TABLE III (*Concluded*)

ANALYSES OF METHYL HYDROXYSTEARATES

Calcd. for $C_{19}H_{18}O_3$: C, 72.55; H, 12.18

No.	Subs., g.	CO_2, g.	H_2O, g.	C, %	H, %
I	0.0961	0.2545	0.1035	72.22	12.06
II	*.1624*	*.4284*	*.1742*	71.94	*12.00*
III	.1384	.3649	.1537	71.90	12.42
IV	.1151	.3084	.1265	72.33	12.29
V	.1080	.2828	.1205	72.04	12.28

ANALYSES OF HYDROXYSTEARIC ACIDS

Calcd. for $C_{19}H_{36}O_3$: C, 71.94; H, 12.08; mol. wt., 300.4

								Mol. wt. detn.		
-Stearic acid	M. p., °C.	Solid p., °C.	Subs., g.	CO_2, g.	H_2O, g.	C, %	H, %	Subs., g.	0.1 *N* NaOH, cc.	Mol. wt. found
9-Hydroxy	74–75	70–68	0.1891	0.4956	0.2018	71.49	11.94	0.3409	11.30	301.6
10-Hydroxy	81–82	78–77	.0894	.2346	.0947	71.56	11.85	.3099	10.29	301.2
11-Hydroxy	76–77	74–73	.1197	.3136	.1277	71.45	11.94	.5950	19.69	302.1
12-Hydroxy	78–79	73–72	.1256	.3304	.1336	71.74	11.91	.6474	21.39	302.1
13-Hydroxy	77–77.5	73–72	.0670	.1762	.0730	71.74	12.19	.5667	18.78	301.8

***n*-Nonyl Bromide.**—A mixture of 74 g. of *n*-nonyl alcohol, 240 g. of (42%) hydrobromic acid and 62 g. of concd. sulfuric acid was refluxed for 11 hours. The yield of product was 80%; b. p., 88°, at 4 mm.; n_D^{20}, 1.4533; d_{20}^{20}, 1.0183.

Summary

1. The 9-, 10-, 11- and 12-hydroxystearic acids have been previously prepared from unsaturated fatty acids or found in nature. 13-Hydroxystearic acid has never been prepared. The synthesis of these five acids and their esters has been accomplished by a procedure leaving no doubt as to their constitution and purity.

2. These acids were synthesized by condensing the proper alkyl magnesium bromide with the proper aldehyde ester, then by saponifying the product: $CH_3(CH_2)_xMgBr + OCH(CH_2)_yCO_2CH_3 \longrightarrow CH_3(CH_2)_x$-$CHOH(CH_2)_yCO_2CH_3 \longrightarrow CH_3(CH_2)_xCHOH(CH_2)_yCO_2H$.

URBANA, ILLINOIS

ETHERS OF DIACETONE ALCOHOL

BY ALFRED HOFFMAN

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In the preparation of mesityl oxide from diacetone alcohol by the action of small amounts of hydrochloric acid[1] the following phenomena were noted. If equal volumes of diacetone alcohol and of water containing a few percent. of hydrochloric acid are sealed in a glass tube and shaken, a homogeneous mixture results, since the alcohol mixes with water in any proportion. If the tube is then heated for an hour to 120°, mesityl oxide is formed by the splitting off of water from the alcohol, and since the former is only slightly soluble in water, the contents of the tube are

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[1] Hoffman, U. S. pat. 1,474,935 (1922).

divided into two approximately equal layers. On standing at room temperature for a few days with occasional shaking, the contents of the tube again become homogeneous, due to the fact that the mesityl oxide has reverted to diacetone alcohol under the catalytic influence of the acid. This cycle can be repeated indefinitely with the same material. The reaction is as follows, the equilibrium depending on the temperature: $(CH_3)_2.C(OH)CH_2{-}CO{-}CH_3 \rightleftarrows (CH_3)_2C{=}CH{-}CO{-}CH_3 + H_2O$. In considering the mechanism of the conversion of mesityl oxide into diacetone alcohol it appeared likely that the hydrogen and the oxygen comprising the hydroxyl group of water were added to the double bond of the former. If this were the case, other hydroxyl compounds, like alcohol, should react with mesityl oxide to form ethers of diacetone alcohol. By experiment it was found that mixtures of mesityl oxide and alcohol containing a few percent. of hydrochloric acid increased in specific gravity on standing at room temperature for several days and at the same time substances of higher boiling point and characteristic odor were formed. The reaction reaches an equilibrium depending on the temperature—the lower the temperature, the greater the conversion. As a rule about 20–25% yields were obtained. Compounds were prepared of a number of primary aliphatic alcohols and benzyl alcohol. *iso*Propyl alcohol, as a secondary alcohol, reacted only to a slight extent, sufficient to show a small rise in specific gravity and to leave a peculiar odor on evaporation, but not to allow the isolation of the compound. Glycerine and cellulose do not seem to react. The compounds are colorless, somewhat oily liquids of pronounced odor, resembling cedarwood oil. They boil with little or no decomposition at about 90° higher than the respective alcohols, the specific gravities are about 0.9 and the lower members are slightly soluble in water.

