[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA, BERKELEY]

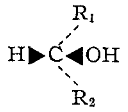
The Direct Chemical Interrelation of the Configuration of Terpenes and Hydroxy Acids[1]

BY DONALD S. NOYCE AND DONALD B. DENNEY

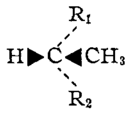
RECEIVED SEPTEMBER 3, 1953

By the successive degradation of (−)*cis*-3-hydroxycyclohexanecarboxylic acid to (+)3-methylcyclohexanone and to (−)α-methoxyadipic acid a direct chemical relationship between the configurations of the terpenes and of α-methoxyadipic acid has been established. This work tends to substantiate the relationships suggested by Fredga by the method of quasi-racemates, and the calculations of Kirkwood and of Eyring.

The problem of the relative configurations of broad series of natural products is of interest both to the biochemist concerned with modes of biogenesis, and to the organic chemist concerned with the mechanism of organic reactions. It is of value, therefore, to attempt to interrelate the configurations of the sugars as typified by the asymmetric center of type I, and the terpenes which may be characterized *via* the asymmetric center of type II.


R_1, H▶C◀OH, R_2

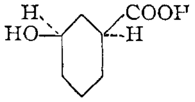
I


R_1, H▶C◀CH_3, R_2

II

Such an interrelationship has been suggested by Fredga[2] by use of the methods of quasi-racemates, and more recently by Lane[3] by a sequence considering Walden inversion. A direct chemical correlation is of interest also, since calculations of the absolute configuration of asymmetric molecules have been carried out for representatives of both series, (+)-2-butanol[4–7] (III), (−)lactic acid[7] (IV), and (+)-2,3-epoxybutane[8] (V) as representative of type I, and of (+)-3-methylcyclopentanone[3,7] (VI) as representative of type II.

It is the purpose of the present communication to report a method for the direct chemical interrelationship of these series. The starting point is *cis*-3-hydroxycyclohexanecarboxylic acid (VII), in which there are present two asymmetric centers, one of type I, and the second of potential type II. In VII, the relationship of these two centers one to another may be established by the *cis*-[illegible] arrangement of the hydroxyl group and the carboxyl group as confirmed by the formation of a lactone.[9] VII was prepared by reduction of *m*-hydroxybenzoic acid, and purified by crystallization from ethyl acetate. Resolution of VII proceeded smoothly, the quinine salt affording the (+)-isomer, and the cinchonidine salt the (−)-isomer. From (−)VII, the degradation proceeded by the utilization of stereospecific methods for the isolation of the two asymmetric centers individually. These reaction sequences are summarized in Chart I.



VII

The conversion of (−)*cis*-3-hydroxycyclohexanecarboxylic acid to (+)*cis*-3-hydroxycyclohexanemethanol, (+)VIII, and thence to (−)*cis*-3-methylcyclohexanol, (−)X, through the monotosylate (IX), has been reported recently[10] by methods which have been shown to be stereospecific.[11] Oxidation of (−)X to (+)3-methylcyclohexanone, (+)-XI, has been carried out by Macbeth and Mills.[12] Since (+)XI has been obtained by the degradation of pulegone,[13] this establishes the configurational relationship between (−)VII and pulegone. By an extended series of chemical transformations, a relationship between pulegone and many of the monoterpenes may be worked out. Such a relationship is summarized by Huckel.[14]

The second major sequence was the conversion of (−)*cis*-3-hydroxycyclohexanecarboxylic acid to (−)α-methoxyadipic acid, (−)XII, to complete the interrelationship of the two series. (−)VII, was converted to methyl (−)*cis*-3-methoxycyclohexanecarboxylate, (−)XIII, by a two-step process. The acid was converted to the ester by treatment with diazomethane, and the free hydroxyl group methylated by the procedure of Bonner.[15] Conversion of the ester to the hydrazide was accomplished with hydrazine hydrate, and the hydrazide XIV was subjected to the Curtius rearrangement to the isocyanate, which was not isolated, but converted directly by acid hydrolysis to (−)*cis*-3-methoxycyclohexylamine (XV).

