[Contribution from the Chemical Laboratory of the University of California, Berkeley]

The Stereochemistry of the 9-Methyldecalins

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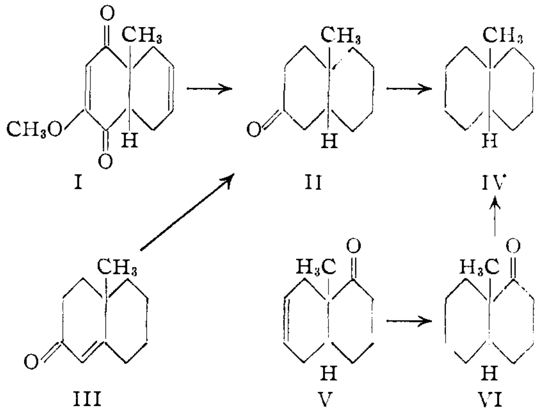
The preparation of *cis*- and *trans*-9-methyldecalin has been reinvestigated utilizing materials of known stereochemical purity in order to unequivocally assign the proper configurations to the hydrocarbons. It has been found that whereas the assignment by Linstead, Millidge and Walpole in the *cis* series was correct, the previously prepared *trans* isomer was a mixture of rearranged hydrocarbons. In addition. it has been found that the allocation of a *cis* structure to a 9-decalincarboxylic acid is incorrect.

Recent work in this Laboratory on the stereochemistry of various 9-substituted-decalins[2] created the need for samples of *cis*- and *trans*-9-methyldecalin as stereochemical standards. In 1931, Ruzicka, Koolhaas and Wind[3] reported the preparation of the *trans* isomer by Clemmensen reduction of 10-methyldecalin-1,3-dione and this work was repeated in 1935 by Clemo and Dickenson.[4] The *cis* isomer was reported to have been prepared by two different methods. In 1936, Hibbit and Linstead[5] hydrogenated a 9-methyl-Δ^2-octalin which was thought to possess a *cis* configuration but degradation products derived from the methyloctalin cast doubt on the stereochemical purity. In 1937, Linstead, Millidge and Walpole[6] reported a second preparation which involved Clemmensen reduction of *cis*-9-methyl-2-decalone. That this starting ketone possessed the assigned configuration was established by degradation to known *cis*-compounds.[6,7] In addition to the individual preparations of the two isomers, it had been reported by Hibbit and Linstead[5] that in the presence of aluminum chloride, the "*cis*" material they prepared was isomerized to the *trans*, suggesting a greater stability of the latter isomer.

Recently, Bachmann, Ross, Dreiding and Smith[8] have investigated the stability of some bicyclic six-membered heterocyclic ring systems with angular methyl groups and they have demonstrated that such compounds are more stable in the *cis* configuration. In addition by re-examination of the available degradative studies in the 9-methyl decalin series, it was also suggested that the hydrocarbon prepared by Hibbit and Linstead[5] was primarily a *trans* isomer while that of Ruzicka, *et al.*,[3] was actually *cis*. If such be the fact, then, the aluminum chloride equilibration of the former authors would indicate a *trans* to *cis* rearrangement. Such a conclusion is of interest in view of the present utilization of empirically calculated conformational energy differences[8,9] Furthermore, the suggestion that the material of Ruzicka, *et al.*,[3] possesses a *cis* configuration makes it difficult to reconcile its purity with the hydrocarbon prepared by Linstead, Millidge and Walpole[6] from intermediates established as being in the *cis* series. In view of our needs for the hydrocarbons, the preparation of *cis*- and *trans*-9-methyldecalin has been reinvestigated.



cis-9-Methyldecalin (IV) was prepared by Clemmensen reduction of either *cis*-10-methyl-2-decalone (II) or *cis*-9-methyl-1-decalone (VI). The solid intermediate ketone II was synthesized either in four steps from *cis*-1,4-diketo-2-methoxy-10-methyl-$\Delta^{2,6}$-hexahydronaphthalene (I) as described by Woodward, *et al.*,[10] or by catalytic hydrogenation of 2-keto-10-methyl-$\Delta^{1(9)}$-octalin (III) which had been prepared from 2-methylcyclohexanone and the methiodide of 1,1-diethylamino-3-butanone by a modification of the method of duFeu, McQuillin and Robinson.[11] The intermediate ketone VI was synthesized by the method of Gaddis and Butz[12] employing butadiene and 2-methylcyclohex-2-en-1-one. The 9-methyldecalin received from either *cis* intermediate was identical and the properties of the highly purified material as well as the properties of the compounds prepared by Linstead[5,6] are listed in Table I. It is readily seen that the material from ketones II or VI possesses properties quite similar to those reported by Linstead, Millidge and Walpole[6] but different from those reported by Hibbit and Linstead.[5] Thus, the method of preparation used in the present work further establishes the *cis* nature of the 9-methyldecalin prepared from 9-methyl-2-decalone.