Since analysis shows that these compounds are formed by the addition of one molecule of alcohol to one of mesityl oxide, there are three possible structures to be considered, two forms of ether and a half-acetal.

$(CH_3)_2{\cdot}C(OR){\cdot}CH_2{-}CO{-}CH_3$ I

$(CH_3)_2{\cdot}CHCH(OR){\cdot}CO{\cdot}CH_3$ II

$(CH_3)_2{\cdot}C{=}CH{-}C(OH)(OR){\cdot}CH_3$ III

A carbon-to-carbon linkage does not exist, as even in the cold a trace of a strong acid breaks down the pure compounds to the equilibrium mixture. No attempt was made to distinguish between I and II. I is by far the more likely as it is analogous to diacetone alcohol. III cannot be the correct formula for the following reasons. The keto group is present as shown by the formation of the semi-carbazone, the oxime and the phenylhydrazone. The ethers can be regenerated from the semicarbazones. The compounds react with sodium hypobromite, giving bromoform and a saturated acid.

The latter, when heated with dil. sulfuric acid, produces the respective alcohol: $(CH_3)_2.C(OR).CH_2.CO—CH_3 + NaOBr \longrightarrow (CH_3)_2.C(OR).CH_2.COOH (+H_2SO_4) \longrightarrow ROH + (CH_3)_2.C=CH—COOH$. The keto group can be reduced with sodium under certain conditions, giving an hydroxy ether. The latter, when heated with a drop of concd. sulfuric acid, gives the alcohol, water and a hexadiene: $(CH_3)_2.C(OR)\cdot CH_2\cdot CO\cdot CH_3 + H_2 \longrightarrow (CH_3)_2\cdot C(OR)\cdot CH_2\cdot CH(OH)\cdot CH_3(+H_2SO_4) \longrightarrow ROH + H_2O + (CH_3)_2.C=CH—CH=CH_2$.

It was not found possible to prepare compounds with sodium bisulfite. However, it will be recalled that mesityl oxide itself reacts only in part with bisulfite.[2] Formula III is also excluded by the fact that the compounds do not contain a double bond. It is true that the products purified by simple distillation do react with dil. permanganate solution and with bromine. This is, however, due to the presence of a small amount of mesityl oxide, as repeated washing with small amounts of dil. permanganate solution removes the unsaturation. The pure ethers regenerated from the semicarbazones are stable to dil. permanganate for several hours and do not decolorize a chloroform solution of bromine.

Experimental Part

Preparation of the Ethers.—The most efficient catalyzer for this purpose is hydrochloric acid, as it brings about the equilibrium several times faster than sulfuric acid. It is not advisable to use it, however, as it forms addition compounds with mesityl oxide which contaminate the product and finally decompose it by the liberation of acid.

Method for Low-Boiling Alcohols, Easily Soluble in Water.—A mixture of 607 g. of mesityl oxide, 561 g. of absolute ethyl alcohol and 32 g. of concd. sulfuric acid is allowed to stand at room temperature for ten days. It is then placed in a copper still equipped with a stirrer, 35 g. of calcium hydroxide is added and the unchanged alcohol distilled off in an oil-bath. It is necessary to use an excess of calcium hydroxide and to stir during the distillation because the ethylsulfuric acid present gradually decomposes with the liberation of sulfuric acid. Finally, the ether is distilled with steam, separated, dried with calcium chloride and fractionated; yield, 185 g. of ether; b. p., 160–170°.

TABLE I

PROPERTIES OF THE DIACETONE ETHERS

Derivative	B. p., °C.	Pressure, mm.	D^{25}_{25}	Anal. C, % Calcd.	Anal. C, % Found	Anal. H, % Calcd.	Anal. H, % Found
Methyl	155–157	760	0.901	64.6	64.4	10.77	10.66
Ethyl	164–166	760	.886	66.6	66.9	11.1	11.09
Propyl	182–183	760	.878	..	..	...	...
Butyl	198–199	760	.877	69.7	69.54	11.6	11.5
	81–84	7	...	..	..	...	...
*iso*Butyl	85–87	15	.876	..	..	...	...
iso-Amyl	85–88	6	.868	..	..	...	...
Benzyl	153–157	12	1.005	75.7	75.2	8.7	8.8

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[2] Harries, *Ber.*, **32,** 1326 (1899).

