

1-(Carbethoxyhydroxybenzyl)-6-methoxy-7-benzyloxy-1,2,3,4-tetrahydroisoquinoline VI.—A suspension of 2.28 g. of the above dihydro compound in 50 cc. of absolute alcohol and 50 mg. of PtO_2 were shaken at room temperature under 25 lb. pressure of hydrogen for 1.5 hours, *i.e.*, until no more hydrogen was absorbed. After filtering, the solution no longer possessed the original blue fluorescence. Upon concentration to a small volume, a non-crystalline precipitate was obtained by the addition of ether. The compound was dissolved in water, made alkaline with dilute sodium hydroxide, and the oil extracted with ether. After drying, the solution was saturated with dry hydrogen chloride, and a gummy product was produced. It was dissolved in benzene and diluted with ligroin (b.p. 60–72°) until turbid. After several days at room temperature, the compound slowly crystallized; m.p. 156–166°. It was recrystallized from ethanol-ether; m.p. 162–165°.

Anal. Calcd. for $\text{C}_{27}\text{H}_{30}\text{NO}_3\text{Cl}$: C, 67.00; H, 6.25; N, 2.90. Found: C, 67.19; H, 5.76; N, 2.94.

The yield was low due to losses during the above crystallization.

dl-Coclaurine Hydrochloride VII.—One gram of the above compound was warmed on the steam-bath with 20 cc. of 20% hydrochloric acid. After one-half hour, the material had dissolved, and the equivalent amount of carbon dioxide was collected. While warming was continued, colorless crystals appeared. After cooling, they were filtered off. The product was recrystallized from water; m.p. 251–254° dec.; dried *in vacuo* over phosphorus pentoxide; m.p. 259–261°.

Anal. Calcd. for $\text{C}_{17}\text{H}_{20}\text{NO}_3\text{Cl}\cdot\text{H}_2\text{O}$: C, 60.00; H, 6.40. Found: C, 60.07; H, 6.41.

Dried *in vacuo* at 120° over P_2O_5 ; m.p. 250–252°.

Anal. Calcd. for $\text{C}_{17}\text{H}_{20}\text{NO}_3\text{Cl}\cdot\frac{1}{2}\text{H}_2\text{O}$: C, 61.72; H, 6.53; Cl, 10.72. Found: C, 61.67; H, 6.40; Cl, 10.71.

dl-Coclaurine Hydrochloride without Isolating the Intermediate Tetrahydroisoquinoline.—A solution of 11.4 g. of 1-(4-carbethoxyhydroxybenzyl)-6-methoxy-7-benzyloxy-3,4-dihydroisoquinoline hydrochloride was prepared in 200 cc. of absolute alcohol with slight warming. After adding 100 mg. of PtO_2 , it was reduced at 25° and 185 lb. pressure of hydrogen until one mole equivalent was absorbed. The clear solution was filtered and concentrated to dryness. To the resinous material obtained, 200 cc. of 20% hydrochloric acid was added, and the mixture warmed on the steam-bath for approximately 1 hour when crystals started to appear. The solution was filtered rapidly and the filtrate cooled. The colorless crystals were collected and dried; yield 6.1 g. or 80%.

dl-Tetramethylcoclaurine Methylsulfate VIII.—A solution of 2.2 g. of *dl*-coclaurine hydrochloride was treated with 33.0 cc. of *N* NaOH and 5.94 g. of methyl sulfate and warmed on the steam-bath. Within 10 minutes the two layers disappeared. The treatment of alkali and dimethylsulfate was repeated twice and cooled. The solution was extracted with ether which was discarded and then three times with chloroform. The chloroform extract was dried and blown down *in vacuo* to a small volume. The oily residue was treated with a small amount of alcohol and ethyl acetate and again blown down *in vacuo*, yielding colorless crystals. Recrystallization was effected from a mixture of alcohol-ethyl acetate; m.p. 174–174.5°; yield 2.2 g.

Anal. Calcd. for $\text{C}_{22}\text{H}_{31}\text{O}_7\text{NS}$: C, 58.27; H, 6.89; N, 3.09. Found: C, 58.13; H, 6.80; N, 3.26.

