[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE POLYTECHNIC INSTITUTE OF BROOKLYN]

Sterol Models. II. 4a-Methyl-*cis*- and -*trans*-decahydronaphthalenes and their -4a-methyl-d_3 Analogs[1,2]

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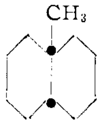
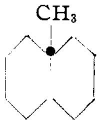
The synthesis of the stereochemically pure compounds referred to in the title has been effected. Their infrared spectra have been examined to determine whether a specific band is associated with the *cis* or *trans* arrangement of the angular group. For the *trans* series 2-ethoxycarbonylcyclohexanone was converted by means of methyl vinyl ketone to 4a-ethoxycarbonyl-4,4a,5,6,7,8-hexahydro-2[3H]naphthalenone (V), reduction of which gave 4a-ethoxycarbonyl-*trans*-3,4,4a,-5,6,7,8,8a-octahydro-2[1H]naphthalenone. Clemmensen reduction gave 4a-ethoxycarbonyl-*trans*-decahydronaphthalene. Conversion of the ester group to methyl was effected by (1) reduction with lithium aluminum hydride, (2) conversion to the tosylate, (3) conversion to the thiobenzyl ether, and (4) hydrogenolysis with Raney nickel. The deuterio series was obtained by substituting lithium aluminum deuteride and deuterium-saturated nickels for the ordinary compounds. For the *cis* series V was converted to the dioxolane by reaction with 2-methyl-2-ethyldioxolane and *p*-toluenesulfonic acid. Reduction with lithium aluminum hydride, and then hydrogen, and finally under Clemmensen conditions afforded *cis*-4a-hydroxymethyldecahydronaphthalene. Again reduction of the thiobenzyl ether, obtained through the tosylate, gave 4a-methyldecahydronaphthalene. Substitution of lithium aluminum deuteride and deuterium-saturated nickel gave the deuterio analogs. The infrared spectra showed that the band at 1380 cm.$^{-1}$ for the methyl group is shifted to 1370 cm.$^{-1}$, but the effect is too small to be of value in determining the configuration of sterols.

Introduction

The purpose of this investigation was to determine whether a specific band in the infrared could be assigned to the *cis* (I) or *trans* (II) configuration of the methyl group in 4a-methyldecahydronaphthalene. Were this assignment possible and capable of extrapolation to the sterols, it would be of general interest. In this paper the syntheses of the decahydronaphthalenes necessary to test the idea are presented and the outcome of their spectral investigation is discussed. The syntheses of the 3a-methylhydrindans required to test the same idea already have been reported.[5]



I



II

Results and Discussion

In order to obtain the stereospecificity required for the successful outcome of the work, the Diels–Alder reaction between a substituted cyclohexene and butadiene appeared to be ideal.[6] However, in attempting the reaction of butadiene with methyl cyclohexene-1-yl ketone, cyclohexene-1-carbonitrile, ethyl cyclohexen-6-one-1-carboxylate 2,5-dihydrobenzoic acid, acetylenedicarboxylic acid and methyl gentisate, no Diels–Alder adduct at all or only a trace was obtained. Temperatures, molar ratios of diene to dienophile and time of reaction were varied, but only starting materials and butadiene dimer could be isolated. Inhibitors, such as phenyl-β-naphthylamine, picric acid and hydroquinone offered no improvement, nor did operating under nitrogen.[7] These results were surprising when compared with the ease with which corresponding cyclopentenes reacted[5] and in view of the fact that cyclohexen-1-aldehyde does react.[8] These observations suggest that with just one group activating the carbon–carbon double bond only –CHO is sufficiently activating to overcome the steric factor in forming the fused octahydronaphthalene system. In any case an alternative route was needed.

The successful route to II was essentially that of Hussey, Liao and Baker[9] with one modification, namely, the conversion of the angular tosylate X to I (see Chart I). In our hands the direct hydrogenolysis of X was not satisfactory (see, however, footnotes[6a,9]). In the preferred route, the tosylate was converted to the angular benzyl thioether XIV without isolation and the latter was hydrogenolyzed with hydrogen-on-nickel.[10,11]

Returning to the main problem, the introduction of deuterium in the angular methyl group next was effected. Reduction of the *trans*-ester VII with lithium aluminum deuteride (LAD) gave decahydro-4a-naphthalenemethanol-d_2 (XII), which was readily converted to the tosylate XIII. Hydrogenolysis of the thiobenzyl ether XIV with deuterated Raney nickel[13] afforded XV.

It is known[14,15] that III hydrogenates to give IV,

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[1] This work was supported by the National Institutes of Health, Grant G-3124.

[2] Presented at the 127th Meeting of the American Chemical Society, Cincinnati, Ohio, March 29–April 7, 1955, Abstracts, p. 49-N.

[3] Taken from the Dissertation submitted to the Graduate Faculty of the Polytechnic Institute of Brooklyn in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1955.

[4] To whom inquiries should be directed.

[5] R. L. Kronenthal and E. I. Becker, THIS JOURNAL, **79**, 1095 (1957).

[6] See (a) W. G. Dauben, J. B. Rogan and E. J. Blanz, Jr., *ibid.*, **76**, 6384 (1954); and (b) W. G. Dauben, R. C. Tweit and R. L. MacLean, *ibid.*, **77**, 48 (1955); for a discussion of some of the limitations of previous syntheses leading ultimately to the 4a-methyldecalins.

[7] For details see the Dissertation of M.I.

[8] J. Szmuszkovicz and E. D. Bergmann, *Bull. Research Council Israel*, **3**, No. 1/2, 93 (1953).

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

[10] An adaptation[9] of the procedure of F. G. Bordwell, B. M. Pitt and M. Knell, *ibid.*, **73**, 5004 (1951).

[11] Independently of one another, Dauben, *et al.*,[6a,b] Dreiding and Tomasewski,[12] and ourselves had found the mistaken assignment in footnote 9. Through the kind coöperation of Drs. Hussey and Baker, intermediates were exchanged. They were, in fact, the first to inform us that the melting point of authentic IV was depressed on admixture with their corresponding ketone (April 3, 1954).

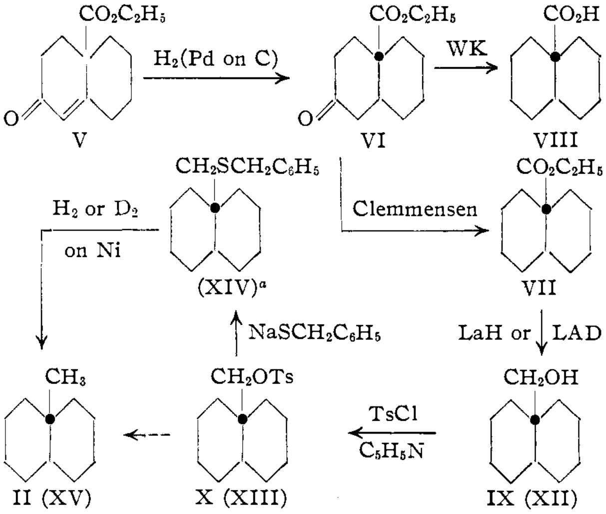
[12] A. S. Dreiding and A. J. Tomasewski, THIS JOURNAL, **77**, 168 (1955).