Method for High-Boiling Alcohols, Slightly Soluble in Water.—A mixture of 1 kg. of butyl alcohol, 1325 g. of mesityl oxide and 70 g. of concd. sulfuric acid is allowed to stand ten days. A concentrated solution of 250 g. of crystalline sodium carbonate is added, the mixture thoroughly shaken and then steam-distilled. The product is purified by fractionation; yield, 590 g. In the case of the benzyl ether, the product is found in the still after steam-distillation, as it is not volatile with steam.

Oxime of Ethyl-D Ether.[3]—Six g. of ethyl-D ether was added to a concd. aqueous solution of 3 g. of hydroxylamine hydrochloride and 3.6 g. of sodium bicarbonate, and methyl alcohol was then added until the solution was homogeneous. This was allowed to stand overnight at about 50°, water was added and the solution was extracted with ether and fractionated; yield, 3 g. The oxime is a colorless, oily liquid of faint odor; b. p., 103°, at 7 mm.

Anal. Calcd. for $C_8H_{17}O_2N$: C, 60.3; H, 10.69. Found: C, 60.2; H, 10.8.

Preparation of a Semicarbazone.—Three and four-tenths g. of butyl-D ether was added to a concd. aqueous solution of 2.5 g. of semicarbazide hydrochloride and 3.2 g. of crystalline sodium acetate and then enough methyl alcohol was added to render the solution homogeneous. The mixture, after being warmed slightly, set to a cake of crystals in a few minutes. The substance was recrystallized from hot methyl alcohol.

In the case of the methyl-D ether, no semicarbazone was formed. After standing several days a small deposit of crystals appeared. They were insoluble in hot methyl alcohol, but could be recrystallized from hot water. They were identified as hydrazine-dicarbonic acid diamide, a condensation product of semicarbazide with itself.

Properties of the Semicarbazones.—These substances form colorless, more or less coarse, flat needles. The hydrazine-dicarbonic acid diamide from methyl-D ether and semicarbazide melted at 248° (corr.).

Anal. Calcd. for $C_2H_6O_2N_4$: N, 47.4. Found: 46.04.

TABLE II

PROPERTIES OF THE SEMICARBAZONES

Derivative	M. p., °C. (corr.)	Anal. C, % Calcd.	Found	H, % Calcd.	Found	N, % Calcd.	Found
Ethyl	163–164	..	..	...	..	20.9	21
Propyl	139–140	..	..	...	..	19.5	19.8
Butyl	134–135	57.6	57.5	10.04	9.85	18.3	18.7
*iso*Butyl	145	..	..	...	..	18.3	18.2
iso-Amyl	142–143	..	..	...	..	17.28	17.6
Benzyl	138–139	..	..	...	..	15.9	16.4

The figures for nitrogen in Table II are in most cases somewhat high due, perhaps, to the presence of traces of mesityl oxide semicarbazide-semicarbazone (N, 36.5%).

Regeneration of an Ether from the Semicarbazone: Preparation of *iso*Butyl-diacetone Ether from its Semicarbazone.—One and four-tenths g. of *iso*butyl-D ether semicarbazone and 9 g. of phthalic anhydride were steam-distilled. An oil came over rapidly which had the characteristic odor of the ether. A semicarbazone prepared from it melted at 145° (corr.), as did its mixture with the original semicarbazone.

Reduction of an Ether: Conversion of Ethyl-diacetone Ether to 4-Ethoxy-4-methyl-pentan-2-ol.—As the ethers of diacetone alcohol are

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[3] "D" denotes diacetone.

sensitive to sodium hydroxide, attempts at reduction of the keto group with sodium and alcohol or sodium and moist ether were not successful. Sodium amalgam and aluminum amalgam were also unsatisfactory. Finally the following method was devised, which seems to be new and may be of value in similar cases.

Twenty-five g. of ethyl-D ether was dissolved in 250 g. of ordinary "washed" ethyl ether, and 67 g. of boric acid added. The mixture was stirred mechanically under a reflux condenser and cooled with water. Twenty-five g. of sodium in small pieces and 125 cc. of water were gradually added, making sure that the sodium actually reacted and did not accumulate. When it did not react, due to crust formation, more water was added. When the reaction was finished, the contents of the flask were divided in two layers. The upper one, on fractionation, gave a crude product which could not be purified over the acid phthalic ester. It gave no oxime, nor did it react with sodium hypobromite, showing the absence of the keto group; yield, 15.8 g.; b. p., 160–173°, d^{25}_{25}, 0.868.

