[A COMMUNICATION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

Catalytic Dehydrogenation of Alcohols in the Liquid Phase Using Ethylene as a Hydrogen Acceptor

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The catalytic dehydrogenation in the vapor phase of alcohols to aldehydes has proved to be a useful process. However, since liquid phase methods of hydrogenation are more useful in the laboratory than vapor phase methods, it seemed worth while to investigate the feasibility of dehydrogenations in the liquid phase. Since the reaction $RCH_2OH \rightleftarrows RCHO + H_2$ is a reversible one, it is necessary to make some provision for the removal of the hydrogen if the dehydrogenation of an alcohol is to be carried out in a closed system. Ethylene is readily hydrogenated to ethane and therefore appeared to be a suitable hydrogen acceptor.

A survey of the available catalysts and a series of preliminary tests made against hexanol-1 indicated that unless the catalyst contained copper chromite the yields of aldehyde were quite low. However, a catalyst which also contained zinc, nickel and barium was, in several cases, more resistant toward deactivation and gave less of condensation products. A catalyst which did not contain barium lost its activity very quickly. The catalyst containing the four metals copper, zinc, nickel and barium would often show as high an activity after being used four times as it would during the first run. The presence of both zinc and nickel in the catalyst seemed rather essential in order to prevent condensation or polymerization of the aldehyde in the reaction mixture. One other advantage of the mixed catalyst was that the exact proportion of catalyst to alcohol was less important than for copper chromite. The latter often gave good results with one ratio of catalyst to alcohol and poor results with a somewhat different ratio.

Raney nickel could also be used as a catalyst, but the yields were low, the reaction time required was much longer and the optimum pressure of ethylene was much lower than for the chromite catalysts.

The yield of aldehyde obtained from a given alcohol is a function of the amount and kind of catalyst, temperature and duration of reaction, type of equipment, and the purity and pressure of the ethylene. In general, however, it was found that the best yields of aldehyde were obtained using 40 g. of the alcohol, 0.5 to 2.5 g. of catalyst under a pressure of 70 to 130 atm. of ethylene at 280° for an hour and a half. Over 100 dehydrogenations were made and serve as the basis for the conclusions given above and the data listed in Table I.

TABLE I

DEHYDROGENATION OF ALCOHOLS[a]

Alcohol	Catalyst, g.	C_2H_4, atm.	Yield ald., %	Alcohol recovered, %
n-Butyl	2.5 (a)	133	26	41
i-Butyl	2.5 (a)	120	51	17
i-Butyl	0.5 (b)	115	39	39
Neopentyl	2.5 (a)	115	62	15
Neopentyl	0.5 (b)	115	45	37
n-Hexyl	.5 (a)	85	34	30
2-Et-hexyl	2.5 (a)	78	63	3
2-Et-hexyl	0.5 (b)	72	60	13
Dodecyl	.5 (a)	48	39	38
Dodecyl	.25 (b)	49	33	41
Heptanol-2	2.5 (b)	105	77	9
Heptanol-4	2.5 (a)	145	60	22

[a] Duration of reactions 1.5 hours except for dodecyl (0.75 hour) and heptanol-2 (3 hrs.). The pressure recorded is that at 280° at which the dehydrogenations occurred. The original pressure at room temperature was about 40% of that at 280°. Catalyst (a) is the copper, zinc, nickel, barium chromite, while (b) is the one without zinc and nickel. Forty grams of the alcohol was used except for *i*-butyl where 30 g. was subjected to dehydrogenation.