When XV was allowed to react with methyl iodide in the presence of potassium carbonate, an excellent yield of (−)*cis*-3-methoxycyclohexyltrimethylammonium iodide, (−)XVI, was obtained. The methiodide XVI was treated with a suspension of silver oxide in water, and the resulting solution was distilled after filtration to remove the

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[1] Presented before the 123rd Meeting of the American Chemical Society in Los Angeles, March, 1953. Taken from the dissertation submitted by D. B. D. to the Graduate Division in partial fulfillment of the requirement for the Ph.D., September, 1952.

[2] A. Fredga, "The Svedberg Memorial Volume," Almquist and Wiksells Boktryckeri, Upsala, 1944, p. 261; see also *Acta Chem. Scand.*, **1**, 361 (1947).

[3] J. F. Lane, *Science*, **113**, 577 (1951).

[4] S. F. Boys, *Proc. Roy. Soc.* (*London*), **A144**, 655, 675 (1934).

[5] W. Kuhn, *Z. physik. Chem.*, **B31**, 23 (1936).

[6] J. G. Kirkwood, *J. Chem. Phys.*, **5**, 479 (1937); see G. W. Wheland, "Advanced Organic Chemistry," John Wiley and Sons, New York, N. Y., p. 319.

[7] W. J. Kauzmann, J. E. Walter and H. Eyring, *Chem. Revs.*, **26**, 339 (1940).

[8] W. W. Wood, W. Fichett and J. G. Kirkwood, *J. Chem. Phys.*, **20**, 561 (1952).

[9] W. H. Perkin, Jr., and G. Tattersall, *J. Chem. Soc.*, **91**, 480 (1907).

[10] D. S. Noyce and D. B. Denney, THIS JOURNAL, **74**, 5912 (1952).

[11] D. S. Noyce and D. B. Denney, *ibid.*, **72**, 5743 (1950).

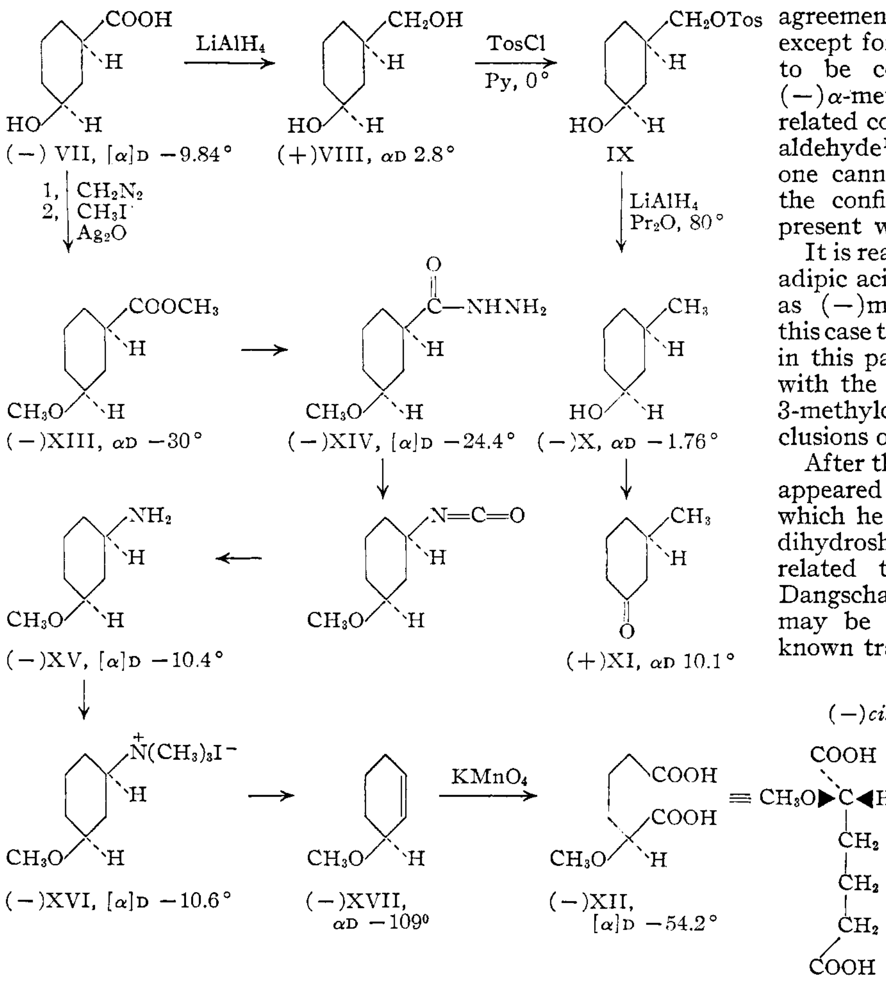
[12] A. K. Macbeth and J. A. Mills, *J. Chem. Soc.*, 205 (1947).

