for those anhydrides not previously reported in the literature.

TABLE II

	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
Tridecylic	76.04	76.27	12.27	12.28
Pentadecylic	77.19	77.68	12.53	12.58
Margaric	78.55	78.31	12.79	12.60

Discussion

The melting points of the anhydrides alternate in the opposite sense to those of the acids. Up to valeric the swing is wide but from there on it is small, each odd anhydride melting only about 2° above the mean evens. From heptylic to stearic, the average of the melting points of the anhydrides is 1.2° above the average of the acids. Above valeric the alternation is much smaller for the anhydrides than for the acids.

The anhydrides crystallize in leafy plates and are soluble in the usual organic solvents. Limited quantities of the acids, usually one gram or less, prevented the determination of other properties.

This problem was suggested by Dr. E. Emmet Reid, Research Adviser, University of South Carolina, and to him the authors wish to express their appreciation for his valuable help. The melting points of the acids given in Fig. 1 were taken from the same authors.[2]

Summary

The anhydrides of the normal aliphatic saturated monobasic acids from heptylic to stearic were prepared and their melting points determined. Curves are given for the melting points, through stearic, of the acids and anhydrides. The melting points, above butyric, of the anhydrides form practically a smooth curve, those derived from the odd carbon acids being slightly higher than the even on the mean curve.

COLUMBIA, SOUTH CAROLINA RECEIVED JULY 31, 1940

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE UNIVERSAL OIL PRODUCTS COMPANY AT ILLINOIS INSTITUTE OF TECHNOLOGY][1]

Catalytic Dehydrogenation and Condensation of Aliphatic Alcohols

BY V. I. KOMAREWSKY AND J. R. COLEY[2]

In the course of our investigation of complex action catalysts it was found that aromatic hydrocarbons were formed by the simultaneous dehydration and dehydrogenation of normal aliphatic alcohols containing six, seven and eight carbon atoms.[3] It was believed that the dehydration was accomplished by alumina and dehydrogenation–cyclization by chromia.

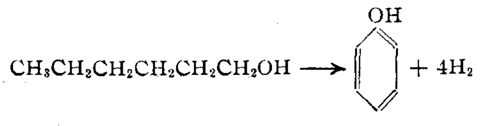
The work of previous investigators[4] indicated, however, that chromia might be a dehydrating as well as dehydrocyclizing catalyst. Therefore, it was of interest to see if chromia alone could carry on a similar complex reaction with alcohols. When the *n*-hexyl, *n*-heptyl, and *n*-octyl alcohols were subjected to the action of various preparations of chromia, complete absence of water in the reaction products indicated that there was no dehydration of the alcohols.

A large percentage of the product obtained was found to be symmetrical ketones formed by the condensation of two molecules of the alcohols charged, according to the equation

$$2RCH_2CH_2OH \longrightarrow RCH_2COCH_2R + CO + 3H_2$$

It seems reasonable that the change takes place through the following steps: (1) dehydrogenation to aldehyde, (2) aldol condensation, (3) removal of carbon monoxide from the aldehyde group of the aldol leaving a secondary alcohol, (4) dehydrogenation to ketone. This mechanism seems to be the most probable since there is no water addition or evolution as in a similar reaction with ethyl alcohol described by Kagan.[5]

At higher temperatures (475–525°) in addition to the ketone formation a direct dehydrocyclization of alcohols took place with the production of small amounts of phenols according to the equation



This result stands out in contrast to the reactions obtained using chromia–alumina catalyst[3] with the same alcohols, and proves that the chro-

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(1) A consolidation of Armour Institute of Technology and Lewis Institute.

(2) Universal Oil Products Company Research Fellow.

(3) Komarewsky, Riesz and Thodos, THIS JOURNAL, **61**, 2525 (1939).

(4) Sabatier, "Catalysis in Organic Chemistry," D. Van Nostrand Co., New York, N. Y., 1923, p. 22.

(5) Kagan, Sobolev and Lyubarskii, *Ber.*, **68**, 1140 (1935).

mia–alumina was a true "complex action" catalyst since alumina performed the dehydrating and chromia the dehydrocyclizing action.

Experimental Part

Apparatus and Procedure.—The alcohols were charged at a rate of 4–5 cc. per hour over 119 cc. of 8–10 mesh catalyst. The Pyrex reaction tube, 15 mm. inside diameter, was contained in a horizontal block type electrically heated furnace with automatic temperature control. The liquid products were condensed by means of a water condenser into a graduated receiver and the gas collected in a gas holder. The average time on stream was seven hours. A close check on the rate and direction of the reaction was kept during the run by means of the rate of gas evolution and periodic measurement of the refractive index of the product. During the run a layer of carbon was deposited on the catalyst surface. The catalyst was regenerated by passing a slow stream of air through the reaction tube until the carbon layer was completely oxidized. After flushing the tube thoroughly with nitrogen, hydrogen was introduced and passed over the catalyst, until the evolution of water stopped. The catalyst was then considered ready for use. The catalyst was freshly regenerated before each run.