Reaction of a Reduced Ether, 4-Ethoxy-4-methyl-pentan-2-ol, with Acid.—To determine the structure of the reduced ethyl-D ether, the crude product was heated in an oil-bath with a drop of concd. sulfuric acid. A mixture of water and oil distilled. After drying with potassium carbonate, fractionation showed the product to consist mainly of ethyl alcohol and a hydrocarbon. The latter was highly unsaturated. On distillation it tended to polymerize to a sticky, rubber-like substance; b. p., 70–77°; d^{25}_{25}, 0.712. It was therefore thought inadvisable to purify it over sodium. Beilstein[4] gives the boiling point of 4-methyl-2,4-pentadiene as 74–75°. The substance was evidently not quite free from ethyl alcohol.

Anal. Calcd. for C_6H_{10}: C, 87.8; H, 12.2. Found: C, 86.13; H, 11.76.

Oxidation of an Ether with Sodium Hypobromite: Conversion of Butyl-diacetone Ether to β-Butoxy-*iso*valerianic Acid.—Twelve g. of butyl-D ether is shaken with a hypobromite solution prepared from 24 g. of sodium hydroxide, 48 g. of bromine and 100 g. of ice and water. The mixture became warm, the oil dissolved and a heavy layer of bromoform appeared which, was separated, and the last traces were extracted with ether. After adding sodium bisulfite, the mixture was acidified with dil. sulfuric acid and extracted with ether; yield, 6.3 g.; b. p., 140–143°, at 10 mm.; d^{20}, 1.053. It was saturated toward bromine. While it was impure, containing some halogen, it may be considered to be mainly β-butoxy-*iso*valerianic acid from the following decomposition. Five g. of acid was refluxed for one and one-half hours with 20 cc. of 50% sulfuric acid, 10 cc. of water was added and 10 cc. distilled off. After saturating the distillate with sodium carbonate, 1.2 cc. of oil was obtained, which had the properties of butyl alcohol; b. p., 115–116°; d. (roughly), 0.81. Heated with acetic anhydride it gave a strong odor of butyl acetate. The other product which should have been produced by the decomposition, β,β-dimethylacrylic acid, could not be isolated from either the distillate or the residue.

Summary

Ethers of diacetone alcohol have not been prepared up to the present time. They could scarcely be obtained by the usual methods because of the great sensitiveness of diacetone alcohol toward acids and alkalies. In this research a series of the ethers with primary aliphatic alcohols and

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[4] Beilstein, "Handbuch der organischen Chemie," Julius Springer, Berlin, **1918**, vol. 1, p. 255.

with benzyl alcohol has been prepared by the direct addition of the alcohols to mesityl oxide with the aid of an acid catalyst. Characteristic derivatives of the keto group and reduction and oxidation products give proof of the structure.

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[CONTRIBUTION FROM THE UNITED STATES DEPARTMENT OF AGRICULTURE]

THE PREPARATION OF CHLOROVANILLIN AND SOME OF ITS DERIVATIVES[1]

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A search of the available chemical literature brought to light only a preliminary note concerning the preparation and properties of a chlorinated derivative of vanillin[2] (3-methoxy-4-hydroxybenzaldehyde). The present paper describes the preparation and properties of chlorovanillin and some of its commoner aldehydic derivatives.

The position occupied by the chlorine atom has not been definitely ascertained, although orientation experiments indicate that it enters the 5 position, *ortho* to the phenolic hydroxyl. This conclusion would be the normal one on the basis of the directing influence of the groups already present. Furthermore, bromine under an environment similar to that used in the experiments here reported enters the 5 position.[3] Finally, it has been observed that while vanillin readily couples with *p*-nitrobenzene diazonium chloride in the *ortho* position to the phenolic hydroxyl, chlorovanillin fails to couple under identical experimental conditions, an indication that the position *ortho* to the hydroxyl is occupied. None of these facts can be held as more than an indication of the position of the chlorine atom. Further study is being made of this phase of the problem.

Experimental Part

Chlorovanillin.—Seventeen g. of vanillin was dissolved in 150 cc. of glacial acetic acid, and a stream of dry chlorine was bubbled through the solution at room temperature. The chlorine was rapidly absorbed, hydrochloric acid copiously evolved and the reaction mixture warmed perceptibly. After absorption had continued for 15 minutes, glistening crystals began to separate from the solution. At this point the passage of gas was discontinued. After standing for several hours the solid was separated by suction and dried. The crude yield was 18 g. A further 3 to 4 g. may be recovered from the mother liquors. The compound is practically pure, but may be completely separated

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[1] Presented at the Los Angeles meeting of the American Chemical Society, August 3–8, 1925.

[2] Menke and Bentley, THIS JOURNAL, **20,** 316 (1898).

[3] Bromovanillin has been oriented by Brady and Dunn [*J. Chem. Soc.*, **107,** 1861 (1915)] through hydrolysis of the benzonitrile from *syn.*-bromovanillin oxime to 3-methoxy-4-hydroxy-5-bromobenzoic acid previously described by Robertson [*J. Chem. Soc.*, **93,** 792 (1908)].