[13] O. Wallach, *Ann.*, **289**, 340 (1896).

[14] W. Huckel, *J. prakt. Chem.*, **157**, 225 (1941); see *Ann. Repts.*, **47**, 192 (1950).

[15] W. A. Bonner, THIS JOURNAL, **73**, 3126 (1951).

CHART I



silver iodide. Decomposition began at a bath temperature of 140°. The product resulting from the Hofmann degradation was shown to be (−)3-methoxycyclohexene (XVII) by comparison of its infrared spectrum with an authentic sample. XVII was distinctly different in absorption spectrum from the other possible product of the Hofmann degradation, 4-methoxycyclohexene.

Oxidation of (−)XVII to give crude (−)α-methoxyadipic acid, (−)XII, was carried out following the procedure of Birch, Oldham and Johnson.[16] The methoxy acid was contaminated with a large amount of glutaric acid, and attempts to purify the (−)α-methoxyadipic acid by crystallization were unsuccessful. The mixture of acids was eventually successfully separated by employing the partition chromatography procedure of Marvel and Rand.[17]

The absolute configuration of (+)tartaric acid has been determined recently by Peerdeman, van Bommel and Bijvoet.[18] The results of all of the calculations of configurations[3-8] are in agreement with the results of Bijvoet, except for those of Boys which appear to be consistently reversed. Since (−)α-methoxyadipic acid has not been related configurationally to (+)glyceraldehyde[19] by a direct chemical method, one cannot state unequivocally what the configurations indicated by the present work are.

It is reasonable that (−)α-methoxyadipic acid has the same configuration as (−)methoxysuccinic acid, and in this case the configurations are as drawn in this paper. This is also consistent with the calculated configurations for 3-methylcyclopentanone[7,3] and the conclusions of Fredga.[2]

After this work was completed, there appeared a report by Freudenberg[20] in which he reported the relationship of dihydroshikimic acid, which had been related to glucose by Fischer and Dangschat,[21] to 3-methylhexane, which may be related to the terpenes by known transformations.

Experimental[22]

(−)*cis*-3-Hydroxycyclohexanecarboxylic Acid, (−)VII.—The preparation and resolution of this acid have been reported previously.[10]

Oxidation of (−)*cis*-3-Methylcyclohexanol.—Following the procedure of Macbeth and Mills[12] oxidation of 2.86 g. of (+)-3-methylcyclohexanol afforded 1.2 g. of (−)3-methylcyclohexanone, b.p. 165°, n^{20}_D 1.4468, α^{20}_D −9.40° (homog. 1 dm.); lit.[12] n^{20}_D 1.4452, α^{20}_D −11.5°. The semicarbazone was crystallized from ethanol–water, m.p. 173–174° dec., $[\alpha]^{23.5}_D$ +30.5° (*c* 0.12 in ethanol).

In a similar manner (−)*cis*-3-methylcyclohexanol (0.8 g.) (from (−)*cis*-3-hydroxycyclohexanecarboxylic acid) afforded (+)3-methylcyclohexanone, 0.28 g., α^{26}_D +10.1° (homog. 1 dm.), semicarbazone, m.p. 171–174° dec., $[\alpha]^{23}_D$ −27° (*c* 0.1 in ethanol).

Conversion of (−)VII to (−)Methyl *cis*-3-Methoxycyclohexanecarboxylate.—In a 500-ml. erlenmeyer flask there was placed 64 g. (0.456 mole) of (−)VII and 50 ml. of ether. Freshly prepared diazomethane in ether was added until all of the acid had dissolved and the solution retained the yellow color evidencing excess diazomethane. After evaporation

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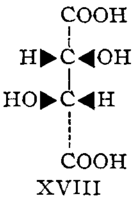
(16) S. F. Birch, W. J. Oldham and E. A. Johnson, *J. Chem. Soc.*, 819 (1947).

(17) C. S. Marvel and R. D. Rand, Jr., THIS JOURNAL, **72**, 2642 (1950).

