potassium permanganate, or performic acid followed with lead tetraacetate, resulted only in the recovery of small amounts of the starting materials. Attempts to cleave the ether linkage of the saturated acid with hydrobromic acid gave inconclusive results.

The unsaturated acid (6.90 g.) was reduced with lithium aluminum hydride in ether. A total of 4.98 g. (78%) of colorless crystals separated from hexane; m.p. 65.5–67.5°. Further recrystallization and sublimation at 50° (0.3 mm.) gave pure 2-methyl-3-methylene-2,3-dihydro-2-benzofurylcarbinol, m.p. 67.6–68.8°. Overheating caused decomposition.

Anal. Calcd. for $C_{11}H_{12}O_2$: C, 74.97; H, 6.87. Found: C, 74.78; H, 6.94.

A solution of 4.20 g. of the alcohol in ethanol absorbed 103% of the theoretical amount of hydrogen over platinum oxide. The product (3.76 g., 89%), 2,3-dimethyl-2,3-dihydro-2-benzofurylcarbinol, also obtained (82% yield) by reducing the saturated ethyl ester with lithium aluminum hydride in ether, was a viscous colorless liquid, b.p. 81–89° (0.5 mm.). The 84–85° cut was analyzed; $n^{20}D$ 1.5383. The best of three samples, it was still impure.

Anal. Calcd. for $C_{11}H_{14}O_2$: C, 74.12; H, 7.92. Found: C, 73.54; H, 8.11.

An attempt to convert the alcohol to the bromide with phosphorus tribromide gave only a trace of recovered alcohol; similar results were observed upon treatment with thionyl chloride, alone or with an equivalent of pyridine.

Eugene, Oregon

[Contribution from the Sterling–Winthrop Research Institute]

1,4-Dimethoxy-5-methyl-6-tetralone and 1,4-Dimethoxy-5,5-dimethyl-6-tetralone

By T. R. Lewis, William B. Dickinson and S. Archer

Received June 7, 1952

The adduct obtained from benzoquinone and 2-ethoxybutadiene upon aromatization and methylation furnished 6-ethoxy-1,4-dimethoxy-5,8-dihydronaphthalene (VI) which isomerized on recrystallization from ethanol in the presence of Darco to yield the conjugated 7,8-dihydro derivative, VIII. In the methoxy series the adduct yields V. This 5,8-dihydronaphthalene gave a ketal, X, when recrystallized from methanol in the presence of Darco. The true 7,8-dihydro compound, VII, was obtained by refluxing the ketal in acidified methanol. Hydrolysis of all the above aromatic ethers gave 1,4-dimethoxy-6-tetralone. Alkylation of this compound with methyl iodide and sodium sand gives a mixture of three compounds: the tetralol, XIII, the dimethyltetralone, XI, and the monomethyltetralone, XII.

Grob and Wicki[1] condensed 2-methoxybutadiene with benzoquinone in petroleum ether and obtained in 58% yield the adduct, III, which they aromatized and methylated in alkaline medium. The resulting dimethyl ether was isolated in 65% yield and melted at 80–82°. It was originally assigned structure V, but in a later paper[2] it was pointed out that the ultraviolet absorption spectrum exhibited two maxima, one of which was due to conjugation of the double bond with the benzene ring. On this basis the substance was assigned structure VII.

When 2-ethoxybutadiene[3] (II) was condensed with benzoquinone in ethanol the desired adduct (IV) was obtained in 85% yield.[4] Grob's procedure for converting the adduct to the dimethyl ether proved to be unsatisfactory in our hands. By suitable modification of his procedure we prepared VI in 79% yield. On hydrolysis this compound furnished the tetralone IX.[5] It showed a maximum at 284 mμ in the ultraviolet. Absorption at this wave length was attributed to the presence of the substituted benzene ring since the tetralone, IX, absorbed at 289 mμ (see Table I).

When a sample of VI was recrystallized from ethanol with the aid of a small amount of Darco, the melting point of the recovered material dropped markedly. The compound that was isolated was isomeric with VI, hydrolyzed to the tetralone, IX, and in contrast to VI, showed two peaks in the ultraviolet, one at 274 mμ and the other at 312 mμ. The conjugated structure, VIII, is compatible with these properties.