[13] N. A. Khan, *Science*, **117**, 130 (1953).

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

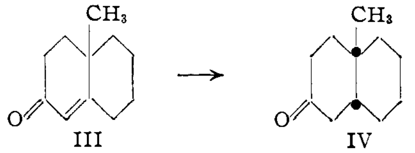
[15] R. B. Woodward, F. Sondheimer, D. Taub, K. Heusler and

CHART I



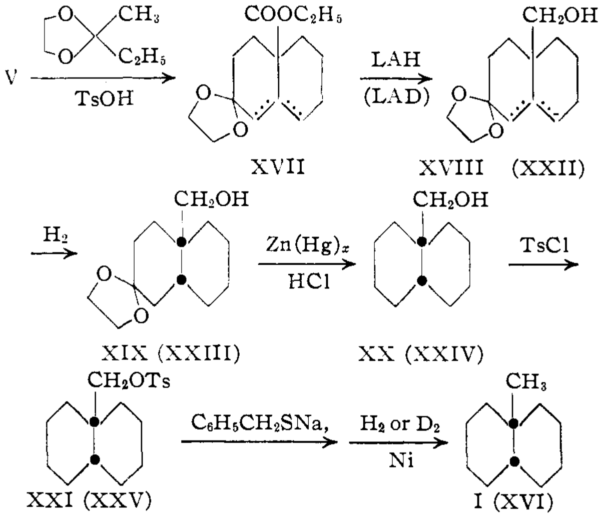
[a] Compounds in parentheses are deuterated.

the *cis*-ketone. Therefore, if V could be converted to III, catalytic hydrogenation followed by Clemmensen reduction would give XVI. In an attempt to change the course of the reduction of V, it was decided to protect the ketone group. Thus,



V was converted to the dioxolane-ester XVII by reaction with 2-ethyl-2-methyl-1,3-dioxolane in the presence of *p*-toluenesulfonic acid according to the elegant method of Dauben[16]

CHART II



[a] Compounds in parentheses are deuterated.

(see Chart II).[16a] During the reaction with *p*-toluenesulfonic acid, the position of the double bond becomes uncertain. Reduction of XVII with LAH afforded the alcohol XVIII. Saturation of the double bond could produce either the *cis* or *trans* isomer or both, but Kronenthal[5] had already prepared the pure *trans* isomer. A sample was reduced to XIX and its infrared spectrum was compared with the spectrum of the *trans* isomer; the fingerprint regions were quite different, so the reduction had probably been *cis*. Clemmensen reduction hydrolyzed the dioxolane and reduced the keto-alcohol to the alcohol XX. Its spectrum showed none of the peaks present in the *trans* isomer IX. The tosylate XXI could not be reduced with LAH, although it had seemed probable to us that in the more open *cis* molecule the displacement might be easier than with the *trans* isomer. The steps through the benzyl thio ether did prove successful, and compound I was obtained. Its spectrum was identical with that obtained *via* Linstead's procedure.

By the use of LAD on V and then the same sequence as described immediately above, XXV was prepared. The final deuteration was carried out *via* deuterated Raney nickel on the benzyl thio ether. However, the product showed only two deuterium atoms. Apparently the nickel had not been completely exchanged this time. Since three deuterium atoms were not necessary for the study of the spectra, the reaction was not repeated.

Experimental[17]

Ethyl Cyclohexene-6-one-1-carboxylate.—2-Ethoxycarbonylcyclohexanone was brominated by the method of Kotz.[18,19] 2-Bromo-2-ethoxycarbonylcyclohexanone was dropped through a pyrolysis tube[20] at 435–450° at a rate of 12 g./min. in a rapid stream of nitrogen.[21] The condensate was taken up in ether, washed with water until neutral, dried over calcium chloride, filtered, concentrated, and distilled. The fraction boiling from 100–130° (20 mm.) was collected and redistilled through a 30-cm. helix-packed column to give 43% of the unsaturated ester, b.p. 118–122° (20 mm.), n^{25}_{D} 1.5150.

4a-Ethoxycarbonyl-4,4a,5,6,7,8-hexahydro-2[3H]naphthalenone (V).—The two-step procedure of Wilds and Werth[22] applied to 2.4 moles of 2-ethoxycarbonylcyclohexanone and 300 ml. of 85% methyl vinyl ketone azeotrope gave an 80% yield of V, b.p. 100–130° (1.5 mm.), n^{24}_{D} 1.5110. Triton B and potassium hydroxide were the two bases used.[7]

The **semicarbazone** formed readily, m.p. 186–188°, after recrystallizations from ethanol and from benzene (reported 205–208°,[6b] 208°[14]).

Anal. Calcd. for $C_{14}H_{21}N_3O_3$: C, 60.19; H, 7.58; N, 15.05. Found: C, 60.07; H, 7.68; N, 14.79.

4a-Ethoxycarbonyl-*trans*-3,4,4a,5,6,7,8,8a-octahydro-2[1H]-naphthalenone (VI).—All of the unsaturated ester V was hydrogenated in 80-g. batches each in 100 ml. of ethanol containing 2 g. of 10% palladium-on-charcoal and 10 g. of

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W. M. McLamore, This Journal, **74**, 4223 (1952), have shown that at least 10% of the *trans* isomer is also present.

(16) H. J. Dauben, Jr., B. Loken and H. J. Ringold, *ibid.*, **76**, 1359 (1954).

(16a) Since our work was completed, the sequence XVII → XIX has been reported in a slightly different way [(b) L. S. Minckler, A. S. Hussey and R. H. Baker, *ibid.*, **78**, 1009 (1956)] and discussed [(c) W. G. Dauben and J. B. Rogan, *ibid.*, **79**, 5002 (1957)].

(17) Melting points are corrected. Microanalyses were carried out by Dr. K. Ritter, Microanalytisches Laboratorium, Basel, Switzerland. Analyses for deuterium were carried out by Mr. Byron Arison, Merck & Co., Inc.

(18) A. Kötz, *Ann.*, **358**, 199 (1907).

(19) A. Kötz and T. Grethe, *J. prakt. Chem.*, [2] **80**, 494 (1909).

(20) E. R. Burns, D. T. Jones and P. D. Ritchie, *J. Chem. Soc.*, 400 (1935).

(21) Kötz[18] had dehydrobrominated the bromo-keto-ester with aniline claiming a quantitative yield. In our hands the product could not be isolated by this procedure. Kötz[19] had also prepared the unsaturated keto-ester by distillation of the bromo-keto-ester at atmospheric pressure; it was this which led us to the successful hot-tube experiment. The conditions cited represent optimum conditions.