Three primary alcohols with no substituent in the α-position, *i. e.*, *n*-butyl, *n*-hexyl and *n*-dodecyl alcohols gave the corresponding aldehydes in yields of 26, 31 and 39%, respectively, under the optimum conditions. Three primary alcohols having a substituent in the α-position, *i. e.*, *i*-butyl, neopentyl and 2-ethylhexyl gave the corresponding aldehyde in yields of 51, 62 and 63%, respectively. If allowance is made for the alcohols recovered, the yields of aldehyde from all of the six alcohols are in the range of 45 to 70%. Two secondary alcohols, *i. e.*, heptanol-2 and heptanol-4, gave the corresponding ketones in yields of 60 to 77%. All of these yields could be increased if larger quantities of the reaction mixtures were submitted to more complete fractionation. Methyl, ethyl and benzyl cellosolves could not be dehydrogenated successfully.

The yield of aldehyde is lower if the pressure of ethylene is much in excess of that required to hold in the reaction vessel an amount of ethylene molecularly equivalent to the amount of alcohol. For example, the yield of aldehyde from 2-ethylhexanol-1 was only a little more than half as great under a pressure of 185 atm. of ethylene as under 68 to 75 atm. Presumably this is because at the higher pressure of ethylene the catalyst is so covered with adsorbed ethylene that it is not effective for dehydrogenation. When nitrogen was substituted for ethylene as a means of keeping the reactants in the liquid phase, the formation of aldehydes proceeded to the extent of only a few per cent.

The extent of dehydrogenation of an alcohol to an aldehyde can be increased by increased time or temperature of reaction, but the actual yield of aldehyde is decreased because it is converted to higher molecular weight compounds. With such an aldehyde as trimethylacetaldehyde or 2-ethylhexanal almost all the alcohol may be caused to react before the aldehyde undergoes condensation to any great extent. However, with the straight chain alcohols better yields of aldehydes are obtained if the reaction is stopped while there is still a considerable amount of unchanged alcohol.

Preparation of Catalysts.—Copper chromite containing barium was prepared by the standard procedure.[1]

The copper, zinc, nickel, barium chromite catalyst was prepared by a similar procedure. A solution of 72 g. of copper nitrate ($Cu(NO_3)_2 \cdot 3H_2O$), 87 g. of nickel nitrate ($Ni(NO_3)_2 \cdot 6H_2O$), 57 g. of anhydrous zinc nitrate, 26 g. of barium nitrate, and 3 ml. of nitric acid in 900 ml. of water was heated to 80° and added to a solution in 900 ml. of water at 25° of 126 g. ammonium dichromate ($(NH_4)_2Cr_2O_7$) and 190 ml. of 28% ammonia. The mixture was allowed to stand for thirty minutes in a cold water-bath with occasional stirring. The precipitate was filtered, the cake well pressed and washed with 50 ml. of water. After the cake was sucked as dry as possible, it was dried at 105–110° for twelve hours and pulverized. The yield was 181 g.

The mixture of ammonium chromates was decomposed in three portions in a casserole as in the case of copper chromite. After the decomposition was apparently complete, the bottom of the casserole was kept at a dull red heat for two minutes. The powder was stirred with 600 ml. of 5% acetic acid at room temperature for five minutes. It was then filtered and washed with 600 ml. of water in several portions. The material was dried overnight at 105°, pulverized and dried for an hour at 105°. The yield was 124 g.

The method of carrying out the dehydrogenations was essentially the same as in a hydrogenation except that ethylene instead of hydrogen was used. In a typical run the ethylene was admitted to a pressure of 47 atm. in a steel reaction vessel having an internal volume of 270 ml. containing 40 g. of an alcohol and 2.5 g. of catalyst. When the reaction vessel was heated with shaking to 280° the pressure in the vessel was 100 atm.

After the completion of the reaction, the reaction vessel was cooled to room temperature, the catalyst removed by centrifuging and the mixture of products submitted to fractionation through a modified Widmer column having a spiral 15 cm. in length with one turn of the helix per cm.