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[CONTRIBUTION FROM THE IPATIEFF HIGH PRESSURE AND CATALYTIC LABORATORY, DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY]

Study in the Terpene Series. X. Isomerization Accompanying Hydrogenolysis of Alcohols

BY V. N. IPATIEFF, W. W. THOMPSON¹ AND HERMAN PINES

Cyclopentylmethanol, 1-cyclopentylethanol, 2-cyclopentylethanol and cyclohexylmethanol, undergo ring expansion or contraction when subjected to hydrogenolysis in the presence of a nickel-alumina catalyst. Cyclohexanol and 2-cyclopentyl-2-propanol undergo hydrogenolysis to the corresponding hydrocarbons. 3,3-Dimethyl-2-butanol formed a mixture of 2,2- and 2,3-dimethylbutane on hydrogenolysis in the presence of nickel-alumina catalyst. 3,3-Dimethylbutanol under similar conditions yielded as the main products of reaction 2,2-dimethylbutane, neopentane and isopentane. The hydrogenolysis of 3,3-dimethylbutanol in the presence of either nickel-kieselguhr or Raney nickel yielded neopentane.

The hydrogenolysis of the oxygen to carbon bond in primary and secondary alcohols proceeds with difficulty in the presence of nickel-kieselguhr or copper oxide-chromium oxide catalyst except when the hydroxyl group is activated by the presence of a phenyl, furyl, pyrrol and other groups.²

The hydrogenolysis of aliphatic primary alcohols in the presence of a nickel-kieselguhr catalyst or in the presence of finely divided nickel is usually accompanied by the splitting of a carbon-carbon bond, which results in the formation of a paraffin having one carbon less than the parent alcohol,^{3,4}; a similar reaction occurs even in the absence of hydrogen.^{5,6}

(1) Universal Oil Products Company Predoctorate Fellow 1946–1947. E. I. du Pont de Nemours and Company, Wilmington, Delaware.

(2) H. Adkins, "Reactions of Hydrogen with Organic Compounds over Copper-Chromium Oxide and Nickel Catalysts," the University of Wisconsin Press, Madison, Wisconsin, 1937.

(3) J. Bösesken and G. H. Van Senden, *Rec. trav. chim.*, **32**, 23 (1913).

(4) B. Wojcik and H. Adkins, *THIS JOURNAL*, **55**, 1293 (1933).

(5) H. Gault, L. Palfray and P. Hsu, *Compt. rend.*, **209**, 999 (1939).

(6) V. N. Ipatieff, G. S. Monroe, L. E. Fischer and E. E. Meisinger, *Ind. Eng. Chem.*, **41**, 1802 (1949).

In the present study a nickel-alumina catalyst has been used for the hydrogenolysis of alcohols; this catalyst has been shown previously to reduce ketones and alcohols of the terpene series to hydrogenated terpenic hydrocarbons.⁷ In some cases the hydrogenolysis was accompanied by isomerization, *e.g.*, fenchyl alcohol was converted to isobornylane, isoborneol to isocamphane.

The present investigation was undertaken in order to determine whether a nickel-alumina catalyst could be applied for converting some monocyclic terpenic alcohols to the corresponding hydrocarbons without causing a skeletal rearrangement to occur. For that reason compounds having structures similar to those of the terpenes have been used in this study.



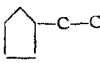

It was observed that when a primary or secondary alcohol having the hydroxy group adjacent to a five or six membered ring was subjected to hydrogenolysis using the nickel-alumina catalyst (com-

(7) (a) V. N. Ipatieff and Matov, *Ber.*, **45**, 3205 (1912); (b) V. N. Ipatieff, "Catalytic Reactions at High Pressures and Temperatures," the Macmillan Company, New York, 1936, p. 340; (c) V. N. Ipatieff and H. Pines, *THIS JOURNAL*, **67**, 1931 (1945).

TABLE I

HYDROGENOLYSIS OF CYCLIC ALCOHOLS

From 3.3 to 25 g. of alcohol and 10% by weight of catalyst, based on the alcohol charged was used in each experiment. The reactions in the presence of NiO-Al₂O₃ were made under 100 atm. of an initial hydrogen pressure at a temperature of 210°; the duration of heating was about 8 hours. The dehydration reaction was made at atmospheric pressure in a flow type apparatus and at a temperature of 400°. ^a 77% NiO-23% Al₂O₃. ^b The analysis was made on the hydrogenated product. ^c The remaining product consisted probably of dimethylcyclopentanes.