(18) A. F. Peerdeman, A. J. van Bommel and J. M. Bijvoet, *Proc. Kon. Ned. Ak. v. Wet., Ser. B*, **54**, 16 (1951); see also J. Waser, *J. Chem. Phys.*, **17**, 498 (1949), and E. E. Turner and K. Lonsdale, *ibid.*, **18**, 156 (1950).

(19) D and L prefixes have not been used in this paper, since these prefixes frequently lead to ambiguity. Tartaric acid has been related to glyceraldehyde by a number of methods, some of which involve carbon 2 and some of which involve carbon 3. Thus (+)tartaric acid has been assigned to the D series by K. Freudenberg ("Stereochemie," F. Deuticke, Leipzig, 1932, p. 575) while it is assigned the L-(+) configuration by Wohl (*Ber.*, **50**, 455 (1917)). It should be pointed out, however, that there is no ambiguity in the spatial representation of (+)tartaric acid as (XVIII) and also no ambiguity in the similar representation of compounds related chemically to (+)glyceraldehyde.



XVIII

(20) K. Freudenberg, paper presented at the March 30, 1953, Chemikertreffen, Innsbruck, *cf. Angew. Chem.*, **65**, 259 (1953).

(21) H. O. L. Fischer and G. Dangschat, *Helv. Chim. Acta*, **20**, 705 (1937).

(22) All melting points are corrected; boiling points are uncorrected. Analyses are by the Microanalytical Laboratory of the University of California.

of the ether, the residual ester was placed in a one-liter three-necked flask. Methyl iodide, 500 g. (3.52 moles), 100 g. of glass beads, 100 g. of drierite and 304 g. (1.31 moles) of freshly prepared silver oxide were added to the flask. To this stirred mixture 500 g. of additional methyl oxide was added, over a period of 40 hours. Filtration and distillation through a one-meter modified Podbielniak column afforded one main fraction of 54.5 g. (71%) of (−)-methyl *cis*-3-methoxycyclohexanecarboxylate (XIII), b.p. 116–120° (26 mm.), n^{20}_{D} 1.4530, α^{20}_{D} −29.85° (homog., 1 deci.).

Anal. Calcd. for $C_9H_{16}O_3$: C, 62.77; H, 9.37. Found: C, 62.31; H, 8.86.

The N-benzylamide, prepared in the usual manner and crystallized from aqueous alcohol melted 119.5–120.3°.

Anal. Calcd. for $C_{15}H_{21}NO_2$: C, 72.84; H, 8.56; N, 5.66. Found: C, 73.16; H, 8.65; N, 5.94.

(−)*cis*-3-Methoxycyclohexanecarboxylic Acid Hydrazide.—A solution of 45.9 g. (0.268 mole) of (−)XIII in 35 ml. of methanol was treated with 25 ml. of 85% hydrazine hydrate, and the mixture heated under reflux for 12 hours. The methanol and water were evaporated under reduced pressure to give 43.1 g. (94%) of crude hydrazide, (−)XIV, m.p. 137–142°. A sample crystallized from ethyl acetate for analysis had m.p. 143.4–144.4°, $[\alpha]^{19}_{D}$ −24.4° (*c* 4 in methanol).

Anal. Calcd. for $C_8H_{19}N_2O_2$: C, 55.79; H, 9.37; N, 16.27. Found: C, 55.87; H, 9.04; N, 16.45.