trans-9-Methyldecalin (IX) was prepared by the Clemmensen reduction of the *trans* isomers (VIII

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[1] Ethyl Corporation Predoctoral Fellow, 1953–1954.

[2] W. G. Dauben, R. C. Tweit and R. L. MacLean, This Journal, **77**, Jan. (1955).

[3] L. Ruzicka, D. R. Koolhaas and A. H. Wind, *Helv. Chim. Acta*, **14**, 1151 (1931).

[4] G. R. Clemo and H. G. Dickenson, *J. Chem. Soc.*, 735 (1935).

[5] D. C. Hibbit and R. P. Linstead, *ibid.*, 470 (1936).

[6] R. P. Linstead, A. F. Millidge and A. L. Walpole, *ibid.*, 1140 (1937).

[7] E. G. Davis, Doctoral Thesis (1942), Summaries of Theses, Harvard University Graduate School (1946).

[8] W. E. Bachmann, A. Ross, A. S. Dreiding and P. A. Smith, *J. Org. Chem.*, **19**, 222 (1954).

[9] R. B. Turner, This Journal, **74**, 2118 (1952).

[10] R. B. Woodward, F. Sondheimer, D. Taub, K. Heusler and W. M. McLamore, *ibid.*, **74**, 4223 (1952).

[11] E. C. duFeu, F. J. McQuillin and R. Robinson, *J. Chem. Soc.*, 53 (1937).

[12] A. M. Gaddis and L. W. Butz, This Journal, **69**, 117 (1947).

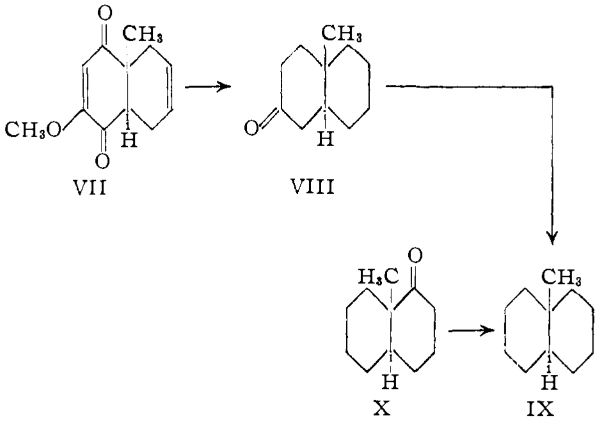
TABLE I

PROPERTIES OF 9-METHYLDECALINS

Compound	B.p. °C.	B.p. Mm.	n^{25}_D	d^{25}_4	[M] Obsd.	[M] Calcd.	$[EM]_D$
cis (present work)	91.5–92.0	20	1.4791	0.8924	48.37	48.60	−0.23
trans (present work)	90.4–90.6	20	1.4764	.8857	48.54	48.60	−0.06
"$AlCl_3$" (present work)	...		1.4638				
"COOH" (present work)	90.0–91.0	20	1.4764	.8855	...	...	...
cis (L, M and W[6])	79	11	1.4786[a]	.8911[a]	48.63	48.60	+0.03
cis (H and L[5])	82	11	1.4771[a]	.8850[a]	48.63	48.60	+0.03
trans (R, K and W[3])	70	12	1.4609[a]	.8550[a]	48.82	48.60	+0.22
"$AlCl_3$" (H and L[5])	70	11	1.4668[a]	.8601[a]	49.03	48.60	+0.43

[a] Converted from lower temperatures to 25° by means of the values d*n*/d*t* = −0.00047/°C. and d*d*/d*t* = −0.00066/°C., which were determined in the present work.