(22) A. L. Wilds and R. G. Werth, *J. Org. Chem.*, **17**, 1149 (1952).

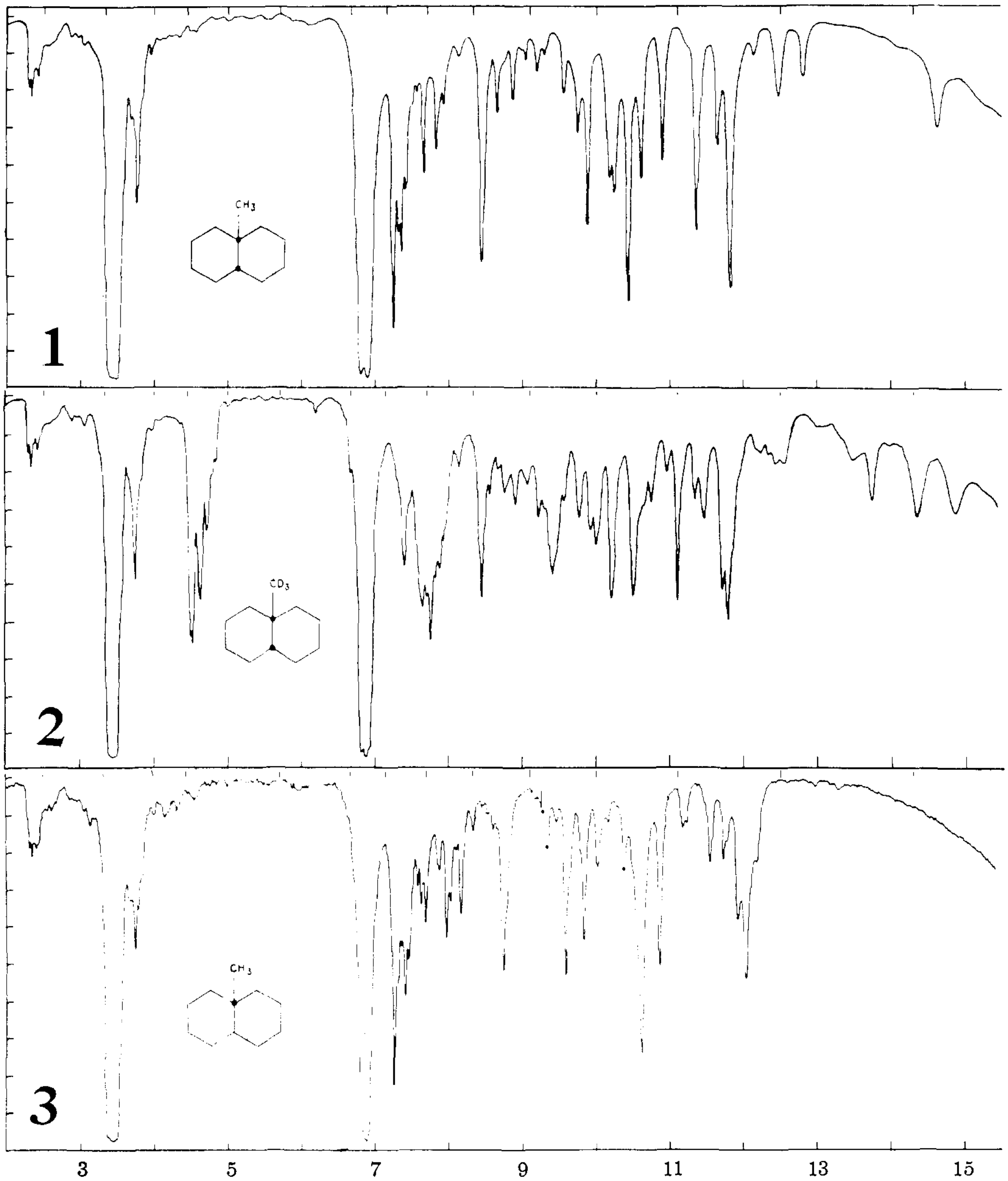

Fig. 1.—Infrared spectra: 1, 4a-methyl-*cis*-decahydronaphthalene (I) (0.0565-mm. cell); 2, 4a-methyl-d_3-*cis*-decahydronaphthalene (XVI) (0.0565-mm. cell); 3, Linstead's "*trans*-9-methyldecalin" (0.0565-mm. cell).

calcium carbonate at 3 atm. The catalyst was filtered and reused without any noticeable decrease in activity after five reactions.

The semicarbazone was prepared from the solution of VI using a 10% excess of semicarbazide hydrochloride. The entire batch was recrystallized from ethanol three times to a melting point of 181–184°. The progress of purification was followed by taking infrared spectra of Nujol mulls. When the above melting point was reached, the spectrum was the same as the analytical sample, which was obtained by two additional crystallizations from benzene, m.p. 186–188° dec. A total of 479 g. (1.75 moles, 92%, based on crude V), m.p. 181–184°, was obtained after concentration of the mother liquors.

Anal. of semicarbazone: Calcd. for $C_{14}H_{23}N_3O_3$: C, 59.76; H, 8.24; N, 14.94. Found: C, 59.56; H, 8.12; N, 14.88.

The free ketone was regenerated from the pure semicarbazone with concentrated hydrochloric acid, steam and vacuum distilled, and finally dried over paraffin for analysis. The constants were b.p. 100° (0.5 mm.), $n^{25}\text{D}$ 1.4801, d^{25}_4 1.077 (reported b.p. 146–148° (2 mm.),[9] 111–113° (0.5 mm.),[6b] 135–136° (3.5 mm.),[6b] $n^{25}\text{D}$ 1.4790[9], $n^{25}\text{D}$ 1.4829[6b]).

Anal. Calcd. for $C_{13}H_{20}O_3$: C, 69.61; H, 8.99; *R*D, 59.45. Found: C, 69.95; H, 8.93; $R^{25}\text{D}$, 59.16.

4a-Ethoxycarbonyl-*trans*-decahydronaphthalene (VII). **A. Usual Procedure.**—The semicarbazone, m.p. 181–184°, 294 g. (1.04 moles), was refluxed with 660 g. of mossy zinc (amalgamated with 66 g. of mercuric chloride) and 500 ml. of concentrated hydrochloric acid. An additional 400 ml. of acid was added in 100-ml. portions during the first four hours. The mixture was refluxed for 18 hours and then distilled with steam to separate the product from resinous by-products. The steam distillate was saturated with salt and extracted with ether. After washing and drying, the product was distilled yielding 97 g. (0.47 mole, 45%), b.p. 70–85° (1.0–1.5 mm.). Redistillation gave b.p. 76–77° (0.5 mm.), $n^{25}\text{D}$ 1.4790, d^{25}_4 1.0179.

Anal. Calcd. for $C_{13}H_{22}O_2$: C, 74.24; H, 10.55; *R*D, 58.28. Found: C, 74.15; H, 10.44; *R*D 58.59.