The isolation of dodecanal by fractionation is difficult and confusing, because of the formation of a solid complex of the aldehyde and dodecanol, because there are solid and liquid forms of the aldehyde, and because of the tendency of the aldehyde to polymerize.[2] The preferred procedure for the isolation of the aldehyde was as follows. The product of dehydrogenation from 40 g. of alcohol was dissolved in ether, separated from the catalyst and rapidly distilled. The portion b. p. 110–190° (18 mm.) (31.5 g.) was dissolved in an equal amount of ether and stirred for six hours with a strong solution of sodium bisulfite composed of 35 g. of bisulfite dissolved in 55 ml. of water. The white solid was then filtered off, sucked as dry as possible, and mixed with 20 ml. of ethyl alcohol. The mixture was again filtered and the solid dried in a desiccator for one day, 25 g. was obtained. The yields given in Table I for dodecanal are based upon the weight of addition product isolated.

The aldehyde was recovered by dissolving the addition product in four times its weight of water and heating with four times the theoretical amount of sodium carbonate for fifteen minutes. After cooling the mixture was extracted with ether and the aldehyde distilled at138–139° (22 mm.). The amount of aldehyde recovered was only 50 to 65% of the theoretical amount based upon the weight of the bisulfite compound. The aldehyde can also be separated from the alcohol by careful fractionation, but due to the length of time required about half of the aldehyde was polymerized in the process. The aldehyde distilled after separation as the bisulfite addition compound analyzed to be 97% pure, while that by fractionation was only 88% pure. Analysis of the crude product distilling in the range 110–190° (18 mm.) showed 49% aldehyde.

Analyses for hexaldehyde and dodecanal were made by means of the 2,4-dinitrophenylhydrazones.[3] The procedure was modified in the case of dodecanal as follows. Approximately 0.4 millimole of aldehyde was dissolved in 35 ml. of ethyl alcohol and 35 ml. of a saturated solution of 2,4-dinitrophenylhydrazine in 2 *N* hydrochloric acid added. The reagent was added drop by drop from a buret until the hydrazone began to precipitate, after which it was added faster. After standing for two hours, it was fil-

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[1] Folkers, Connor and Adkins, THIS JOURNAL, **53**, 2012 (1931); **54**, 1138 (1932); Adkins, "Reactions of Hydrogen, etc., "Univ. of Wisconsin Press, Madison, Wis., 1937, p. 13; "Organic Syntheses," Vol. 19, John Wiley and Sons, Inc., New York, N. Y., 1939, note 11, p. 33.

[2] Zaar, *J. prakt. Chem.*, **132**, 163 (1931).

[3] Iddles, Low, Rosen and Hart, *Ind. Eng. Chem., Anal. Ed.*, **11**, 102 (1939).

tered on a Gooch crucible, washed with a mixture of 25 ml. of 2 *N* hydrochloric acid and 25 ml. of ethyl alcohol, then with 75 ml. of 2 *N* hydrochloric acid. The precipitate was then washed with water until free of chlorides, and dried in an oven at 95° until it reached a constant weight.

The purest sample of dodecanal (0.1431 g.) gave 0.2744 g. of the hydrazone, or 97.2% of the amount which should be obtained if the aldehyde were pure and was quantitatively converted to the hydrazone which was isolated and purified without loss.

The aldehydes and ketones were characterized by the following derivatives: *n*-butyraldehyde, b. p. 70–75° (740 mm.), 2,4-dinitrophenylhydrazone, m. p. 121–122°; *i*-butyraldehyde, b. p. 63–68° (740), gave isobutylidene malonic ester; trimethylacetaldehyde, b. p. 74–76° (739); 2,4-diphenylhydrazone, m. p. 210–211°, semicarbazone, m. p. 191–192°; *n*-hexanal, b. p. 126–129° (740), 2,4-dinitrophenylhydrazone, m. p. 106°, semicarbazone, m. p. 112–113°; 2-ethylhexanal, b. p. 161–166° (737), 2,4-dinitrophenylhydrazone, m. p. 122–123°; *n*-dodecanal, b. p. 138–139° (22), 2,4-dinitrophenylhydrazone, m. p. 107–108°, semicarbazone, m. p. 102–103°; heptanone-2, b. p. 147–148° (747), m. p. semicarbazone, 122–123°; heptanone-4, b. p. 142–145°.

