R. L. Shriner and R. C. Fuson, "Identification of Organic Compounds," Third Edition, John Wiley and Sons, Inc., New York, N. Y., 1948, p. 60.

TABLE III

2,4-DINITROPHENYLHYDRAZONES[a]

Aldehyde	M.p. of DNP, °C.	Nitrogen, % Calcd.	Nitrogen, % Found
5-Methoxypentanal	79–79.5	18.91	19.10
6-Hydroxyhexanal	104–105	18.91	19.09
6-Methoxyhexanal	74–74.5	18.06	18.36
8-Hydroxyoctanal	91–93	17.28	17.33
8-Methoxyoctanal	73–74	16.56	16.48
9-Methoxynonanal	73–74	15.90	15.98
10-Hydroxydecanal	80[b] 101–103	15.90	16.33
10-Methoxydecanal	77	15.29	15.25

[a] These derivatives were prepared by standard procedures as given by Shriner and Fuson[25] and A. I. Vogel, "Practical Organic Chemistry," Longmans, Green and Co., Inc., New York, N. Y., 1948, p. 342. [b] Double m.p. sintered at 80° and melted 101–108°.

"75% dioxane" was prepared by mixing three volumes of dried and purified[26] dioxane with one volume of distilled water. The samples measured were generally the same as those submitted for analysis or were purified as described under their preparation. Equilibrium conditions in solutions of the hydroxy aldehydes were obtained within one to three days. Initial absorption was usually considerably lower than that at equilibrium. The existence of equilibrium was verified by rechecks on different solutions or by returning to the original temperature after measurements at another temperature. The equilibria were quite mobile once established, about one-half hour at a given temperature generally being sufficient for the attainment of stable readings. The precision of the results may vary somewhat, since a few of the measurements were made at high transmittancies where the spectrophotometer is less accurate.[27] Data on the methoxy aldehydes are given in Table I.

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[26] L. Fieser, "Experiments in Organic Chemistry," D. C. Heath Co., New York, N. Y., 1941, p. 369.

[27] G. H. Ayres, *Anal. Chem.*, **21**, 652 (1949).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NEW HAMPSHIRE]

Rates of Chromic Acid Oxidation of Some Cyclanols[1,2]

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The rates of chromic acid oxidation of isopropyl alcohol and four cyclanols follow the order $C_8H_{15}OH > C_7H_{13}OH > C_4H_7OH > C_5H_9OH > C_6H_4OH > C_3H_7OH$.

It is well known that the rates and equilibria of reactions involving alicyclic compounds often vary profoundly with ring size. Several factors appear to be involved. Some of these have been embraced in the concept of I-strain by Brown and co-workers.[3] Thus a quadricovalent cyclopropane derivative will be less strained due to the bond angles imposed by the ring structure than a tricovalent (*e.g.*, ion, radical or ketone) or pentacovalent (transition state in an S$_N$2 displacement) species. Transformation from the first to either of the latter two is therefore relatively difficult; the reverse transformation is relatively easy. A similar argument applies to cyclobutane derivatives where the differences in strain are smaller. However, complications can be introduced, for example, by the fact that the cations from some cyclobutyl and cyclopropylmethyl derivatives may be identical.[4] For the 5- and 7-membered rings torsional forces due to hydrogen–hydrogen repulsions[3,5] appear to account for the greater ease of the quadricovalent-to-tricovalent transformation of a carbon atom compared with the 6-membered ring; in the latter hydrogen–hydrogen repulsions are at a minimum because of the possibility of a completely "staggered" configuration.

In order to obtain additional quantitative information on the reactivities of alicyclic derivatives we have measured the rates of chromic acid oxidation of isopropyl alcohol and the series cyclobutanol through cycloöctanol. As a result of the elegant investigations of Westheimer and co-workers[6] the mechanisms of oxidation of secondary alcohols are fairly well understood. The slow step in the reaction involves participation by the alcohol, acid chromate ion and one or two protons as kinetically distinguishable species in water. Furthermore, removal of the hydrogen on the carbinol carbon is part of this step, as evidenced by the fact that 2-deutero-2-propanol reacts only about one-sixth as fast as ordinary 2-propanol.[6b] The mechanisms may be represented as

$$R_2CHOH + HCrO_4^- + H^+ \overset{\text{fast}}{\rightleftharpoons} R_2CHOCrO_3H + H_2O \overset{H^+}{\rightleftharpoons} [R_2CHOCrO_3H_2]^+ \quad (1)$$

$$R_2CHOCrO_3H + H_2O \xrightarrow[k_1]{\text{slow}} H_3O^+ + R_2C{=}O + HCrO_3^- \quad (2)$$

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[1] Taken in part from the Master's Thesis of W. J. Becker, III, June, 1951.

[2] The authors gratefully acknowledge the assistance provided by a Frederick Gardner Cottrell grant of the Research Corporation.

[3] H. C. Brown and M. Gerstein, THIS JOURNAL, **72**, 2926 (1950); H. C. Brown, R. S. Fletcher and R. B. Johannsen, *ibid.*, **73**, 212 (1951). The latter paper contains a summary of pertinent data for 5-, 6- and 7-membered ring compounds. See also H. C. Brown and M. Borkowski, *ibid.*, **74**, 1897 (1952).

[4] J. D. Roberts and R. H. Mazur, *ibid.*, **73**, 2509, 3542 (1951).

[5] K. S. Pitzer, *Science*, **101**, 672 (1945); J. Kilpatrick, K. S. Pitzer and R. Spitzer, THIS JOURNAL, **69**, 2483 (1947); C. W. Beckett, K. S. Pitzer and R. Spitzer, *ibid.*, **69**, 2488 (1947).

[6] (a) F. H. Westheimer and A. Novick, *J. Chem. Phys.*, **11**, 506 (1943); (b) F. Westheimer and N. Nicolaides, THIS JOURNAL, **71**, 25 (1949); (c) F. Holloway, M. Cohen and F. H. Westheimer, *ibid.*, **73**, 65 (1951).