Alcohols.—*n*-Hexyl alcohol, Eastman Kodak Company, b. p. 155.0–156.0, $n^{25}D$ 1.4170; *n*-heptyl alcohol, Eastman Kodak Company, b. p. 173.5–175°, $n^{25}D$ 1.4225; *n*-octyl alcohol, E. I. du Pont de Nemours & Company, b. p. 194–195°, $n^{25}D$ 1.4295. Each alcohol was carefully distilled and dried before using.

Catalysts.—Four different chromia catalysts were used in this investigation. Catalyst 1 was prepared by the precipitation of chromium hydroxide from a cold 1 *N* solution of chromium nitrate by 1 *N* sodium hydroxide. The precipitate was washed anion free, dried at 110°, screened to 8–10 mesh, and then heated in an atmosphere of hydrogen at slowly increased temperatures up to 500°. Catalyst 2 was made by redissolving precipitated chromium hydroxide in excess sodium hydroxide. The chromite solution on standing overnight gave a fine precipitated chromium hydroxide gel. Catalyst 3 was made by the ignition of chromium nitrate followed by heating in a stream of hydrogen up to 500°. Catalyst 4 was made by precipitation of chromium hydroxide gel from a cold 0.1 *N* chromium nitrate solution by 0.1 *N* ammonium hydroxide. The precipitate was washed and dried as with catalysts 1 and 2.

The activity of the catalysts was tested by the reaction of aromatization of *n*-heptane to toluene at 475° and at a charging rate of 5 cc. per hour. The results were as follows: Catalyst 1, 100% aromatization; 2, 7%; 3, 7%; 4, 100%.

It is important to note that with the exception of catalyst 4 all the catalysts had the same activity in the reaction of ketone and phenol formation. No phenol was formed using catalyst no. 4 at 475°, and only 3.6% of ketone was produced at 425° with this catalyst. Since catalyst no. 4 was found to be a very active cyclizing catalyst when tested with *n*-heptane, the inability of this catalyst to produce phenols requires an explanation. This catalyst gave a highly aromatic product with alcohols, but it consisted of light boiling fractions such as benzene and toluene. This catalyst was in effect too active, since all of the alcohol was probably immediately dehydrogenated to the aldehyde thus eliminating the possibility of the formation of phenols. Catalyst 2 was used for the majority of the runs.

(1) **Analysis of Products. Analysis of Liquid Product Obtained at Temperature Range** (350–450°).—The product was fractionated in a Podbielniak type column. The column was eighty-five centimeters long and was calculated to be equivalent to twelve theoretical plates as shown by the distillation of various mixtures of pure hydrocarbons. The product was found to consist largely of unreacted alcohols, ketone and high boiling bottoms. The ketones were identified by boiling and melting point, elementary analysis, molecular weight as well as the formation of derivatives (secondary alcohol and oximes). The secondary alcohols were obtained by high pressure hydrogenation in the presence of nickel–silica catalyst[6] at 120° and 80 atmospheres of initial pressure of hydrogen. The oximes were prepared by the standard procedure.

(2) **Analysis of Liquid Products Obtained at High Temperatures (475–525°).**—A characteristic phenolic odor showed that a certain amount of the alcohol underwent a dehydrocyclization to a phenol. The phenol was separated by repeated extractions with 0.2 *N* potassium hydroxide. The alkaline solution of the phenol was neutralized with 0.2 *N* sulfuric acid. The phenol content of a portion of this solution was estimated by means of a colorimetric analysis as suggested by Wetlaufer, Van Natta and Quattlebaum.[7] The other part of the solution was extracted with ether. The ether extract after drying and separation of ether was distilled and resulted in a material boiling 190–210°. This material was identified as phenols by the formation of aryloxyacetic acid and phenyl urethan derivatives. The product remaining after extraction of the phenol was washed, dried, distilled and analyzed as before.

Gas Analysis.—The gaseous product was analyzed by the Gockel method.[8]

Discussion of Results.—Table I represents the results of the experiments. The optimum temperature for the ketone formation varied with the alcohol charged, but the average temperature

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[6] Ipatieff and Corson, *Ind. Eng. Chem.*, **30**, 1039 (1938).

[7] Wetlaufer, Van Natta and Quattlebaum, *Ind. Eng. Chem., Anal. Ed.*, **11**, 438–439 (1939).

[8] "U. O. P. Laboratory Test Methods for Petroleum and its Products," Universal Oil Products Company, Chicago, 1937, p. 162.