Alcohol	Catalyst	Alcohol reacted %	Composition of product, %			
						
Cyclopentylcarbinol	NiO-Al ₂ O ₃ ^a	75	70	30		
Cyclopentylcarbinol	Al ₂ O ₃	100	43 ^b	57 ^b		
Cyclohexanol	NiO-Al ₂ O ₃	85		100		
2-Cyclopentyl-1-ethanol	NiO-Al ₂ O ₃	45			65	18
1-Cyclopentyl-1-ethanol	NiO-Al ₂ O ₃	50			61	36
Cyclohexylcarbinol	NiO-Al ₂ O ₃	50				70 ^c
Dimethylcyclopentylcarbinol	NiO-Al ₂ O ₃	60				100

posed of 77 mole per cent. of NiO and 23 mole per cent. of Al₂O₃), isomerization of the ring occurred. Cyclopentylmethanol yielded a mixture of methylcyclopentane and cyclohexane, 1-cyclopentylethanol formed ethylcyclopentane and methylcyclohexane, while cyclohexylmethanol was reduced to methylcyclohexane and ethylcyclopentane. Even when the cyclopentyl group was removed one carbon atom further from the hydroxy group as in 2-cyclopentylethanol, isomerization of the ring was observed. That compound yielded mostly ethylcyclopentane, with an admixture of 18% of methylcyclohexane and probably some dimethylcyclopentanes.

No isomerization was observed with cyclohexanol or with 2-cyclopentyl-2-propanol; these compounds were hydrogenolyzed to cyclohexane and isopropylcyclopentane, respectively.

The isomerization occurring during the hydrogenolysis was probably due to the presence of alumina, since by passing cyclopentylmethanol over activated alumina at 400° a mixture of hydrocarbons was obtained which after hydrogenation consisted of 43% of methylcyclopentane and 57% of cyclohexane.

The compositions of the hydrogenolyzed products were determined by infrared analysis.

The experimental results are summarized in Table I.

Since many of the terpenic alcohols contain a quaternary carbon atom, it was decided to study the behavior of similar compounds toward hydrogenolysis. It was observed that the hydrogenolysis of 3,3-dimethyl-2-butanol in the presence of a nickel-alumina catalyst was also accompanied by isomerization; a mixture of 2,2- and 2,3-dimethylbutane was obtained.

In the case of a primary alcohol such as 3,3-dimethylbutanol the hydrogenolysis is much more pronounced and occurs not only on the carbon-oxygen but also on the carbon-carbon bond; the skeletal rearrangement proceeds only to a small extent. The liquid and in Dry Ice-acetone condensable product was composed of 2,2-dimethylbutane, neopentane and isobutane and of a small amount of 2,3-dimethylbutane. Part of the isobutane was formed most probably from the decomposition of 2,2-dimethylbutane inasmuch as the gaseous prod-

uct contained ethane, amounting to about 6 mole per cent. based on the alcohol reacted.

A skeletal isomerization also occurred when 3,3-dimethyl-2-butanol was passed over activated alumina; the dehydrated product, after hydrogenation, contained 51% of 2,3-dimethylbutane. In the case of 3,3-dimethyl-1-butanol, the extent of skeletal isomerization was only 9%.

The hydrogenolysis of 3,3-dimethylbutanol in the presence of nickel-kieselguhr was accompanied by a carbon-carbon scission; a 95% yield of neopentane was produced; the gases contained mainly methane and some unreacted hydrogen. It is very probable that the first step in this reaction consisted of the dehydrogenation of 3,3-dimethylbutanol to pivalic aldehyde, which in the presence of the nickel-kieselguhr catalyst decomposes to neopentane and carbon monoxide; the latter then undergoes hydrogenation to methane.

Raney nickel yielded results similar to that of nickel-kieselguhr.

The hydrogenolysis of 1-octanol by means of nickel-alumina catalyst is not accompanied by a skeletal isomerization. The main product consisted of *n*-octane and of smaller amounts of *n*-heptane.

The experimental results are given in Table II.