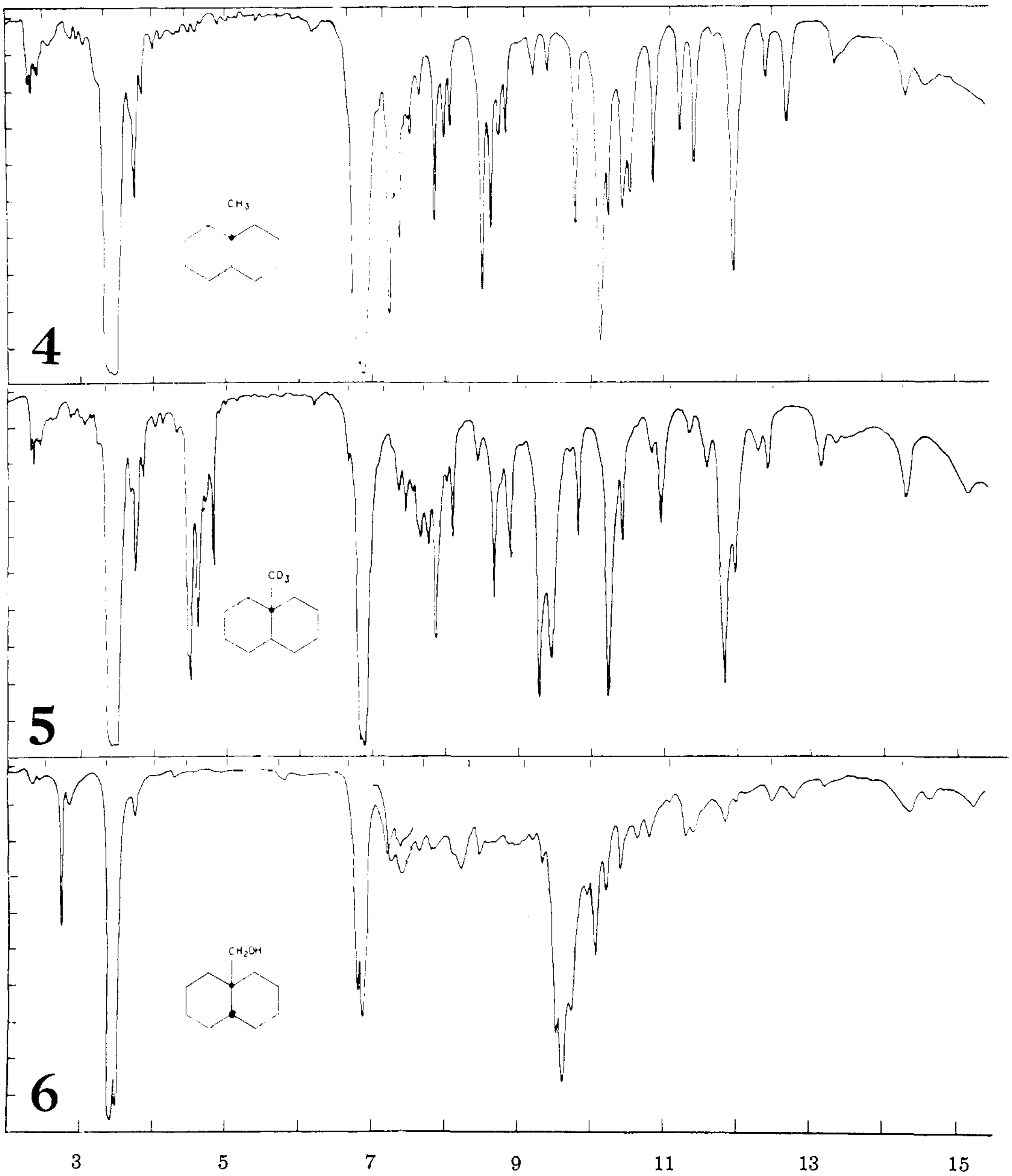

Fig. 2.—Infrared spectra: 4, 4a-methyl-*trans*-decahydronaphthalene (II) (0.0565-mm. cell); 5, 4a-methyl-d_3-*trans*-decahydronaphthalene (XV) (0.0565-mm. cell); 6, *cis*-decahydro-4a-naphthalenemethanol (XX) in carbon tetrachloride from 2.0–7.5 m., 0.063 molar; carbon bisulfide from 7.0–15.5 m., 0.060 molar.

B. With Rapid Distillation of Product.—In a 3-l., 3-necked flask fitted for steam distillation and bearing two dropping funnels were placed 300 ml. of water and 400 g. of amalgamated mossy zinc. One of the dropping funnels was filled with 217 g. (0.97 mole) of VI, which had been distilled, but not purified through the semicarbazone. Through the other dropping funnel 250 ml. of concentrated hydrochloric was added to the water, and the mixture was heated to boiling. The steam was then turned on, and the keto-ester slowly dropped into the boiling mixture. The distillate became cloudy almost immediately and had the characteristic sweet odor of VII. Additional hydrochloric acid was added slowly through the second dropping funnel while the keto-ester was added. After all of VI had been added, steam distillation was continued until no more oil distilled with the steam. The distillate was worked up as in A, yielding 156 g. (0.74 mole, 76.5%) of colorless VII. Practically no tarry residue remained in the reaction flask.

***trans*-4a-Decahydronaphthalenemethanol (IX)** was obtained in 80% yield according to Dauben,[6b] but substituting the ester VII for the acid VIII and using ethyl ether instead of *n*-butyl ether as the reaction solvent, m.p. 78–79.5° (reported 77–78°,[6b] 84°[9]) (see infrared spectrum 12).

Anal. Calcd. for $C_{11}H_{20}O$: C, 78.51; H, 11.98. Found: C, 79.06; H, 12.14.

Since purification by distillation or sublimation did not raise the melting point, derivatives were made and cleavage of them was tried to see if a pure sample could be obtained. The tosylate, described below, could be cleaved only with LAH, but the resulting alcohol exhibited the same characteristics on recrystallization.

The *p*-nitrobenzoate formed readily using *p*-nitrobenzoyl chloride in pyridine. After three crystallizations from ethanol, it melted at 89–89.5°.