and X) of the two ketones employed in the *cis* synthesis. The intermediate *trans* ketone (VIII) was obtained following the procedure of Woodward, *et al.*,[10] and the ketone X was synthesized by the method of Johnson and Highet[13] which started with 1-decalone. The hydrocarbon IX obtained



from each *trans* ketone was identical and the properties of the highly purified *trans*-9-methyl decalin are listed in Table I. For comparison, the properties of the hydrocarbon synthesized directly by Ruzicka[3] and the material obtained by Hibbit and Linstead[5] by aluminum chloride isomerization of their "*cis*"-9-methyldecalin are listed in the same table. It is apparent that the 9-methyldecalin prepared from ketones VIII and X differs markedly from the earlier preparations. In view of the proved stereochemistry of the *trans* intermediates VIII and X employed in the present work, it must be concluded that the hydrocarbons obtained by Ruzicka[3] and Hibbit and Linstead[5] were not pure 9-methyldecalins. Upon re-examination of the methods of synthesis utilized by these later two investigators, it is not unexpected that such is the case. For example, Ruzicka[3] prepared his "*trans*-9-methyldecalin" by a Clemmensen reduction of a cyclic 1,3-diketone and Dey and Linstead[14] have shown that such a reduction of 5,5-dimethylcyclohexane-1,3-dione (dimedone) does not yield the expected 1,1-dimethylcyclohexane but the rearrangement products, 2,4,4-trimethylcyclopentanone and 1,1,3-trimethylcyclopentane. Therefore, it seems reasonable to suggest that the material obtained by Ruzicka[3] contained some dimethylhydrindane. On the other hand, Hibbit and Linstead[5] prepared their *trans* material by aluminum chloride isomerization of a hydrocarbon and it is not uncommon to obtain carbon skeleton rearrangements of cycloparrafins under the similar mild conditions.[15] Indeed, it has been shown that in such an isomerization of *cis*-decalin itself but under more vigorous conditions, skeletal rearrangement occurs to a small extent.[16] As a further indication of a rearrangement in the aluminum chloride treatment, it has been found that when the pure *trans*-9-methyldecalin prepared in the present work was subjected to such a reaction, it gave rise to a hydrocarbon with a refractive index similar to that reported by Hibbit and Linstead.[5] Also, the infrared spectrum of such isomerized material (see Fig. 1) displayed several bands not present in either the authentic *cis*- or *trans*-9-methyldecalin. To date, no chemical proof is available as to the actual composition of the rearranged material.[17]

Returning to the properties listed in Table I, it is of interest to note that the densities and refractive indices of the authentic isomeric 9-methyldecalins differ less than with the unsubstituted *cis*- and *trans*-decalins (n^{20}_D 1.4811, d^{20}_4 0.8963 and n^{20}_D 1.4697 and d^{20}_4 0.8699, respectively).[18] This greater similarity in physical properties in the 9-methyl series perhaps is a reflection of a lesser energy difference than between the decalins themselves (2.4 kcal.). It is of further interest to note that utilizing the new values found for the *trans*-9-methyldecalin, the difference between the values for the molecular refractivity of the two isomers (0.29) is of the same order of magnitude as in decalin itself (0.38) and in the usual direction. The infrared spectra of the two isomeric 9-methyldecalins are shown in Fig. 1 and the differences are only readily discernible when thick films are employed.

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[13] W. S. Johnson and R. J. Highet, private communication; see also W. S. Johnson, THIS JOURNAL, **65**, 1317 (1943); W. S. Johnson and H. Posvic, *ibid.*, **69**, 1362 (1947).

[14] A. N. Dey and R. P. Linstead, *J. Chem. Soc.*, 1063 (1935).

[15] C. A. Thomas, "Anhydrous Aluminum Chloride in Organic Chemistry," A.C.S. Monograph 87, Reinhold Publ. Corp., New York, N.Y., 1941, p. 787.

[16] R. L. Jones and R. P. Linstead, *J. Chem. Soc.*, 616 (1936); G. Chiurdoglu and J. L. Jaminet, *Bull. soc. chim. Belg.*, **62**, 448 (1953).

[17] Although recently it has been shown (E. J. Eisenbraun, S. M. McElvain and B. F. Aycock, THIS JOURNAL, **76**, 607 (1954)) that substituted 9-methyldecalins give a poor yield of acetic acid in the Kuhn-Roth oxidation and values of 0.34–0.56 of one C–CH_3, the results obtained on the pure *trans*-9-methyldecalin and on the rearranged material perhaps are indicative of a higher C–CH_3 content in the latter compound. The results are: *trans*, 0.41, 0.44, 0.44; rearranged, 0.64, 0.67.

