[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE UNIVERSAL OIL PRODUCTS COMPANY AT ILLINOIS INSTITUTE OF TECHNOLOGY]

Catalytic Dehydrogenation and Condensation of Aliphatic Alcohols. II[1]

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In a recent paper[3] a catalytic method was presented for the preparation of ketones by the simultaneous dehydrogenation and condensation of primary alcohols. The present investigation includes extension of this method to other primary alcohols ranging from *n*-propyl to *n*-octadecyl alcohol. In addition this method was extended to the preparation of unsymmetrical ketones.

Two mixed ketones, methyl *n*-heptyl ketone and *n*-butyl *n*-nonyl ketone, were prepared from the proper mixture of alcohols. The method is recommended in particular for the preparation of unsymmetrical methyl ketones since no acetone is formed.

It was found that aldehydes undergo the same type of condensation, producing ketones in yields considerably superior to those obtained from the corresponding alcohol.

When the aldols of *n*-butyraldehyde and *n*-heptaldehyde were subjected to the same reaction conditions, excellent yields of ketones were produced directly by a catalytic decomposition reaction. The order of percentage conversion of the reactants to ketones was aldol > aldehyde > alcohol. These facts are in agreement with the previously proposed mechanism.[3]

During the course of our investigation, several compounds were made which to our knowledge have not been prepared previously. The compounds are *n*-butyl *n*-nonyl ketone, *n*-butyl-*n*-nonylcarbinol, and di-nonylcarbinol.

Experimental Part

Apparatus and Procedure.—The apparatus and procedure employed were similar to the previous investigation,[3] with the exception that a vertical furnace was used for the aldol experiments and a water-jacketed feeding buret with a needle valve for the *n*-octadecyl alcohol experiment. The chromic oxide catalyst employed was prepared similarly to catalyst 2 of the previous investigation.[3]

Reactants.—*n*-Propyl alcohol, Eastman Kodak Company, b. p. 96.0–98.0°, $n^{20}\mathrm{D}$ 1.3871; *n*-butyl alcohol, Eastman Kodak Co., b. p. 116.0–118.0, $n^{20}\mathrm{D}$ 1.3999; *n*-butyraldehyde, Carbide and Carbon Chemicals Corporation, b. p. 75.0–76.0°, $n^{20}\mathrm{D}$ 1.3810; aldol of *n*-butyraldehyde, b. p. 94.0–96.0° (6 mm.), $n^{20}\mathrm{D}$ 1.4129; *n*-hexyl alcohol, C. & C. C. C., b. p. 155.0–156.0°, $n^{20}\mathrm{D}$ 1.4190; *n*-heptyl alcohol, E. K. C., b. p. 173.5–175.0°, $n^{20}\mathrm{D}$ 1.4245; *n*-heptaldehyde, E. K. C., b. p. 154.0–155.0°, $n^{20}\mathrm{D}$ 1.4159; aldol of *n*-heptaldehyde, b. p. 135–145° (6 mm.), $n^{20}\mathrm{D}$ 1.4489; *n*-octyl alcohol, E. I. du Pont de Nemours & Company, b. p. 194.0–195.0°, $n^{20}\mathrm{D}$ 1.4315; *n*-decyl alcohol, du Pont, b. p. 230.0–231.0°, $n^{20}\mathrm{D}$ 1.4379; *n*-octadecyl alcohol, du Pont, m. p. 58.0°.

The two aldols were prepared according to the procedure of Batalin and Slavina.[4] Aldol of *n*-butyraldehyde, b. p. 94.0–95.0° at 6 mm., $n^{20}\mathrm{D}$ 1.4426. Oxime of aldol: found, b. p. 138–140° at 6 mm.; literature, b. p. 138–140° at 6 mm.[4] Aldol of *n*-heptaldehyde, b. p. 135–145° at 6 mm., $n^{20}\mathrm{D}$ 1.4489. 2,4-Dinitrophenylhydrazone of aldol: found, m. p. 125.5–126.5°; literature, m. p. 124.5°.[5]

Analysis and Identification of Products.—The products were fractionated in a Podbielniak type column. It was necessary to form the sodium bisulfite addition compound of methyl *n*-heptyl ketone in order to effect its separation from the unreacted *n*-octyl alcohol which boiled at practically the same temperature.