In view of these results it was thought advisable to reinvestigate the methoxy series. Methoxybutadiene (I)[6] and benzoquinone were refluxed in methanol for three hours to furnish the adduct, III, in 52% yield. It was converted to an aromatic ether, m.p. 80–81°, by the procedure used in the ethoxy series. The tetralone, IX, was obtained on hydrolysis and the ultraviolet absorption spectrum revealed only one maximum at 284 mμ (Table I). This is the same wave length at which the 5,8-dihydro isomer in the ethoxy series (VI) absorbed. Accordingly, the ether was assigned structure V in contrast to Grob's later claim.[2]

When a dry methanol solution of V was refluxed in the presence of Darco a new substance was formed, the analysis of which agreed well with structure X. In harmony with this formulation were the facts that the compound hydrolyzed to yield IX and showed a maximum only at 286 mμ (Table I). This ketal was probably formed by the addition of a molecule of methanol across the double bond of V.

In an attempt to prepare an authentic specimen of X the tetralone, IX, was treated with methyl orthoformate. The reaction mixture was resolved into two components by means of chromatography on alumina. The minor product proved to be the desired ketal X. The substance present in major amounts was an isomer of V. The tetralone, IX, was formed on hydrolysis of this isomer and the ultraviolet absorption spectrum revealed two maxima, one at 274 mμ and the other at 312 mμ. Thus this new ether must be the conjugated compound, VII. It was prepared from X by simply refluxing a methanol solution containing a small amount of hydrogen chloride for a few hours.

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(1) C. A. Grob and H. Wicki, *Helv. Chim. Acta*, **31**, 1706 (1948).

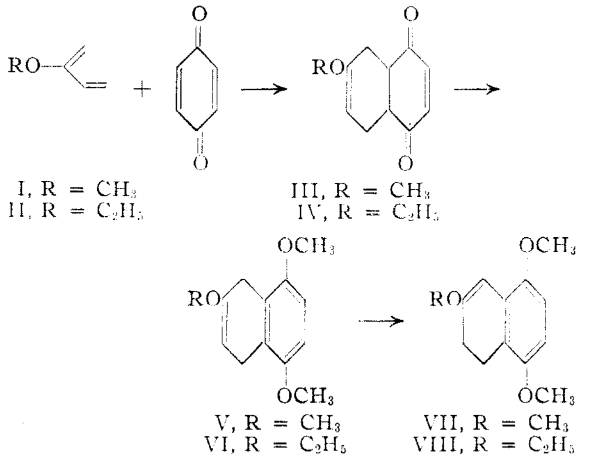
(2) C. A. Grob, N. Jundt and H. Wicki, *ibid.*, **32**, 2127 (1949).

(3) H. L. Holmes and K. M. Mann, This Journal, **69**, 2001 (1947).

(4) This compound was first prepared by Dr. R. L. Clarke of this Laboratory; purification and analyses will be reported by him.

(5) C. A. Grob and W. Jundt, *Helv. Chim. Acta*, **31**, 1691 (1948).

(6) Reference 1 gives the pertinent literature on the preparation of this diene.

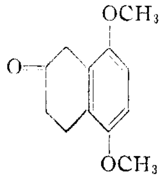


I, R = CH_3
II, R = C_2H_5

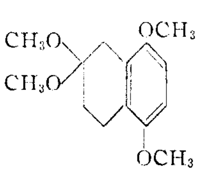
III, R = CH_3
IV, R = C_2H_5

V, R = CH_3
VI, R = C_2H_5

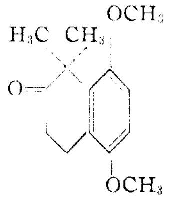
VII, R = CH_3
VIII, R = C_2H_5



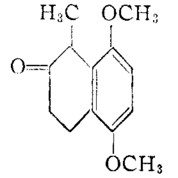
IX



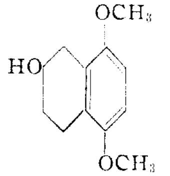
X



XI



XII



XIII

The ethers V and VI do not appear to be alkali sensitive as implied by Grob.[2] On the contrary it is in weakly acidic alcohols that the double bond migration was effected, probably through the formation of acid-sensitive ketals in both the ethoxy and methoxy series.

When the tetralone, IX, was alkylated in sodium methoxide solution with methyl iodide, Grob[5] obtained some unchanged starting material and an oil, the analysis of which was in agreement with structure XI, the dimethyltetralone. It formed a semicarbazone which melted at 175–176° after many crystallizations from chloroform–ethanol. When the methylation was carried out with potassium sand in benzene it was reported that the monomethyltetralone XII was obtained in 90% yield. The yield of XII was lower when sodium was substituted for potassium. The semicarbazone of XII melted at 165–167° after purification by chromatographic adsorption on alumina. It was also stated that the semicarbazones of XI and XII gave no melting point depression on admixture.