[18] W. F. Seyer and R. D. Walker, THIS JOURNAL, **60**, 2125 (1938).

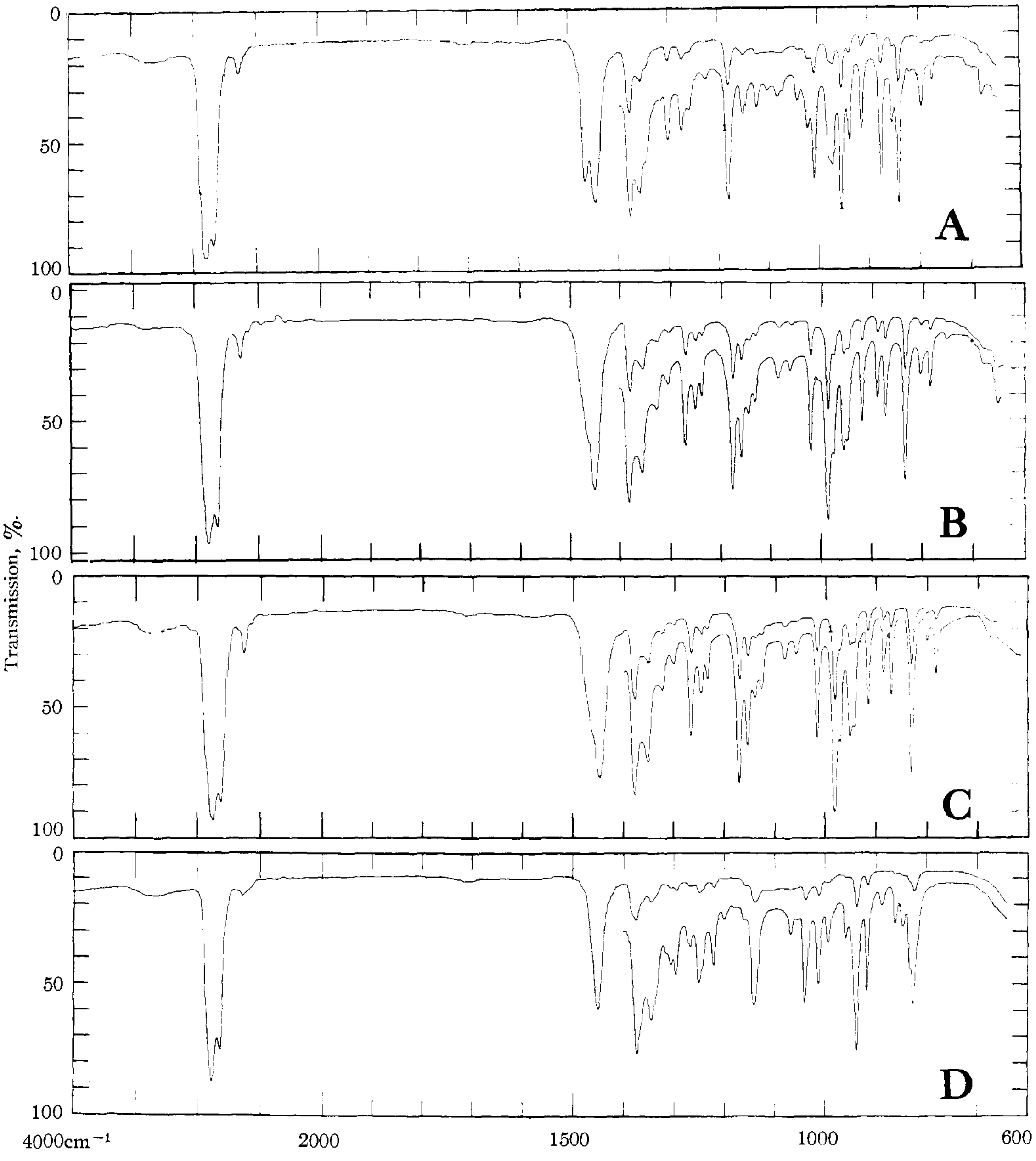

Fig. 1.—Infrared spectra of the isomeric 9-methyldecalins: A, *cis*-9-methyldecalin from *cis*-10-methyl-2-decalone; B, *trans*-9-methyldecalin from *trans*-10-methyl-2-decalone; C, *trans*-9-methyldecalin from *trans*-9-carboxydecalin; D, $AlCl_3$ isomerization product of *trans*-9-methyldecalin. All spectra were run as liquid films using a Perkin-Elmer Model 21 instrument. The cell length for the lower curve in each case is 0.08 mm.