All derivatives prepared for the identification of the products were made by standard procedures with the exception of the secondary alcohols by the high pressure hydrogenation of the ketones as previously described.[3]

TABLE I

Reactant charged	Temp., °C.	% of theoretical yield of ketone	% unconverted reactant
n-Propyl alcohol	425	48.8	5.2
n-Butyl alcohol	400	27.8	28.3
n-Butyraldehyde	400	31.4	23.6
Aldol of *n*-butyraldehyde	400	61.0	0.0
n-Butyl alcohol	425	46.9	12.2
n-Butyraldehyde	425	58.5	0.0
n-Amyl alcohol	375	55.5	8.85
n-Amyl alcohol	425	47.0	5.5
n-Hexyl alcohol	425	46.5	16.7
n-Heptyl alcohol	425	57.5	11.6
n-Heptaldehyde	400	66.9	2.5
Aldol of *n*-heptaldehyde	400	82.8	0.0
n-Octyl alcohol	400	56.0	13.3
n-Octyl alcohol (125–135 mm. pressure)	400	73.9	8.3
n-Decyl alcohol	400	83.2	3.5
n-Octadecyl alcohol	400	47.6	19.8
25% by vol. ethyl alcohol 75% by vol. *n*-octyl alcohol	425	CH_3COCH_3 0.0 $CH_3COC_7H_{15}$ 41.7 $C_7H_{15}COC_7H_{15}$ 26.2	C_2H_5OH 0.0 $C_8H_{17}OH$ 5.85
50% by vol. *n*-amyl alcohol 50% by vol. *n*-decyl alcohol	400	$C_4H_9COC_4H_9$ 13.5 $C_4H_9COC_9H_{19}$ 27.2 $C_9H_{19}COC_9H_{19}$ 20.9	$C_5H_{11}OH$ 2.4 $C_{10}H_{21}OH$ 1.5

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(2) Universal Oil Products Company Research Fellow.

(3) Komarewsky and Coley, THIS JOURNAL, **63**, 700 (1941).

(4) Batalin and Slavina, *J. Gen. Chem.* (U. S. S. R.), **7**, 202 (1937).

(5) Backes, *Compt. rend.*, **196**, 277 (1933).

(a) IDENTIFICATION OF PRODUCTS

Compound	Found m. p., °C.	Lit. m. p., °C.	Derivative	Found m. p., °C.	Lit. m. p., °C.
Diethyl ketone	...	...	Semicarbazone	138.0	138.0[12]
Di-*n*-propyl ketone	...	...	Semicarbazone	134–135	134.0[12]
Di-*n*-butyl ketone	...	...	Semicarbazone	89.5–90.0	90.0[13]
Di-*n*-amyl ketone	14–15	14.0[7]	Di-*n*-amylcarbinol	15–16	16+[14]
Di-*n*-hexyl ketone	32.0–32.5	33.0[7]	Di-*n*-hexylcarbinol	40.0–40.5	41–42[15]
Di-*n*-heptyl ketone	39.0–40.0	39.0[8]	Di-*n*-heptylcarbinol	49.0	49.5–50[16]
			Oxime	21.5	19.5–20[16]
Methyl *n*-heptyl ketone	...	...	Semicarbazone	119.0	119.0–120[17]
n-Butyl *n*-nonyl ketone[9]	25.5–26.0	...	*n*-Butyl-*n*-nonylcarbinol[18]	28.5	......
Di-*n*-nonyl ketone	58.0	58–59[10]	Di-*n*-nonylcarbinol[19]	65.5	......
Di-*n*-heptadecyl ketone (Stearone)	88.0	88.0[11]	Di-*n*-heptadecylcarbinol	89.5–90.0	89.5[11]

Gas Analysis.—The gaseous product was analyzed by the Gockel method.[6]

Tables I and Ia represent the results of the experiments. A single experiment was carried out to see whether the yields might be improved with the use of reduced pressure. *n*-Octyl alcohol at 125–135 mm. pressure yielded 73.9% di-*n*-heptyl ketone, compared to 56.0% conversion obtained at atmospheric pressure.