TABLE II

HYDROGENOLYSIS OF ALIPHATIC ALCOHOLS

Alcohol, kind	Catalyst, kind	Alcohol reacted, %	Composition of product:		Neopentane
			2,2-Dimethylbutane	2,3-Dimethylbutane	
3,3-Dimethylbutanol	NiO-Al ₂ O ₃	76	35	2	24 ^c
3,3-Dimethylbutanol	Ni(k)	100			95
3,3-Dimethylbutanol	Ni(R)	100			97
3,3-Dimethylbutanol	Al ₂ O ₃	100	91 ^a	9 ^a	
3,3-Dimethyl-2-butanol	NiO-Al ₂ O ₃	75	23	77	
3,3-Dimethyl-2-butanol	Al ₂ O ₃	100	49 ^a	51 ^a	
1-Octanol	Ni-Al ₂ O ₃				

^a The analysis was made on the hydrogenated product. ^b The product consisted of octane admixed with a small amount of heptane. ^c The product contained also 25 mole per cent. of isobutane.

Experimental Part

Hydrogenolysis Reactions.—Five to twenty-five grams of alcohol and 10% by weight of finely powdered catalyst were charged into a 125-cc. rotating type autoclave and pressured with 100 atmospheres of hydrogen. The autoclave was brought rapidly up to temperature of 210–225° in an

electric furnace and held there for the indicated period of time. After being cooled, the excess hydrogen was released through ice and Dry Ice-acetone cooled traps, the liquid products and the catalyst were removed. The catalyst was separated by filtration and the liquid products were dried with anhydrous sodium sulfate. This liquid mixture was then distilled to remove any unchanged alcohol and the composition of the hydrocarbons was determined by infrared spectral analysis.

Fifteen to twenty-five grams of alcohol and 3 g. of hydrogenation catalyst were used in each experiment. The hydrogenolysis was carried out in a 125-ml. capacity rotating autoclave, at 210–225°, and under 100 atmospheres of initial hydrogen pressure. The duration of heating was 3–4 hours. The dehydration reactions in the presence of activated alumina were made at atmospheric pressure in a flow type apparatus and at a temperature of 400°. NiO-Al₂O₃ consisted of 77% NiO and 23% Al₂O₃; Ni(k)—nickel kieselguhr; Ni(R)—Raney nickel.

Dehydration Reactions.—The dehydration reactions were made by passing at atmospheric pressure 15–20 ml. of the alcohols over activated alumina at 400° and an hourly liquid space velocity of 0.5.^{8a} The olefinic hydrocarbons thus obtained were hydrogenated at 60–70° in the presence of a nickel-kieselguhr catalyst and with an initial hydrogen pressure of 70 atmospheres.

Materials Used

Cyclopentylmethanol. a. **Bromocyclopentane** (b.p. 134–135°) was prepared in 90% yield from cyclopentanol by bromination with phosphorus tribromide at 0°.

b. **Ethylcyclopentane Carboxylate.**—Cyclopentylmagnesium bromide prepared from 180 g. (1.2 M) of bromocyclopentane and 29 g. (1.2 g. atom) of magnesium was added with stirring to 236 g. (2 M) of purified^{8b} ethyl carbonate.

The product was separated, washed and distilled according to the procedure described in the literature.^{8b} The ethyl ester of cyclopentane carboxylic acid, 97 g., distilled at 169–170°, *n*_D²⁰ 1.4354, yield 57%.

c. **Cyclopentylmethanol.**—Ninety-five grams of the ethyl ester of cyclopentane carboxylic acid was added to 19 g. of lithium aluminum hydride in 500 g. of anhydrous ethyl ether, according to the method of Nystrom and Brown.⁹ Owing to mechanical difficulties during the decomposition of the excess of the reducing agent, the yield of cyclopentylmethanol was only 60%. The alcohol distilled at 160–161°, *n*_D²⁰ 1.4576; (recorded in the literature,¹⁰ b.p. 162–162.5, *n*_D²⁰ 1.4579).

1-Cyclopentylethanol was synthesized by the method of Edwards and Reid,¹¹ b.p. 162–164°, *n*_D²⁰ 1.4578.

2-Cyclopentylethanol was prepared by the method of Yohe and Adams,¹² yield 20%, b.p. 179–181°, *n*_D²⁰ 1.4615.

2-Cyclopentyl-2-propanol was prepared via a Grignard reaction using 35 g. of bromocyclopentane, 8.5 g. of magnesium and 15 g. of acetone. The 2-cyclopentyl-2-propanol distilled at 66–70° (10 mm.), *n*_D²⁰ 1.4548; yield 18%.

Cyclohexylmethanol was obtained by hydrogenation of benzyl alcohol.¹³

3,3-Dimethyl-2-butanol (pinacolyl alcohol) which was prepared by hydrogenation of pinacolone¹⁴ distilled at 118–119°, *n*_D²⁰ 1.4148; yield 80%.