Curtius Degradation of (−)XIV.—Crude (−)XIV, 42.5 g. (0.247 mole), was dissolved in a solution which was made up by adding 43.3 ml. of 6 *N* hydrochloric acid to 90 ml. of water. The resulting solution was filtered into a one liter, three-necked flask which was equipped with a dropping funnel, stirrer, thermometer, and which contained 300 ml. of ether. The stirred solution was cooled to 3°; to it there was added dropwise a solution of 17.25 g. (0.250 mole) of sodium nitrite in 35 ml. of water. The rate of addition was adjusted so that the temperature never became greater than 9°. After the addition of the sodium nitrite was complete, the layers were separated, and the aqueous solution was extracted with two 70-ml. portions of ether. The combined, yellow, ether extracts were washed with 15 ml. of cold sodium bicarbonate solution, and dried at ice temperatures briefly over magnesium sulfate. After the addition of 200 ml. of benzene, the solution was distilled slowly through a short column. The azide underwent rearrangement as soon as heat was applied, and nitrogen was given off continuously during the distillation. When the temperature at the top of the column reached 76° a reflux condenser was substituted for the column, and the solution was refluxed until no more nitrogen was evolved. The solution of isocyanate was cooled in an ice-bath, and 150 ml. of concentrated hydrochloric acid was added. Refluxing was then continued for two hours to hydrolyze the isocyanate. The cooled solution was washed with benzene, and then basified with cold 6 *N* sodium hydroxide solution. The basic solution was continuously extracted with ether. A considerable amount of water was carried over in the extraction process, consequently methanol was added until the mixture became homogeneous. The solution was dried over magnesium sulfate, and then distilled through a three-foot modified Podbielniak column, to afford 8.5 g. (27%) of (−)*cis*-3-methoxycyclohexylamine, (−)XV, b.p. 97–98° (45 mm.), n^{28}_{D} 1.4610, $[\alpha]^{28}_{D}$ −10.4° (*c* 4 in methanol). The amine was very basic and absorbed carbon dioxide rapidly.

The **benzamide**, prepared in the usual manner crystallized from methanol, m.p. 137.8–138.8°.

Anal. Calcd. for $C_{14}H_{19}NO_2$: C, 72.07; H, 8.21; N, 6.05. Found: C, 71.94; H, 8.12; N, 5.74.

The ***p*-nitrobenzamide**, crystallized from aqueous methanol, had m.p. 171.7–172.3°, $[\alpha]^{22}_{D}$ −15.1° (*c* 1.4 in methanol).

Anal. Calcd. for $C_{14}H_{18}N_2O_4$: C, 60.43; H, 6.53; N, 10.07. Found: C, 60.45; H, 6.41; N, 9.95.

Conversion of (−)XV to (−)*cis*-3-Methoxycyclohexyltrimethylammonium Iodide (XVI).—To a mixture of 8 g. (0.062 mole) of (−)XV and 13 g. (0.094 mole) of potassium carbonate in 30 ml. of anhydrous methanol, there was added dropwise over a period of 30 minutes 23 ml. of methyl iodide. The mixture was refluxed and stirred for four hours. The solution was cooled and 5 g. (0.036 mole) of potassium carbonate was added, followed by the dropwise addition of an additional 23 ml. of methyl iodide. The mixture was heated under reflux with stirring for 19 hours. The resulting mixture was cooled, and the methanol and methyl iodide were removed at room temperature. The precipitated salt cake was triturated with three 60-ml. portions of chloroform. Evaporation of the chloroform afforded 16.5 g. (88%) of crude (−)*cis*-3-methoxycyclohexyltrimethylammonium iodide, (−)XVI, m.p. 175–177.5°.

A small sample, crystallized from methanol–ethyl acetate for analysis melted 176.7–177.5°, $[\alpha]^{20}_{D}$ −10.6° (*c* 2.6 in methanol).

Anal. Calcd. for $C_{10}H_{22}NOI$: C, 40.14; H, 7.41; I, 42.42. Found: C, 40.25; H, 7.40; I, 42.42.

Formation of (−)3-Methoxycyclohexene from (−)XVI.—To a solution of 15.5 g. (0.052 mole) of (−)XVI in 100 ml. of carbon dioxide-free water, there was added a supension of 24.8 g. (0.107 mole) of freshly prepared silver oxide in 100 ml. of carbon dioxide-free distilled water. The suspension was placed on a shaking machine and agitated for three hours. The solution was filtered directly into a 300-ml. round-bottomed flask, and the precipitated silver salts were washed well with water. The aqueous solution was directly distilled. When the bath temperature had reached 140°, decomposition began, and the alkene steam distilled from the mixture. When the bath temperature reached 175°, the decomposition became quite rapid, and the head temperature dropped to 88°. When distillation was complete, the alkene was taken up in 25 ml. of ether, and the aqueous solution further extracted with two 10-ml. portions of ether. The combined, dried, ether extracts were distilled to afford 4.5 g. (78%) of (−)3-methoxycyclohexene, (−)XVII, b.p. 134–137°, $n^{22.5}_{D}$ 1.4630, $\alpha^{22.5}_{D}$ −54.82° (homogeneous in a 1/2 dm. tube).