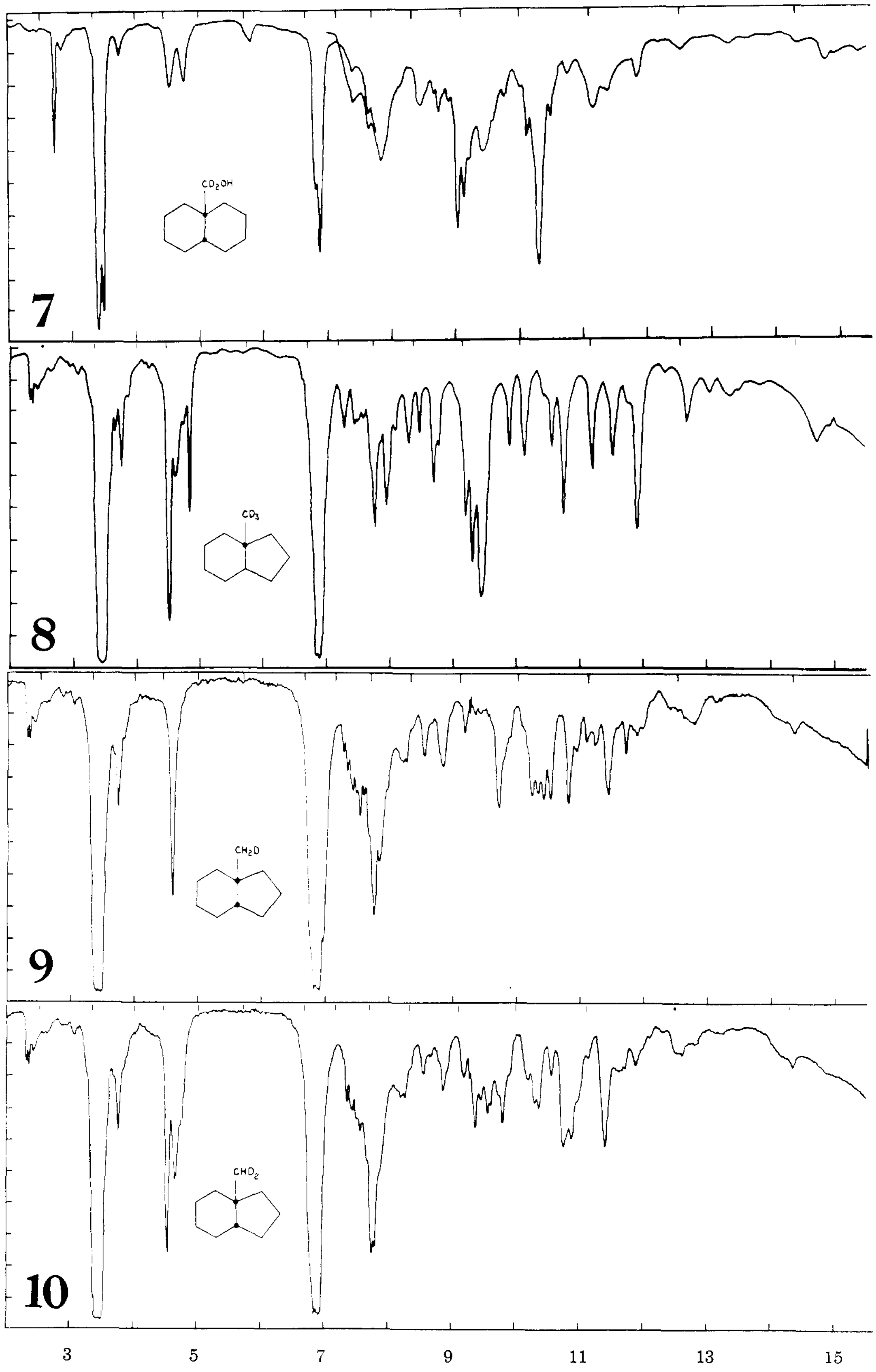

Fig. 3.—Infrared spectra: 7, *cis*-decahydro-4a-naphthalenemethanol-d_2 (XXIV) in carbon tetrachloride from 2.0–7.5 m., 0.058 molar; carbon bisulfide from 7.0–15.5 m., 0.057 molar; 8, 3a-methyl-d_3-*trans*-hexahydroindan (0.0565-mm. cell); 9, 3a-methyl-*d*-*cis*-hexahydroindan (0.0565-mm. cell); 10, 3a-methyl-d_2-*cis*-decahydroindan (0.0565-mm. cell).