In our hands the alkylation of IX with sodium sand and methyl iodide furnished a mixture from which three products were isolated. The first was the tetralol, XIII. The alcoholic nature of the compound was demonstrated by the preparation of its 3,5-dinitrobenzoate. A molecular weight determination eliminated the possibility that the compound was a pinacol or another high molecular weight molecule. After removal of the tetralol the residue was chromatogrammed to give first a crystalline compound, m.p. 94–95°. The analysis indicated that it was the dimethyltetralone, XI. It formed a semicarbazone which melted at about 215°. The analysis of this derivative was also in excellent agreement with the assigned structure. The remaining fractions of the eluate gave an oil which also formed a semicarbazone, m.p. 185–186°. The analysis was in good agreement for the semicarbazone of the monomethyltetralone XII. Hydrolysis of this semicarbazone by Hershberg's method[7] gave an oil which was XII. A mixture of the semicarbazones of XI and XII melted in the range 170–182°. Thus it is apparent that Grob's methylated tetralones were quite impure and the corresponding semicarbazones were approximately eutectic mixtures.[8]

Experimental[9]

Ethoxy Series

6-Ethoxy-1,4,4a,5,8,8a-hexahydronaphthalene-1,4-dione (IV).—A solution of 53.8 g. of 2-ethoxybutadiene (0.55 mole) and 57.3 g. (0.54 mole) of benzoquinone in 200 ml. of absolute alcohol was refluxed on the steam-bath for two hours with the exclusion of moisture. The whole was poured into a beaker while still hot and the flask rinsed with 25 ml. of dry alcohol. After cooling for one hour, the suspension was filtered and pressed dry. It was finally dried *in vacuo* over calcium chloride; m.p. 88–90°, wt. 97.7 g. (88%). Clarke reports m.p. 92–94°.[4]

5,8-Dihydro-1,4-dimethoxy-6-ethoxynaphthalene (VI).—A suspension of 43.7 g. of the above adduct, IV, in 120 ml. of absolute alcohol was kept in an atmosphere of nitrogen as a solution of 14.7 g. of sodium in 300 ml. of absolute alcohol was added in a thin stream with stirring. To effect complete solution the mixture was heated and then cooled to room temperature. Then 96.5 g. of methyl iodide was added over a one-half hour period. A slight rise in temperature was noted and the reaction was completed by refluxing the mixture for one hour. The mixture was then cooled and filtered. The tan crystals were dried at 70° for 4 hr.; wt. 39.0 g. (79%), m.p. 100–103°. When a sample was crystallized from ethanol without Darco it melted at 102.4–103.4° (cor.).

Anal. Calcd. for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74. Found: C, 71.42; H, 8.07.

7,8-Dihydro-1,4-dimethoxy-6-ethoxynaphthalene (VIII).—Six grams of VI (m.p. 99–101°) was dissolved in 100 ml. of boiling 95% ethanol and treated with Darco. On cooling, 4.3 g. of crystalline material separated, m.p. 73–76°. Further crystallization from ligroin with the aid of Darco furnished white crystals, m.p. 83.5–85.5° (cor.).

Anal. Calcd. for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74. Found: C, 71.76; H, 7.54.

1,4-Dimethoxy-6-tetralone (IX). A. From 7,8-Dihydro-1,4-dimethoxy-6-ethoxynaphthalene.—One gram of VIII was dissolved in 25 ml. of ethanol. After cooling to room temperature the suspension was treated with 5 ml. of 2 *N* hydrochloric acid. The whole was swirled for 15 minutes, treated with ice and filtered. The light tan solid weighed 0.9 g. and melted at 96–99°. After recrystallization from ethanol the ketone melted at 98.6–99.4° (cor.).

Anal. Calcd. for $C_{12}H_{14}O_3$: OCH_3, 30.10. Found: OCH_3, 30.26.

The 2,4-dinitrophenylhydrazone prepared in the usual fashion melted at 195° after recrystallization from ethyl acetate.

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(7) E. B. Hershberg, *J. Org. Chem.*, **13**, 544 (1948).

(8) After this work was completed, L. H. Sarett, *et al.*, This Journal, **74**, 1393 (1952), reported the condensation of ethoxypentadiene and benzoquinone. Aromatization and methylation of this adduct followed by hydrolysis should give a sample of XII which would be known to be free of the dimethyltetralone, XI.

(9) All melting points are uncorrected unless otherwise specified. Analyses were carried out under the supervision of Mr. K. D. Fleischer and the spectra measured under Dr. F. C. Nachod's direction.