The infrared spectrum showed characteristic bands at 1453, 1396, 1346, 1320, 1188, 928 and 816 cm.$^{-1}$ in the fingerprint region. Authentic 3-methoxycyclohexene, prepared from 1,2-dibromocyclohexane and sodium methoxide, showed the same bands, whereas authentic 4-methoxycyclohexane, prepared by the boric acid dehydration of 4-methoxycyclohexanol,[23] showed bands at 1440, 1370, 1352, 1250, 1226, 1184, 1105, 1041, 1008, 925, 914 and 872 cm.$^{-1}$.

Oxidation of (−)XVII to (−)α-Methoxyadipic Acid, (−)-XII.—A solution of 4.0 g. (0.036 mole) of (−)XVII in 15 ml. of isoöctane, added to 100 ml. of water, was treated with stirring with a solution of 19 g. (0.097 mole) of sodium permanganate in 110 ml. of water at such a rate that the temperature was maintained at 15–18° (about one-half hour was required for the addition) while a slow stream of carbon dioxide was bubbled through the two-phase mixture. The two phase mixture was filtered with the aid of Celite, and the filter cake was triturated with dilute sodium hydroxide. The basic aqueous solution was acidified with ice-cold 18 *N* sulfuric acid and continuously extracted with ether overnight. Evaporation of the dried ether extract afforded an oil which crystallized on standing. The yield of crystalline material was 4.0 g. (about 65%). After two crystallizations from ether–petroleum ether, the mixture had m.p. 67–85°, neutral equivalent 79. The neutral equivalent of α-methoxyadipic acid is 88 while that for glutaric acid is 66.

Further purification and separation of the (−)α-methoxyadipic acid from the glutaric acid was effected by the use of partition chromatography, following the procedure of Marvel and Rand.[17] A column containing 500 g. of silicic acid and 300 ml. of water was prepared in a tube of 59 mm. diameter, and 40 cm. in length. A solution of the mixture of acids in 4 ml. of *t*-amyl alcohol and 6 ml. of chloroform was carefully placed on top of the column, and elution was carried out with butanol–chloroform, 8%, 2500 ml., followed by butanol–chloroform 9%, 2500 ml. Fractions of 500 ml. were collected. Titration of fractions 5 and 8 accounted for 90% of the acidity. Hence fractions 4 and 5 were combined, extracted with sodium carbonate solution, the extracts washed with ether, and acidified with 50% sulfuric acid. Continuous extraction with ether afforded a solution which was dried and concentrated to yield 0.54 g. of (−)XII. The acid, after one crystallization from ether–petroleum ether, had m.p. 99.2–99.9°, 0.48 g., $[\alpha]^{22.6}_{D}$ −54.2° (*c* 2 in ethyl acetate). Neutral equivalent found 88.0.

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(23) W. Brandenberg and A. Galat, THIS JOURNAL, 72, 3275 (1950).

Anal. Calcd. for $C_7H_{12}O_5$: C, 47.72; H, 6.87. Found: C, 48.04; H, 6.87.

The cinchonidine salt, m.p. 181.8–182.7°, was crystallized from ethyl acetate–methanol.

Anal. Calcd. for $C_{45}H_{56}O_7N_4$: C, 70.65; H, 7.37; N, 7.32. Found: C, 70.25; H, 7.81; N, 6.82.

The *p*-phenylphenacyl ester crystallized from ethanol–ethyl acetate, m.p. 131–132°.

Anal. Calcd. for $C_{35}H_{32}O_7$: C, 74.45; H, 5.71. Found: C, 73.86; H, 5.65.

The benzyl isothiuronium salt crystallized from acetone, m.p. 151.6–152.6.

Anal. Calcd. for $C_{21}H_{28}O_5N_4S_2$: C, 52.46; H, 5.87. Found: C, 52.37; H, 6.31.

Acknowledgment.—We wish to thank Mr. William A. Klemperer for determining the infrared spectra, and the Graduate Fellowship committee of the University of California for the award of the Abraham Rosenberg Fellowship to D. B. D.