The fact that no acetone was obtained when a mixture of ethyl and *n*-octyl alcohols was subjected to the catalytic reaction is interesting, but will require further study before any detailed discussion can be presented.

Summary

1. The preparation of ketones by the catalytic dehydrogenation and condensation of primary aliphatic alcohols was extended to *n*-propyl, *n*-butyl, *n*-amyl, *n*-decyl and *n*-octadecyl alcohols.

2. Two mixed ketones, *n*-butyl *n*-nonyl ketone and methyl *n*-heptyl ketone, were prepared by subjecting mixtures of *n*-amyl and *n*-decyl alcohols, and of ethyl and *n*-octyl alcohols to the same reaction.

3. Aldehydes and aldols were found to undergo the same reaction with the production of higher ketones.

4. The following new compounds were prepared for the first time: *n*-butyl *n*-nonyl ketone, *n*-butyl-*n*-nonylcarbinol and di-nonylcarbinol.

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(6) "U. O. P. Laboratory Test Methods for Petroleum and its Products," Chicago, 1940, p. 33.

(7) Sabatier and Mailhe, *Compt. rend.*, **158**, 832 (1914).

(8) Mailhe, *ibid.*, **157**, 220 (1913).

(9) *Anal.* Calcd. for $C_{14}H_{28}O$: C, 79.17; H, 13.29. Found: C, 78.50; H, 12.76.

(10) Briese and McElvain, THIS JOURNAL, **55**, 1697 (1933).

(11) Easterfield and Taylor, *J. Chem. Soc.*, **99**, 2300 (1911).

(12) Michael, THIS JOURNAL, **41**, 417 (1919).

(13) Pickard and Kenyon, *J. Chem. Soc.*, **101**, 629 (1912).

(14) Hess and Bappert, *Ann.*, **441**, 137 (1925).

(15) Kipping, *J. Chem. Soc.*, **57**, 535 (1890).

(16) Kipping, *ibid.*, **63**, 452 (1893).

(17) Haller and Lassieur, *Compt. rend.*, **150**, 1018 (1910).

(18) *Anal.* Calcd. for $C_{14}H_{30}O$: C, 78.43; H, 14.10. Found: C, 78.04; H, 13.57.

(19) *Anal.* Calcd. for $C_{19}H_{40}O$: C, 80.28; H, 14.08. Found: C, 80.64; H, 14.02.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MISSOURI]

Isomerization of Naphthalyl Chloride[1]

BY H. E. FRENCH AND J. E. KIRCHER

The space relationships of the carboxyl groups of 1,8-naphthalic acid permit the easy elimination of water with the formation of the unusually stable cyclic anhydride. The ease of formation, and the stability of this cyclic structure suggest the possibility of a cyclic, unsymmetrical structure for the di-acid chloride, in addition to the symmetrical compound which would normally be expected from this acid. The existence of such isomers appears probable by analogy with the structurally similar phthalyl chloride, which gives reactions of both structures depending on experimental conditions. That the naphthalyl chloride exists in the symmetrical form has been demonstrated. Mason[2] obtained symmetrical dialkyl esters by the action of various alcohols on the chloride, and the symmetrical di-anilide by the action of aniline.

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[1] This work is part of the thesis material to be submitted by Mr. Kircher to the graduate faculty of the University of Missouri.

[2] Mason, *J. Chem. Soc.*, **125**, 2116, 2119 (1924).