Anal. Calcd. for $C_{18}H_{18}N_4O_6$: N, 14.50. Found: N, 14.59.

The semicarbazone melted at 201–202° after recrystallization from methanol (Grob[4] reported m.p. 202–204°).

B. From 5,8-Dihydro-1,4-dimethoxy-6-ethoxynaphthalene.—A suspension of 104 g. of VI in 700 ml. of ethanol was treated with a solution of 40 ml. of concentrated hydrochloric acid in 210 ml. of water and left for 30 minutes. Then 460 g. of ice was added. The solid was collected and dried *in vacuo;* wt. 83.5 g. (91%), m.p. 98.5–100°.

Methoxy Series

6-Methoxy-1,4,4a,5,8,8a-hexahydronaphthalene-1,4-dione (III).—A mixture of 27.0 g. (0.25 mole) of benzoquinone and 21.0 g. of 2-methoxybutadiene in 63 ml. of absolute methanol was heated under gentle reflux for three hours. The whole was cooled to room temperature, seeded and then chilled in ice. Finally it was cooled in a freezing mixture for about one hour, filtered and washed with about 30 ml. of dry, cold methanol. The crystalline adduct was air-dried; wt. 25.2 g. (52.5%), m.p. 80–83° (Grob[1] reported m.p. 88–89°).

The filtrate was concentrated to about 50 ml. and cooled. The crop of crystals was collected, washed with methanol and dried; wt. 1.6 g., m.p. 112–114°. This substance did not depress the melting point of an authentic specimen of benzoquinone.

1,4,6-Trimethoxy-5,8-dihydronaphthalene (V).—In a three-necked flask equipped with a stirrer, condenser and nitrogen inlet tube there was placed 43.0 g. of the above adduct and 70 ml. of dry methanol. Then 98.5 ml. of 5.06 *N* sodium methoxide in methanol was added under a nitrogen atmosphere. During the very early stages of the addition the mixture became warm enough to require external cooling and a heavy gray solid appeared, presumably the aromatized adduct. After all the base had been added 85.2 g. of methyl iodide was dropped into the stirred suspension. The mixture was heated under reflux for two hours. The solution was then cooled for several hours and filtered. The tan crystals were washed with cold methanol and air-dried; m.p. 78.5–81°, wt. 28.4 g. (58%). After two crystallizations from methanol the compound melted at 80–81° (Grob[1] reported 80–82°).

Anal. Calcd. for $C_{13}H_{16}O_3$: C, 70.89; H, 7.32; OCH_3, 42.27. Found: C, 70.95; H, 7.23; OCH_3, 42.89.

1,4,6,6-Tetramethoxy-5,6,7,8-tetrahydronaphthalene (X). A. From the Ether, V.—Ten grams of the above ether was dissolved in 50 ml. of dry methanol, treated with 0.75 g. of Darco and then the suspension was refluxed for 15 minutes. The solution was filtered and the filtrate was concentrated to dryness. On cooling and seeding the entire residue solidified. It was filtered and washed with petroleum ether, m.p. 71–74°.

A 5-g. portion was dissolved in 100 ml. of petroleum ether and chromatographed on a column of 100 g. of alumina. Elution was carried out with benzene–petroleum ether mixtures. The eluates which contained 30 to 50% benzene on evaporation gave oils which solidified on seeding. The crystalline material was bulked (wt. 3.26 g.) and recrystallized from petroleum ether, m.p. 75–76.5° (cor.).

Anal. Calcd. for $C_{14}H_{20}O_4$: C, 66.64; H, 7.99; OCH_3, 49.20. Found: C, 67.10, 66.10; H, 8.37, 8.14; OCH_3, 48.90.

A one-gram sample of the crude ketal (m.p. 71–74°) was dissolved in 7 ml. of methanol by warming and the resulting solution was treated with 2 ml. of 3 *N* hydrochloric acid. The mixture was shaken for 30 minutes and the crystalline material was collected and dried; wt. 0.976 g. After recrystallization from dilute ethanol the white needles melted at 98.5–99.5° and did not depress the melting point of an authentic specimen of the tetralone, X.