Lack of knowledge of the proximity in physical properties of the 9-methyldecalins has resulted in at least one incorrect structural assignment. Recently, Hussey, Liao and Baker[19] reported the preparation of a 9-carboxydecalin which in turn was converted to a 9-methyldecalin having properties similar to the literature values of the *cis* isomer.[20] On the basis of this evidence and the fact that their material was isomerized by aluminum chloride, it was assumed that the starting acid was of the *cis* configuration. This same acid has been investigated in this Laboratory[2] and it has been found that the 9-methyldecalin obtained from it possessed physical properties (see Table I) and an infrared spectrum (see Fig. 1) identical with the authentic *trans*-9-methyldecalin. Accordingly, all the compounds prepared by Hussey and his collaborators should be assigned the *trans* configuration at the ring juncture.

As a result of the work in the present investigation, it can be stated that the 9-methyldecalin pre-

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[19] A. S. Hussey, H. P. Liao and R. H. Baker, THIS JOURNAL, **75**, 4727 (1953).

[20] The refractive index ($n^{25}D$ 1.4802) reported is higher than the pure *cis* hydrocarbon but it has been found in the present work that unless care is taken to remove the 9-decalyl carbinol present in the mixture, such a high value is always obtained.

pared by Linstead, Millidge and Walpole[6] was predominantly the *cis* isomer as assigned. In view of the proximity of the physical properties of the stereochemically isomeric hydrocarbons, however, the exact purity is difficult to ascertain unless great care has been taken in the purification. With regard to the suggestion of Bachmann, *et al.*,[8] that the 9-methyldecalin prepared by Hibbit and Linstead[5] from 9-methyl-Δ^2-octalin possessed a large amount of the *trans* isomer, such would appear to be the case as is readily seen by comparison of its physical properties with those of the pure *trans* material. The suggestion of the former authors with regard to the *cis* nature of the hydrocarbon prepared by Ruzicka, *et al.*,[3] appears to be incorrect and in actuality the material most likely is a mixture of various hydrocarbons. Finally, all comments with regard to the thermodynamic stability of the isomeric 9-methyldecalins must be withheld since it has been shown that the aluminum chloride isomerization brings about deep-seated rearrangements of the actual carbon skeleton.

Acknowledgment.—The authors are indebted to the Organic Chemicals Division of the Monsanto Chemical Company for generously supplying the *trans*-10-methyl-$\Delta^{3,6}$-hexahydronaphthalene used in this investigation.

Experimental[21]

2-Keto-10-methyl-$\Delta^{1(9)}$-octalin (III).—The compound was prepared by the method of duFeu, McQuillin and Robinson[11] as modified by Hussey, Liao and Baker.[19] It was found, however, that if the ratio of 1-diethylamino-3-butanone methiodide to 2-methylcyclohexanone was adjusted to 1.9/1 the yield was increased from 28 to 42%. The product boils from 140–143° (16 mm.), n^{25}_{D} 1.5203.

***cis*-1-Keto-9-methyl-Δ^6-octalin (V).**—The procedure employed was similar to that described by Gaddis and Butz[12] except for modifications which increased the yield.

2-Methylcyclohex-2-en-1-one (100 g., 0.91 mole, b.p. 102–104° (75 mm.), n^{25}_{D} 1.4839), prepared according to Warnoff and Johnson,[22] was placed in a Pyrex liner of a high pressure hydrogenation bomb. While cooling in a Dry Ice-bath, 200 ml. of butadiene was condensed into the liner, 0.1 g. of hydroquinone added and the reaction mixture placed into the bomb. After heating at 230° for 7 hours, the material was distilled and yielded the following fractions: (1) b.p. 75–77° (150 mm.), 81.1 g., n^{25}_{D} 1.4620; (2) b.p. 60–100° (75 mm.), 16.0 g., n^{25}_{D} 1.4791; (3) b.p. 100–104° (75 mm.), 64.1 g., n^{25}_{D} 1.4833; (4) b.p. 72–118° (20 mm.), 16.6 g., n^{25}_{D} 1.4850; (5) b.p. 100–111° (10 mm.) 18.0 g., n^{25}_{D} 1.5020. The distillation residue was 37 g.