BERKELEY, CALIFORNIA

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

Dehydroxymethylation of Primary Alcohols

BY HERMAN PINES, H. G. RODENBERG[1] AND V. N. IPATIEFF[2]

RECEIVED SEPTEMBER 21, 1953

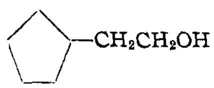
The dehydroxymethylation of 2-cyclopentylethanol, 1-methyl-1-hydroxymethylcyclohexane and 4-hydroxymethylcyclohexanol was studied at about 190° in the presence of a nickel–Kieselguhr catalyst and under 100 atmospheres of hydrogen pressure. The respective products in 80–100% yield obtained from this reaction were methylcyclopentane, methylcyclohexane and cyclohexanol.

It was shown previously[3] that the dehydroxymethylation of primary alcohols proceeds in the presence of a nickel catalyst and hydrogen according to the general formula

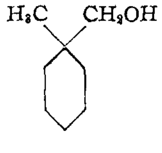
$$RCH_2OH + H_2 \longrightarrow RH + CH_4 + H_2O$$

Thus good yields of neopentane were obtained from 3,3-dimethylbutanol,[3a] 6,6-dimethylnorpinane from myrtanol,[3b] pinane from nopol[3b] and cyclobutane from cyclobutylmethanol.[3c]

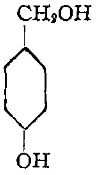
In order to determine the applicability of this reaction, as a method of degradation of primary alcohols, this study was extended to three other representative types of alcohols, namely, to: (1) 2-cyclopentylethanol (I), which on hydrogenolysis in the presence of nickel–alumina catalyst undergoes a skeletal rearrangement forming methylcyclohexane[3a]; (2) 1-methyl-1-hydroxymethylcyclohexane (II), in which the hydroxymethyl group is attached to a tertiary carbon atom; and (3) 4-hydroxymethylcyclohexanol (III), which besides a hydroxymethyl group contains also a secondary hydroxy group.



I



II



III

The experiments were carried out according to the procedure described previously[3] using nickel–Kieselguhr catalyst and initial hydrogen pressure of 100 atmospheres.

Compound I underwent 93% reaction at 171–190° forming, according to infrared spectral analysis, methylcyclopentane as the only liquid hydrocarbon. Compound II underwent over 90% hydrogenolysis at 194° forming methylcyclohexane. The hydrogenolysis of compound III proceeds stepwise; the dehydroxymethylation occurs at a lower temperature than the hydrogenolysis of the hydroxy group attached to the ring. At 174°, 80% of compound III reacted to form only cyclohexanol. At 208° the reaction went to completion and the product consisted of 55% cyclohexane and 40% cyclohexanol.

The present results and those obtained from previous study show that the dehydroxymethylation method could be used as an indirect method for degradation of acids, if the latter are reduced to the corresponding alcohols.

Experimental Part

Dehydroxymethylation.—The dehydroxymethylation reactions were made in a 450-ml. capacity rotating autoclave. The carbinol, 0.1–0.3 mole, and 10% by weight of UOP nickel–Kieselguhr catalyst[4] were placed in the autoclave and heated in the presence of 100 atmospheres of initial hydrogen pressure. The experimental results are summarized in Table I. The gases recovered from the reaction consisted, according to mass spectrographic analyses, of hydrogen and methane.[5] Only about 0.1–0.2% of carbon monoxide was formed.

The structures of the compounds produced were determined by physical constants and infrared spectral analyses.

TABLE I

DEHYDROXYMETHYLATION OF PRIMARY ALCOHOLS

Expt.	Alcohol used	Conditions of reacn. Temp., °C.	Hr.	Alcohol reacted, %	Product formed
1	I	171	19	100	Methylcyclopentane
2	I	190	5	94	Methylcyclopentane
3	II	194	3	94	Methylcyclohexane
4	III	174	6	80	Cyclohexanol
5	III	208	9	100	55% Cyclohexane 40% Cyclohexanol

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[1] Universal Oil Products Company Research Fellow, 1951.

[2] Deceased, November 29, 1952.

[3] (a) V. N. Ipatieff, W. W. Thompson and H. Pines, THIS JOURNAL, **73**, 553 (1951); (b) V. N. Ipatieff, G. Czajkowski and H. Pines, *ibid.*, **73**, 4098 (1951); (c) H. Pines, H. G. Rodenberg and V. N. Ipatieff, *ibid.*, **75**, 6065 (1953).

[4] V. N. Ipatieff and B. B. Corson, *Ind. Eng. Chem.*, **26**, 1838 (1934).

[5] The mass spectrographic analyses were made by J. B. Grutka, Universal Oil Products Company.