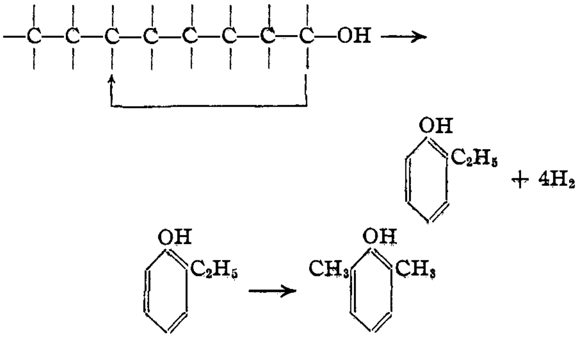
TABLE I

			Liquid product					Reaction gases								
										Gas analysis, %						
Alcohol charged	Temp., °C.	Grams charged	Liquid recovery, g.	n^{25}_D	% ketone by wt.	% unconverted alcohol	% phenols	Air free, g.	Total vol. in cc.	H_2	CO	CO_2	Total olefins	Paraffins	Paraffin index
n-Hexyl	425	18.8	14.6	1.4310	39.0	16.7	0	2.37	6450	78.2	7.9	8.6	2.8	2.5	1.9
n-Hexyl	525						2.5								
n-Heptyl	400	26.8	24.8	1.4283	30,7	36.2	0	1.11	4550	88.5	4.1	6.5	0.0	0.9	2.5
n-Heptyl	425	25.6	20.7	1.4335	49.0	11.6	0	2.60	7490	80.5	8.8	6.5	1.7	2.5	1.7
n-Heptyl	450	27.9	19.2	1.4465	35.2	0	0	5.22	12800	70.7	13.3	5.4	4.5	6.1	1.4
n-Heptyl	525						2.5								
n-Octyl	350	39.2	27.4	1.4300	0	49.5	0	0.470	2153	91.5	3,3	3.1	0.0	2.1	2.5
n-Octyl	400	52.2	43.65	1.4348	48.7	13,3	0	2.95	10570	83.5	8.5	5.0	1.0	2.2	1.1
n-Octyl	475	100	37.0	1.4750	6.1	0.0	2.7	25.15	47850	65.1	12.0	4.1	6.6	11.7	2.0

Identification of Products

Compound	Found m. p., °C.	Lit. m. p., °C.	Derivative	Found m. p., °C.	Lit. m. p., °C.
Di-*n*-amyl ketone	14.5	14–16[9]	Di-*n*-amylcarbinol	15–16	16+[10]
Di-*n*-hexyl ketone	32–33	33.0[11]	Di-*n*-hexylcarbinol	40.0–40.5	41–42[11]
Di-*n*-heptyl ketone	39–40	39–40[12]	Di-*n*-heptylcarbinol	49.0	49.5–50[12]
			Oxime	21.5	19.5–20[12]
Phenol			Aryloxyacetic acid	99	99[13]
o-Cresol			Aryloxyacetic acid	149–152	152[13]
2,6-Dimethylphenol			Aryloxyacetic acid	136–138	139[13]
			Phenyl urethan	131.5–133	133[14]

was 425°. The maximum time on stream for which the catalyst was effective was not determined. At the end of a ten-hour run the catalyst was still functioning with undiminished activity. The *n*-hexyl and *n*-heptyl alcohols were dehydrocyclized, as expected, to phenol and *o*-cresol, respectively. However, 2,6-dimethylphenol was formed from octyl alcohol. This phenol is perhaps formed by the isomerization of an intermediate product *o*-ethylphenol.



The temperature at which phenol production began was 475°. The per cent. of phenol in the product increased with increased temperature beyond 475°, but the liquid recovery dropped off proportionally, so the optimum temperature for phenol formation may be said to be 475°. Catalysts 1, 2 and 3 were equally effective in the production of both ketones and phenols. Catalysts nos. 2 and 3 had relatively poor activity for cyclization; however, their ability to cyclize hydrocarbons and to produce phenols from alcohols was approximately equal.

If the ketone is produced by the mechanism we have proposed, there should be present in the gaseous product twenty-eight grams of carbon monoxide and six grams of hydrogen for each mole of ketone produced. The average weight of carbon monoxide and hydrogen obtained per mole of ketone formed was twenty-four and seven grams, respectively.

Summary

1. Under the action of chromia catalyst the aliphatic alcohols undergo a reaction of dehydrogenation–condensation of two molecules of alcohols to form a symmetrical ketone.

2. This reaction was accomplished with normal alcohols containing six, seven, and eight carbon atoms.

3. The mechanism of this reaction is proposed through the formation of an aldol.

4. At higher temperatures in addition to the ketone formation, a direct dehydrocyclization of the alcohols takes place with the formation of small amounts of phenols.

CHICAGO, ILLINOIS RECEIVED AUGUST 3, 1940

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(9) Beilstein, "Handbuch der organischen Chemie," Vol. I, p. 714.

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

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

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

(13) Field, Dempster and Tilson, *Ind. Eng. Chem.*, **32**, 489 (1940).

(14) Steinkopf and Hopner, *J. prakt. Chem.*, **113**, 137 (1926).