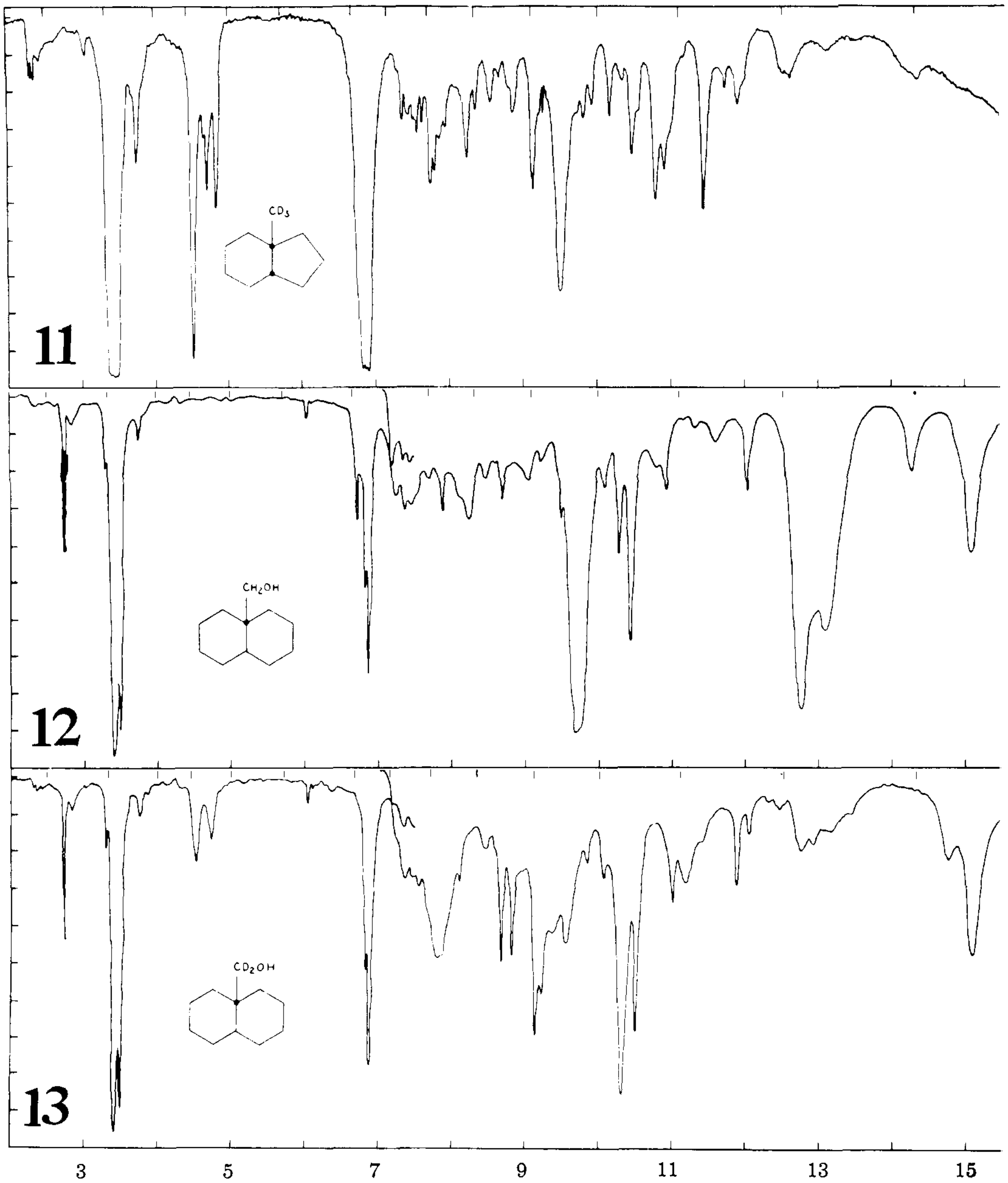

Fig. 4.—Infrared spectra: 11, 3a-methyl-d_3-*cis*-hexahydroindan (0.0565-mm. cell); 12, *trans*-decahydro-4a-naphthalenemethanol (IX) in carbon tetrachloride from 2.0–7.5 m., 0.055 molar; carbon bisulfide from 7.0–15.5 m., 0.062 molar; 13, *trans*-decahydro-4a-naphthalenemethanol-d_2 (XIX) in carbon tetrachloride from 2.0–7.5 m., 0.059 molar; carbon bisulfide from 7.0–15.5 m., 0.069 molar.

Anal. Calcd. for $C_{18}H_{23}NO_4$: C, 68.12; H, 7.30; N, 4.41. Found: C, 68.29; H, 7.46; N, 4.36.

The *p*-toluenesulfonate (X)[6b] melted at 137.5–139° (reported 139.7–141.7°,[6b] 142°[9]).

Anal. Calcd. for $C_{18}H_{26}O_3S$: C, 67.04; H, 8.13; S, 9.94. Found: C, 67.06; H, 8.01; S, 9.94.

***trans*-Decahydronaphthalenemethanol-d_2 (XII).**—The ester VII used for this preparation was obtained by distillation only and not by hydrolysis of its semicarbazone. From VII (n^{25}D 1.4757, 74 g., 0.352 mole) and 10.5 g. (0.250 mole) of LAD in 350 ml. of anhydrous ether refluxed for one week, there was obtained 57 g. (0.332 mole, 94%) of XII, b.p. 94–98° (0.8–1.3 mm.), m.p. 63–77°. Recrystallization from nitromethane raised the m.p. to 73–76°, unchanged by further crystallizations.

Anal. Calcd. for $C_{11}H_{18}D_2O$: C, 77.58; H + D as H, 11.97; D/H + D, 10.0. Found: C, 76.99; H + D as H, 12.09; D/H + D, 9.8.

Prepared according to Dauben, 51 g. (0.30 mole) of XII gave 77.5 g. of XIII, m.p. 138–140°. A final recrystallization from ethanol raised the melting point to 139–140° (71.5 g., 0.22 mole, 74%). From the mother liquors another 7 g. was isolated, m.p. 136–138°.

Anal. Calcd. for $C_{18}H_{24}D_2O_3S$: C, 66.62; H + D as H, 8.16; S, 9.88; D/H + D, 7.7. Found: C, 66.48; H + D as H, 8.00; S, 10.09; D/H + D, 7.6.

Reduction of X with LAH in ethyl ether or in *n*-butyl ether[9] gave at best 18% of II in our hands. The following procedure was adopted.

Using Hussey's[9] directions, 16.2 g. (0.05 mole) of the tosylate was refluxed in a solution of 2 g. of sodium and 10 ml. of benzyl mercaptan in 100 ml. of diethylene glycol monomethyl ether for five hours. It was then cooled, diluted with water and hydrochloric acid, and the excess mercaptan was distilled with steam. The whole was then poured into water, extracted three times with ether, washed with water, and dried over magnesium sulfate. Distillation of the ether left 13 g. of yellow oil, $n^{21}\text{D}$ 1.5452.

Using the minimum value of 125 ml. of hydrogen per 4 g. of Raney nickel,[23] about 70 g. of catalyst was required for the next reaction. It was difficult to get accurate weights of the catalyst. The pyrophoric nature of the metal made it necessary to weigh it wet with solvent. It could not be safely filtered with suction because it rapidly became warm as air was sucked through it. A satisfactory method for handling it was found to be centrifugation in tared bottles. After centrifuging for about five minutes at 2000 r.p.m., the nickel formed a thick, heavy sludge, and was assumed to consist of not less than 80% Raney nickel.

To the above oil in dioxane about 110 g. of Raney nickel slurry, weighed by this method, was added, and the mixture was refluxed with stirring for 12 hours. The nickel was removed by centrifugation, washed once with dioxane and centrifuged again, and the combined dioxane solutions were concentrated on a 12-plate column to about 50 ml. The residue was poured into water and extracted with petroleum ether (b.p. 30–40°), washed with water and dried over magnesium sulfate. Distillation gave a liquid, b.p. 80–83° (10 mm.), $n^{19.5}\text{D}$ 1.4798, which was heated at 170° for 0.5 hour with potassium and distilled giving 4.1 g. (53%) of II, b.p. 80–82° (11 mm.), $n^{25}\text{D}$ 1.4780, $d^{25}{}_4$ 0.8883. Its infrared spectrum was identical with that from B and it crystallized in Dry Ice.

Anal. Calcd. for $C_{11}H_{20}$: C, 86.76; H, 13.24; $R^{25}\text{D}$, 48.60. Found: C, 86.68; H, 13.15; $R^{25}\text{D}$, 48.55 (see infrared spectrum 4).

4a-Methyl-d_3-*trans*-decahydronaphthalene (XV).—Raney nickel, 160 g. according to the procedure above, was placed in a 2-l. suction flask with 250 ml. of pure dioxane and deuterated according to Khan.[13] Then 32.4 g. XIII was treated as before with 4 g. of sodium and 20 ml. of benzyl mercaptan in 200 ml. of diethyleneglycol monomethyl ether. The dried ether solution of the sulfide was flash-concentrated from a previously flamed out apparatus. After flushing the flask with nitrogen, the deuterated nickel was transferred to the flask, which was fitted with a mercury-seal stirrer and reflux condenser with drying tube; 10 ml. of 99.5% heavy water also was added to swamp out any remaining hydrogen. The mixture was stirred under reflux for 16 hours and then worked up as for the ordinary hydrocarbon to give 11.2 g. (0.072 mole, 64%) of liquid, b.p. 75–80° (10–12 mm.), $n^{23}\text{D}$ 1.4805. It solidified in Dry Ice. Distillation from potassium metal gave 9 g. (0.058 mole, 52%) of XV, b.p. 74–75° (11 mm.), $n^{25}\text{D}$ 1.4787, $d^{25}{}_4$ 0.9046.

Anal. Calcd. for $C_{11}H_{17}D_3$: D/H + D, 15.0; $R\text{D}$, 48.60. Found: D/H + D, 14.9; $R^{25}\text{D}$, 48.66 (see infrared spectrum 5).