Fractions 3 and 4 were shown to consist mainly of recovered starting material and were reused and fraction 5 was the desired condensation product, contaminated with a considerable amount of a side-reaction product, probably the trimer of butadiene. Gaddis and Butz[12] report the following properties for their compound, b.p. 58–65° (0.4 mm.), n^{25}_{D} 1.5031–1.5078.

The crude 1-keto-9-methyl-Δ^6-octalin (17.95 g.) was converted to the oxime by the procedure of McElvain.[23] After recrystallization from aqueous ethanol, the oxime was washed twice with cold petroleum ether and then recrystallized from ethanol–hexane, yield 7.0 g. (22.4% based upon recovered starting ketone), m.p. 118.2–121.0° (lit.[12] 123.2–125.0°).

***cis*-9-Methyl-1-decalone (VI).**—*cis*-1-Keto-9-methyl-Δ^6-octalin oxime (13.5 g., 0.075 mole) was heated under reflux with 75 g. (0.60 mole) of oxalic acid dihydrate and 350 ml. of water for one hour. After cooling and extraction with ether, the extracts were washed with water and saturated sodium bicarbonate solution and then dried. Following removal of the ether on the steam-bath, the 13.4 g. of crude *cis*-1-keto-9-methyl-Δ^6-octalin was dissolved in 50 ml. of ethanol and hydrogenated over 0.50 g. of 2% palladium on strontium carbonate. The theoretical amount of hydrogen was absorbed in 50 minutes and then the catalyst was removed by suction filtration through Super-cel and the saturated ketone converted directly to the oxime by the procedure of McElvain.[18] After recrystallization, first, from aqueous ethanol and then from benzene–petroleum ether, 10.23 g. (75%) of *cis*-9-methyl-1-decalone oxime, m.p. 114.8–115.7°, was obtained. Johnson[13] reports m.p. 114.5–115.5° for the oxime of the *cis* and 141.5–142.0° for the oxime of the *trans* isomer.

The oxime (10.2 g., 0.036 mole) was converted to the free ketone following the oxalic acid procedure above and the crude ketone distilled, b.p. 123.5–124.5° (20 mm.), n^{25}_{D} 1.4893 (lit.[13] 1.4897), yield 8.27 g. (88%).

***cis*-9-Methyldecalin (IV). (a) From *cis*-10-Methyl-2-decalone (II).**—The starting ketone (8.00 g., 48.2 moles, m.p. 43.4–47.2°, n^{25}_{D} 1.4908 (supercooled), prepared by hydrogenation of 2-keto-10-methyl-$\Delta^{1(9)}$-octalin as described by deFeu, McQuillin and Robinson[11] or from *cis*-1,4-diketo-2-methoxy-10-methyl-$\Delta^{2,6}$-hexahydronaphthalene as described by Woodward, *e tal.*,[10] was heated under reflux for 7 hours with 40 g. of amalgamated zinc, 17.5 ml. of concentrated hydrochloric acid and 35 ml. of glacial acetic acid with the addition of 2 ml. of concentrated hydrochloric acid every 2 hours. Water (60 ml.) was added and the reaction mixture directly steam distilled. The distillate was neutralized with aqueous sodium carbonate solution and extracted with pentane. After removal of the pentane on the steam-bath, the residue was heated with excess potassium at 170° for 30 minutes and then distilled from fresh potassium. The yield of *cis*-9-methyldecalin 6.57 g. (90%), b.p. 91.5–92.0° (20 mm.), n^{25}_{D} 1.4791, d^{25}_{4} 0.8926.

Anal. Calcd. for $C_{11}H_{20}$: C, 86.76; H, 13.24. Found, C, 87.08; H, 12.99.

(b) From *cis*-9-Methyl-1-decalone (VI).—The ketone (6.90 g., 41.5 mmoles) was reduced by the Clemmensen reaction and processed as described above. The yield of *cis*-9-methyldecalin was 3.49 g. (55%), b.p. 91.5–92.0° (20 mm.), n^{25}_{D} 1.4791, d^{25}_{4} 0.8923.

Anal. Found: C, 86.96; H, 13.22.

***trans*-9-Methyldecalin (IX). (a) From *trans*-9-Methyl-1-decalone.**—The starting ketone was prepared according to the procedure of Johnson and Highet[13] and purified as the semicarbazone. Regeneration from the semicarbazone yielded *trans*-9-methyl-1-decalone, b.p. 127.5–128.0° (20 mm.), n^{25}_{D} 1.4882. When 3.60 g. (23.7 mmoles) of the ketone was reduced by the Clemmensen method and isolated as described for the *cis* isomer, there was obtained 1.54 g. (47%) of *trans*-9-methyldecalin, b.p. 90.0–90.5° (20 mm.), n^{25}_{D} 1.4763.