Summary

A practical and useful method has been described whereby the alcohols of four or more carbon atoms per molecule may be dehydrogenated to aldehydes or ketones in the liquid phase. The reaction is carried out under a pressure of ethylene, which serves as an acceptor for the hydrogen split out of the alcohol under the influence of a suitable catalyst, such as copper chromite or preferably a mixed catalyst containing copper, zinc, nickel and barium chromites.

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Optical Properties of Phenylthiourea Derivatives[1]

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Phenylthiourea derivatives are useful for the characterization of primary and secondary amines.[2] To enhance this usefulness, and particularly to make it possible to distinguish more readily between members of homologous series, the optical properties of these substances have now been studied.

The symmetrical derivatives were prepared from aromatic amines and carbon bisulfide; the unsymmetrical from phenyl isothiocyanate and various amines. Their melting points, which are in reasonable agreement with the values recorded in the literature, and the observed optical properties are collected in the table.

TABLE I

DERIVATIVES OF PHENYLTHIOUREA

Derivative	M. p., °C.	Habit	Ext.	Opt. ax. angle 2 *V* Obsd.	Calcd.	Refractive index α	β	γ
N-Methyl-N′-	112–113	Tab.	Par.		88	1.662	1.695	1.730
N-Ethyl-N′-	101–102	Tab.	Par.		82	1.650	1.680	1.720
N-*n*-Propyl-N′-	64	Aci.	Par.	$56^{1}/_{3}$	56	1.690	1.700	1.735
N-*n*-Butyl-N′-	63	Tab.	Sym.	$36^{2}/_{3}$		1.590	1.603	1.775 (est.)
N-*n*-Amyl-N′-	68–69	Tab.	Sym.	$20^{1}/_{2}$		1.620	1.630	1.76 (est.)
N-*i*-Amyl-N′-	101–102	Tab.	Sym.	Large[c]		1.620	1.700	
N-β-Hydroxyethyl-N′-	138	Aci.	Par.	. .[c]		1.675	1.692	
N,N′-Di-[a]	154	Tab.	Sym.	82		1.645	1.720	High
N-*o*-Tolyl-N′-	138	Aci.	Par.	$35^{1}/_{3}$	36	1.655	1.663	1.74 (est.)
N-*p*-Tolyl-N′-	139–140	Aci.	Par.	63		1.610	1.675	1.8 (est.)
N,N′-Di-*o*-tolylthiourea	158	Aci.	Par.	$66^{2}/_{3}$	$64^{1}/_{2}$	1.655	1.663	1.725
N,N′-Di-*p*-tolylthiourea[b]	178	Aci.	Par.[d]	$42^{1}/_{2}$	46	1.675	1.685	1.74 (est.)
N-*o*-Chlorophenyl-N′-	158	Aci.	Par.	$29^{1}/_{3}$			1.72	

[a] Arzruni (*Ber.*, **19,** 1821 (1886)) reports this substance to form rhombic crystals of short prismatic habit, with positive double refraction and apparent axial angle in sodium light, 2H in bitter-almond oil, of $95^{2}/_{3}$°. [b] Levin (*Z. Krist.*, **7,** 519 (1883)) reports this substance as rhombic. [c] Sign negative (doubtful). [d] Sometimes oblique.

As can be seen from the table the normal propyl, butyl and amyl derivatives, all of which melt within a range of 6°, can be distinguished

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(1) Presented before the Division of Microchemistry at the 99th meeting of the American Chemical Society, Cincinnati, Ohio.

(2) The preparation and properties of the primary aromatic amine derivatives have been given by Otterbacher and Whitmore (THIS JOURNAL, **51,** 1909 (1929)).