(8a) The hourly liquid space velocity is defined as volume of liquid per volume of catalyst per hour.

(8b) "Organic Syntheses." Coll. Vol. II, edited by A. H. Blatt, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 282.

(9) R. F. Nystrom and W. G. Brown, *THIS JOURNAL*, **69**, 1197 (1947).

(10) C. R. Noller and R. Adams, *ibid.*, **48**, 1085 (1926).

(11) W. R. Edwards and E. E. Reid, *ibid.*, **82**, 3238 (1930).

(12) G. R. Yohe and R. Adams, *ibid.*, **50**, 1505 (1928).

(13) H. Adkins and L. W. Covert, *J. Phys. Chem.*, **35**, 1684 (1931).

(14) H. Adkins and H. I. Cramer, *THIS JOURNAL*, **52**, 4349 (1930).

3,3-Dimethylbutanol was synthesized from 3,3-dimethylbutyl chloride; the latter was prepared from *t*-butyl chloride and ethylene according to Schmerling's method.¹⁵ One hundred twenty grams of the chloride and 105 g. of potassium carbonate dissolved in one liter of water were sealed in a 3000 cc. capacity autoclave and heated for 4 hours at 230°. The product was distilled and the upper layer, constituting the organic part, was separated, dried and distilled over potassium carbonate. The 3,3-dimethylbutanol boiled at 141–142°, yield 65% (literature data,¹⁶ b.p. 140–143°).

Catalysts

Nickel-Alumina.—To a solution of 703 g. of NiSO₄·6H₂O dissolved in 10 liters of water and heated to 60° was added slowly with constant stirring 103 g. of activated alumina, calcined at 350° (procured from Harshaw Chemical Company). The temperature was then raised to 70° and to the mixture was added 483 g. of sodium carbonate dissolved in 2 liters of water and stirred for an additional 15 minutes. The precipitate was washed several times by decantation, filtered and again washed until the test for SO₄²⁻ was negative. The precipitate was dried at 120° for 24 hours, ground to 40 mesh size and mixed with 4% of graphite; the powder was piled into 1/8 × 1/8 inch cylinders. The pills were placed in a glass tube and the carbonate of nickel decomposed by heating at 350° in the presence of a stream of nitrogen. When the test for carbon dioxide was negative, the catalyst was reduced by passing over it a mixture of hydrogen and nitrogen in a ratio of 1:2; and the temperature was raised slowly to 450° and maintained at this temperature until no more water was formed.

Nickel-Kieselguhr.—Universal Oil Products Company hydrogenation catalyst.¹⁷

Raney Nickel.—Prepared according to the description of Covert and Adkins.¹⁸

Alumina.—In the form of 1/8 inch diameter spheres, obtained from Harshaw Chemical Company.

Infrared Analyses.—The analyses were made by Dr. W. S. Gallaway and Ed. Baclawski, at the Universal Oil Products Company according to the method described by Webb and Gallaway.¹⁹ The spectra of the samples were obtained and the spectrograms were then compared with those of pure hydrocarbons; the quantitative determinations were made on the basis of appropriate absorption band. Typical spectrograms of the various hydrocarbons may be found in the catalog issued by the American Petroleum Institute Project 44.

The several wave lengths used for calculating the composition of the various samples are given in Table III.

TABLE III

WAVE LENGTHS OF CHARACTERISTIC INFRARED ABSORPTION,

IN μ					
2,2-Dimethylbutane	2,3-Dimethylbutane	Methylcyclopentane	Ethylcyclopentane	Cyclohexane	Methylcyclohexane
12.80	11.50	10.20	11.18	11.60	11.85
10.77	10.85	8.76	10.74	11.07	11.47
10.05	10.10		8.82	9.63	11.00
9.81	9.63			7.92	10.34
9.30	9.38				7.90
8.22	8.87				
7.99	8.68				

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(15) L. Schmerling, *ibid.*, **67**, 1152 (1945).

(16) P. Sutter, *Helv. Chim. Acta*, **21**, 1269 (1938).

(17) V. N. Ipatieff and B. B. Corson, *Ind. Eng. Chem.*, **30**, 1039 (1938).

(18) L. W. Covert and H. Adkins, *THIS JOURNAL*, **54**, 4116 (1932).

(19) G. M. Webb and W. S. Gallaway, *Petroleum Processing*, **2**, 356 (1947).