Anal. Calcd. for $C_{11}H_{20}$: C, 86.76; H, 13.24. Found: C, 86.48; H, 12.76.

(b) From *trans*-10-Methyl-2-decalone.—The starting ketone was prepared by catalytic hydrogenation of *trans*-2-keto-10-methyl-$\Delta^{3,6}$-hexahydronaphthalene according to the procedure of Woodward, *et al.*,[10] b.p. 133.0–134.5° (20 mm.), n^{25}_{D} 1.4883. Clemmensen reduction of the saturated ketone (12.00 g., 72.3 mmoles) and processing in the usual manner yielded *trans*-9-methyldecalin, yield 9.30 g. (84%), b.p. 90.0–90.5° (20 mm.), n^{25}_{D} 1.4765, d^{25}_{4} 0.8857.

Anal. Found: C, 86.56; H, 13.28.

(c) From *trans*-9-Decalylcarbinyl Tosylate.—The tosylate (20.0 g., 62.0 mmoles, m.p. 141.0–141.8°), prepared from *trans*-9-carboxydecalin as described elsewhere,[2,19] was added to 4.50 g. (121 mmoles) of crushed lithium aluminum hydride suspended in 100 ml. of anhydrous di-*n*-butyl ether. After heating under reflux for 3 hours, the reaction mixture was cooled, the excess hydride decomposed with water and the inorganic salts dissolved with 6 *N* hydrochloric acid. The ether layer was separated, washed with aqueous sodium bicarbonate and dried over magnesium sulfate. After removal of the di-*n*-butyl ether by distilla-

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(21) All melting points are corrected and all distillations were conducted with a 20″ wire-screen filled column of 12-plate efficiency. All analyses were performed by the Microanalytical Laboratory of the Department of Chemistry and Chemical Engineering, University of California, Berkeley.

(22) E. W. Warnoff and W. S. Johnson, THIS JOURNAL, **75**, 494 (1953).

(23) S. M. McElvain, "The Characterization of Organic Compounds," The Macmillan Co., New York, N. Y., 1946, p. 198.

tion at atmospheric pressure through a column, the residue was distilled under reduced pressure. After a small forerun, a fraction of 3.20 g. was collected, b.p. 91–94° (20 mm.), $n^{25}\mathrm{D}$ 1.4776. This fraction then was heated at 165° for 30 minutes with excess potassium and redistilled, yield 2.44 g. (26%), b.p. 90.0–91.0° (20 mm.), $n^{25}\mathrm{D}$ 1.4764, d^{25}_4 0.8855.

Anal. Found: C, 87.05; H, 12.61.

A higher boiling fraction and the distillation residue were combined and chromatographed on alumina. Elution with pentane yielded an additional 2.74 g. (29%) of *trans*-9-methyldecalin. Elution with ether and recrystallization from aqueous ethanol gave 0.70 g. (6.8%) of *trans*-9-decalylcarbinol, m.p. 83.8–84.5° (lit.[2,19] 84.2–84.6°).

Aluminum Chloride Isomerization of *trans*-9-Methyldecalin.—The pure hydrocarbon (0.75 g.) was allowed to stand over 0.25 g. of aluminum chloride for 6 days. The product was extracted with pentane, washed with sodium bicarbonate solution and the pentane removed by distillation. The residue was distilled through a short-path molecular type still at a pressure of 70 mm. and a block temperature of 90°. This afforded 0.61 g. (81%) of material, $n^{25}\mathrm{D}$ 1.4638.

BERKELEY 4, CALIFORNIA

[CONTRIBUTION FROM THE ROLLIN H. STEVENS MEMORIAL LABORATORY OF THE DETROIT INSTITUTE OF CANCER RESEARCH]

The Reformatsky Reaction with 2-Hydroxymethylenecyclohexanone. 5,6,7,8-Tetrahydrocoumarin[1]