4a-Ethoxycarbonyl-2,2-ethylenedioxy-1,2,3,4,4a,5,6,7- or -2,3,4,4a,5,6,7,8-octahydronaphthalene (XVII).—A mixture of 133 g. (0.6 mole) of VII, 464 g. (4 moles) of 2-ethyl-2-methyl-1,3-dioxolane[6] and 2 g. of *p*-toluenesulfonic acid was fractionally distilled, the methyl ethyl ketone discarded, and the excess dioxolane recovered. The residue was cooled, diluted with benzene, washed with water and dried over potassium carbonate. Distillation afforded 121 g. (0.455 mole, 76%) of XVII, b.p. 122° (0.5 mm.), 146° (1.5 mm.), $n^{25}\text{D}$ 1.5000. A redistilled sample boiled at 122–124° (0.6 mm.), $n^{25}\text{D}$ 1.5013 [115–115° (0.4 mm.), $n^{25}\text{D}$ 1.4996[16b]].

Anal. Calcd. for $C_{15}H_{22}O_4$: C, 67.64; H, 8.32. Found: C, 67.65; H, 8.25.

2,2-Ethylenedioxy-1,2,3,4,4a,5,6,7- or -2,3,4,4a,5,6,7,8-octahydro-4a-naphthalenemethanol (XVIII).—To 6.0 g. (0.16 mole) of LAH in 100 ml. of ether, 52.5 g. (0.2 mole) of XVII in 50 ml. of ether was added with stirring and then refluxed overnight. The excess LAH was destroyed with ethyl acetate and the complex was decomposed with just enough water to make the solid gummy. The ether solution was dried with magnesium sulfate, extracting the solid twice with ether. Removal of the ether at reduced pressure gave 44.2 g. (0.196 mole, 98%) of crude product. Distillation gave a liquid b.p. 140° (0.6 mm.), $n^{25}\text{D}$ 1.5265, 132–134° (0.4 mm.), $n^{25}\text{D}$ 1.5297.[16b]

Anal. Calcd. for $C_{13}H_{20}O_3$: C, 69.61; H, 8.99. Found: 69.43; H, 8.90.

2,2-Ethylenedioxy-*cis*-decahydro-4a-naphthalenemethanol (XIX).—A solution of 27.5 g. (0.123 mole) of XVIII in 50 ml. of ethanol was completely hydrogenated at room temperature over 0.7 g. of 5% palladium-on-charcoal in six hours. A twice-distilled sample boiled at 134–135° (0.5 mm.), $n^{25}\text{D}$ 1.5160.

Anal. Calcd. for $C_{13}H_{22}O_3$: C, 68.99; H, 9.80. Found: C, 68.81; H, 9.72.

***cis*-Decahydro-4a-naphthalenemethanol (XX).**—The crude XIX obtained from 0.2 mole of XVII without isolation of intermediates was refluxed with 300 g. of amalgamated mossy zinc in 100 ml. of water and 120 ml. of concentrated hydrochloric acid for 4.5 hours. The product was extracted from the cooled reaction mixture with petroleum ether (b.p. 30–40°), dried with magnesium sulfate and distilled. There was obtained 12.1 g. (0.072 mole, 36% from XVII) of XX, b.p. 95° (1.0 mm.), which became a soft solid on standing. Redistillation gave b.p. 88° (0.5 mm.).

Anal. Calcd. for $C_{11}H_{20}O$: C. 78.51; H. 11.98. Found: C, 78.58; H, 11.82 (see infrared spectrum 6).

***cis*-Decahydro-4a-naphthalenemethyl *p*-Tosylate (XXI).** Prepared as previously from 12.1 g. (0.072 mole) of XX and 15 g. (0.079 mole) of *p*-toluenesulfonyl chloride there was obtained 7.3 g. (0.021 mole, 31%) of XXI, m.p. 60–74°. Recrystallizations from methanol and from petroleum ether (b.p. 30–40°)–benzene (10:1) raised the melting point to 74–75.5°.

Anal. Calcd. for $C_{18}H_{26}O_3S$: C, 67.04; H, 8.13; S, 9.94. Found: C, 66.77; H, 7.95; S, 9.78.

4a-Methyl-*cis*-decahydronaphthalene (I).—Treatment of XXI with benzyl mercaptan and Raney nickel in ethanol (Davison sponge nickel catalyst is also satisfactory) in exactly the same manner as before gave I which had an infrared spectrum identical with that obtained from Linstead's ketone, *cis*-3,4,4a,5,6,7,8,8a-octahydro-2[1H]naphthalenone.[24]

***cis*-Decahydro-4a-naphthalenemethyl-d_2 *p*-Tosylate (XXV).**—A solution of 53 g. (0.20 mole) of XVII in 50 ml. of ether was added with stirring to 5.0 g. (0.12 mole) of LAD in 200 ml. of ether, and then the mixture was refluxed with continued stirring for 2.5 days. Ethyl acetate was added to destroy excess LAD. A saturated aqueous solution of magnesium sulfate was then added to decompose the complex until the mixture became slightly gummy. At this point solid, anhydrous magnesium sulfate was added until the gummy material became powdery. The solution was filtered, washing the solid with ether and combining the organic layers. Distillation removed most of the ether, the last traces being removed at reduced pressure on the steam-bath, leaving a residue of XXII.

The residue, in 100 ml. of ethanol containing 1.2 g. of 5% palladium-on-charcoal, absorbed the theoretical quantity of hydrogen in 11 hours at 3 atm. After filtering the catalyst, most of the solvent was distilled and the residue was refluxed with a mixture of 150 g. of amalgamated mossy zinc in 80 ml. of water and 100 ml. of concentrated hydrochloric acid for 4.5 hours. After cooling, the mixture was extracted with petroleum ether (b.p. 30–40°), the extract was washed once with water and dried over anhydrous magnesium sulfate. Distillation afforded 14.6 g. (0.086 mole, 43%) of XXIV, b.p. 90–93° (0.5–0.6 mm.).

From 12 g. (0.070 mole) of XXIV and 15 g. (0.078 mole) of *p*-toluenesulfonyl chloride in pyridine, there was obtained 16 g. of tosylate, m.p. 71–95°. Recrystallization from 250 ml. of methanol gave 2 g. of material, m.p. 130–134°. From the filtrate there was obtained 10 g. of XXV, m.p. 74–75.5°, and a second crop of 4 g., m.p. 73–75.5° (total yield of 61%, 26% based on XVII).

Anal. Calcd. for $C_{18}H_{24}D_2O_3S$: C, 66.62; H + D as H, 8.16; S, 9.88; D/H + D, 7.7. Found: C, 66.60; H + D as H, 8.15; S, 9.84; D/H + D, 7.4.