B. From the Tetralone (IX).—A suspension of 2.06 g. (0.01 mole) of the tetralone, X, in 22 ml. of dry methanol and 1.27 g. of methyl orthoformate (Kay–Fries) was treated with two drops of 6.2 *N* ethanolic hydrogen chloride whereupon a clear solution resulted. After refluxing for 3.5 hours the solution was taken to dryness. The residue was dissolved in 50 ml. of petroleum ether and placed on a column of activated alumina (40 g.). Elution was carried out with petroleum ether–benzene which became progressively richer in the aromatic component. The fraction containing 5% benzene gave an oil on evaporation. Cooling and scratching resulted in crystallization. This solid melted at 36–38°. It was processed further as described below.

The fraction containing 15 to 40% benzene on evaporation yielded crystalline material which melted at 75–76.5°. It did not depress the melting point of the sample prepared from the enol ether V.

The low-melting solid (m.p. 36–38°) crystallized readily when its petroleum ether solution was cooled in a Dry Ice–acetone-bath. The crystals were collected rapidly and recrystallized again for analysis; m.p. 64–65° (cor.). This is **1,4,6-trimethoxy-7,8-dihydronaphthalene** (VII).

Anal. Calcd. for $C_{13}H_{16}O_3$: C, 70.89; H, 7.32; OCH_3, 42.27. Found: C, 70.65; H, 7.69; OCH_3, 42.18.

1,4,6-Trimethoxy-7,8-dihydronaphthalene from the Ketal, X.—A solution of 2.0 g. of the ketal IX in 25 ml. of dry methanol was treated with 20 drops of 1.5 *N* methanolic hydrogen chloride and was gently refluxed for four hours with the exclusion of moisture. It was then concentrated *in vacuo.* The residue was leached with two 25-ml. portions of boiling petroleum ether and the small insoluble gum was rejected. The petroleum ether solution was poured on a column of 45 g. of activated alumina and eluted with petroleum ether–benzene mixtures. •Most of the material was found in the fractions containing 5 to 20% benzene. Evaporation of these fractions yielded an oil which readily solidified; wt. 0.935 g. (54%), m.p. 64–65°. It did not depress the melting point of the sample described above.

TABLE I

LIGHT ABSORPTION DATA OF THE ENOL ETHERS AND 1,4-DIMETHOXY-6-TETRALONE AND ITS KETAL

Compound	λ_{max}	ϵ
VIII	274	10,132
	312	6,939
VI	284	3,327
V	284	3,527
VII	274	9,884
	312	6,580
IX	289	3,513
X	286	3,856

Alkylation of 1,4-Dimethoxy-6-tetralone.—Sodium (2.3 g.) was powdered under xylene and the solvent was then replaced with 35 ml. of dry benzene. A solution of 20.0 g. of the tetralone, IX, in 100 ml. of dry benzene was added dropwise to the rapidly stirred suspension in a nitrogen atmosphere. The addition required one-half hour. The suspension was stirred 90 minutes longer before 28.4 g. of methyl iodide was added in one portion. The whole was refluxed for three hours. After standing overnight the mixture was washed successively with dilute solutions of sulfuric acid, salt, sodium bisulfite, and finally salt. The oil layer was dried over Drierite, filtered and concentrated. After standing for three days, 10 ml. of benzene was added and the crystals that had deposited were collected on a filter. The compound which was **1,4-dimethoxy-6-tetralol** was washed with ligroin and then with benzene. After drying it weighed 1.08 g. It was recrystallized from benzene with the aid of Darco; m.p. 130.5–132°.

Anal. Calcd. for $C_{12}H_{16}O_3$: C, 69.1; H, 7.72; mol. wt., 208. Found: C, 69.0; H, 7.72; mol. wt., 210.

The tetralol gave a **3,5-dinitrobenzoate** when treated with 3,5-dinitrobenzoyl chloride in pyridine. After two recrystallizations from ethanol the ester melted at 120–123°.

Anal. Calcd. for $C_{19}H_{18}N_2O_8$: C, 56.71; H, 4.51; N, 6.96. Found: C, 57.22; H, 4.94; N, 7.25.

The filtrate that remained after the removal of the tetralol was taken to dryness and dissolved in a mixture of 50 ml. of ligroin and 20 ml. of benzene. It was chromatogrammed on a column of activated alumina (300 g.). A crystalline material was eluted with the 70:30 ligroin–benzene fraction. It weighed approximately 5 g. The solid was recrystallized from ligroin with the aid of Darco. The resulting white plates melted at 94–94.4° (cor.). This was the **1,4-dimethoxy-5,5-dimethyl-6-tetralone (XI).**

Anal. Calcd. for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74. Found: C, 71.94; H, 7.74.

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, 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

BY CHARLES D. HURD AND WILLIAM H. SAUNDERS, JR.

RECEIVED APRIL 21, 1952

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).

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

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