BY ANDRE S. DREIDING AND ARTHUR J. TOMASEWSKI

RECEIVED APRIL 26, 1954

The Reformatsky reaction of 2-hydroxymethylenecyclohexanone (II) with methyl bromoacetate produced a 25% yield of 5,6,7,8-tetrahydrocoumarin (I) and a 30% yield of a diene–diester fraction. The structure of I was proven by its conversion with alkali to β-(2-ketocyclohexylidene)-propionic acid (VII, R = H) under mild conditions and to cyclohexanone under stronger conditions. The pyrone (I) readily reacted with maleic anhydride. Saponification of the diene–diester fraction gave β-(2-carboxymethyl-1-cyclohexene)-acrylic acid (XII, R = H) (or possibly a double bond isomer). An examination of the Reformatsky product from the benzoate of 2-hydroxymethylenecyclohexanone (XVI) and ethyl bromoacetate verified the previously assigned structure as 2-benzoyloxymethylene-1-carbethoxymethylcyclohexanol (XVII, R = C_2H_5). It was converted to 2-carbethoxymethyl-1-cyclohexenecarboxaldehyde (X, R = C_2H_5) with acid and to 1-acetylcyclohexene (XXI) with alkali.

In continuation of our investigation of the use of hydroxymethylene ketones as starting materials for certain syntheses,[2] we have subjected 2-hydroxymethylenecyclohexanone (II) to a Reformatsky reaction with 3.1 moles of methyl bromoacetate in ether. The two major products were separated by fractional distillation.

The lower boiling product, $C_9H_{10}O_2$, m.p. 64.5–65°, 25% yield, was soluble in concentrated hydrochloric acid and in 10% sodium hydroxide, but not in water. It did not react with 2,4-dinitrophenylhydrazine in 50% sulfuric acid, but it did form a red 2,4-dinitrophenylhydrazone after being treated with alkali and then acidified. These reactions, as well as the absorption spectrum, $\lambda^{\mathrm{alc}}_{\mathrm{max}}$ 309 mμ (ε 7,000), are consistent with an α-pyrone structure.[3]

Two alternative structures can be proposed for an α-pyrone of this empirical formula, formed in this Reformatsky reaction. It is likely, as it was in the case of the reaction of II with Grignard reagents,[2] organolithium compounds[2] and lithium aluminum hydride,[4] that the Reformatsky reagent first reacted with the active hydrogen of II to give the enolate salt V. The latter could condense further with the reagent at position a or b, and thus form either IV or VI. By a loss of a molecule each of bromozinc methoxide and bromozinc hydroxide, IV could be converted to 5,6,7,8-tetrahydrocoumarin (I) directly in the Reformatsky medium, while VI could form 4,5-tetramethylene-α-pyrone (III) in the same manner.

An α-pyrone with structure I has not been previously described while structure III has been assigned by Plattner, Treadwell and Scholz[5] to an unstable oil, b.p. 120–130° at high vacuum, which solidified on cooling and liquefied at about 28°. This incomplete characterization as well as some uncertainty as to the structure (see below) did not allow a conclusion on the structure of the Reformatsky product and it was thus necessary to adduce independent evidence: A treatment of the pyrone with 5% alkali produced an 81% yield of cyclohexanone. This can best be rationalized on the basis of structure I for the pyrone, which must have suffered a hydrolysis, ring opening followed by hydration and retroaldolization.[6] Confirmation of structure I was obtained from the mild alkaline hydrolysis which yielded β-(2-ketocyclohexylidene)-propionic acid (VII, R = H) as the 2,4-dinitrophenylhydrazone, whose ultraviolet absorption spectrum was almost identical with that of the derivative of 2-ethylidenecyclohexanone,[2] but differed from that of 2-methyl-1-cyclohexenecarboxaldehyde (XVIII)[2] (see below).

On this basis, it can be concluded that the lower boiling fraction of the Reformatsky product is 5,6,7,8-tetrahydrocoumarin (I). It is of interest that the palladium-catalyzed dehydrogenation did not yield coumarin. I readily underwent a Diels–Alder reaction with maleic anhydride in boiling xylene to give a high melting product (possibly XIII), which may have resulted from the introduc-

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[2] A. S. Dreiding and S. N. Nickel, THIS JOURNAL, **76**, 3965 (1954).

[3] J. Fried and R. C. Elderfield, *J. Org. Chem.*, **6**, 266 (1941).

[4] A. S. Dreiding and J. A. Hartman, THIS JOURNAL, **75**, 939 (1953).

[5] Pl. A. Plattner, P. Treadwell and C. Scholz, *Helv. Chim. Acta*, **28**, 771 (1945).

[6] This term is used to designate the reverse process of an aldolization or aldol condensation.