***cis*-Decahydro-4a-methyl-d_2-naphthalene (I).**—Treatment of 14 g. (0.0432 mole) of XXV with 2 g. of sodium and 10 ml. of benzyl mercaptan as for XXI (see above), followed by 100 g. of deuterated Raney nickel in dioxane afforded 4.0 g. (0.026 mole, 59.7%) of twice-distilled XVI, b.p. 89–91° (20 mm.), $n^{20}\text{D}$ 1.4810, $n^{25}\text{D}$ 1.4798, $d^{25}{}_4$ 0.9036.

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[23] N. A. Khan, THIS JOURNAL, **74**, 3018 (1952).

[24] R. P. Linstead, A. F. Millidge and A. S. Walpole, *J. Chem. Soc.*, 1140 (1937).

Anal. Calcd. for $C_{11}H_{18}D_2$: C, 85.63; H + D as H, 13.21; R_D, 48.60. Found: C, 85.48, 85.63; H + D as H, 13.30, 13.12; R_D, 48.49 (see infrared spectrum 1).

Infrared Spectra.—The infrared spectra were measured on a Perkin–Elmer model 21 recording spectrophotometer. All optics were of rock salt, including the sample windows. The liquid intermediates were spread between two rock salt plates without spacers. The spectra so obtained are qualitative only because the thickness is unknown. Solids were measured as mulls in Nujol, again giving qualitative spectra. The angular acid VIII and the alcohols—IX, XX and XXIV—were dissolved in carbon tetrachloride for the region 2.0–7.5 m. and in carbon bisulfide for the region 7.0–15.5 m. Because of the volatility of these solvents, the concentrations probably are not accurate to more than about 5%. All of the hydrocarbons were observed in a cell 0.0565-mm. thick.

The principal purpose of the work was to ascertain what changes are produced in the spectrum of a hydrocarbon by the deuteration of a methyl group. Certain predictions could be made; the well-known band at 1380 cm.$^{-1}$ should disappear and new C–D stretching bands should appear. The fate of the fingerprint region was not certain, but some changes were to be expected.

An isolated methyl group has three stretching modes, a symmetric frequency and two doubly degenerate asymmetric frequencies.[25] On deuteration these bands should shift inversely as the square roots of the reduced masses, but because they occur in the same region as ordinary methylene stretching frequencies, the precise locations of the new C–D bands could not be predicted. Hence, the location of the deuterium bands could not be checked. The steric environment of the methyl group might influence these frequencies, perhaps causing splitting of the degenerate bands, but the maximum number of deuterium bands to be expected should be three. Experimentally, the hexahydroindans showed four and the decalins at least five bands. By the method of synthesis and the deuterium content of the hydrocarbons it is improbable that deuterium is located anywhere else in the molecules. No explanation for the extra bands is offered.

A methyl group also has three bending modes[25]—a doubly degenerate asymmetric frequency occurring in the same region as the methylene bending absorption near 1450 cm.$^{-1}$ and a symmetric bending frequency at 1380 cm.$^{-1}$. The deuteromethyl groups should exhibit the symmetric mode at about 1055 cm.$^{-1}$. All of the methyl-d_3 compounds show this band very near the correct frequency.

The infrared curves of the six decalins and of three hexahydroindans are shown in infrared spectra-1,2 and 4–10 (see footnote 5 for the spectra of 3a-methyl-*trans*- and -*cis*-hexahydroindans). Some similarities can be observed. For example, a few bands in the *trans* isomers are absent in the *cis* and *vice versa*. Some bands are common to all of the compounds, and others are present only in the deuterated molecules. From the curves only the following generalizations can be made: The symmetric bending frequency of the methyl group occurs near 1380 cm.$^{-1}$ in CH_3 and near 1055 cm.$^{-1}$ in CD_3. Introduction of even a single deuterium atom causes profound changes in the fingerprint region and disappearance of the CH_3 band at 1380 cm.$^{-1}$.

The decahydro-4a-naphthalenemethanols (infrared spectra 6, 12) illustrate an interesting feature in the methylene bending region. These compounds were studied in carbon tetrachloride solution in this region so that extinction coefficients could be compared. It is seen that the steric environment has a pronounced influence on the position of the absorption of the methylene group. The ordinary *trans* isomer has a peak at 1490 cm.$^{-1}$, absent in the deuterated analog. The ordinary *cis* isomer has no such peak, but the intensity of the band at 1470 cm.$^{-1}$ is markedly reduced in its deuterated analog. Therefore, in the *cis* isomer, the corresponding methylene group absorbs at 1470 cm.$^{-1}$. That the effect is real is further borne out by the very close similarity of the absorption at 1470 and 1450 cm.$^{-1}$ in the deuterated alcohols; this absorption is likely due to the ring methylenes, which would be virtually unaffected by going from two *trans*-fused chair forms of cyclohexane to two *cis*-fused forms. This observation lends support to the suggestion made earlier that the steric environment of the methyl group affects the frequency of some of its vibrational modes. The symmetric bending mode, however, seems entirely independent of steric factors, for it occurs at 1380 cm.$^{-1}$ in both isomers as well as in the hexahydroindans.

The extension of the above results to the sterols themselves did not prove fruitful. After studying a number of infrared spectra of sterols related to androstane and etiocholane,[26] no peaks were found that were common to either series. Thus, the only structural feature which can be deduced as a result of the present infrared study relates to the angular methyl group. It absorbs at 1380 cm.$^{-1}$ as an isolated methyl group does. Jones' assumption[27] has been confirmed within the limitations of the model approach.

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[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE UPJOHN CO.]

Ozonolysis. II.[1] The Effect of Pyridine on the Ozonolysis of 4,22-Stigmastadien-3-one[2]

BY GEORGE SLOMP, JR., AND JAMES L. JOHNSON

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A quantitative infrared method was developed for determining the side-chain and nuclear double bonds of stigmastadienone. The rate of reaction of these double bonds with ozone was accordingly determined under various conditions. Presence of a small amount of pyridine had a striking effect on the selectivity of the reaction. A yield of 3-ketobisnor-4-cholen-22-al, the selective ozonolysis product, of over 90% is reported. Pyridine also caused the reaction to follow a different course. The formation of two aldehydes instead of the expected ozonolysis intermediates is attributed to a reaction of the zwitterion intermediate with the pyridine. Reductive "decomposition" with formaldehyde and a reaction of pyridine oxide and 3-ketobisnor-4-cholen-22-al are reported.

In the preparation of aldehydes by the ozonolysis of olefins it is of utmost importance to add exactly the correct amount of ozone to the solution because excess ozone causes undesirable side reactions which decrease the yield. Aldehydes are oxidized by ozone to acids and peracids,[3] and alcohols,

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[1] Preceding paper, G. Slomp, Jr., *J. Org. Chem.*, **22**, 1277 (1957).

[2] Presented in part before the Division of Organic Chemistry at the 129th Meeting of the American Chemical Society, Dallas, Texas, April 8–13, 1956, Abstracts p. 30-N.

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