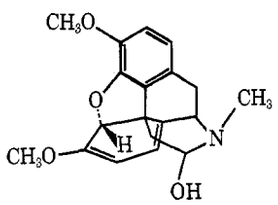
hydroxyamine form. The nmr spectrum[10] in deuteriochloroform with internal TMS standard also showed distinct similarities to that of thebaine: two methoxyl singlets at 3.86 and 3.62 (thebaine, 3.84 and 3.59) and a *N*-methyl group at 3.40 ppm (thebaine, 2.46). The spectrum further showed a one-proton singlet (C-5) at 5.41 (thebaine, 5.29) and two doublets (J = 6–7 cps) representing the C-7 and C-8 protons, resonating at 5.82 and 5.11 (thebaine, 5.54 and 5.02), and two aromatic protons in an AB quartet at 6.65 and 6.68 ppm (thebaine, 6.61 and 6.64). The strong downfield shift of the *N*-methyl protons indicated the presence of an electron-withdrawing group on an adjacent carbon atom.

It seems reasonable that the 16-hydroxy function may exist in solution in both epimeric forms interconvertible *via* the amino aldehyde.[11] However, the axial orientation of the hydroxy group in a half-chair conformation of the piperidine ring (II) may be considered the most prominent molecular species based on the downfield shift of the protons at C-5, C-7, and C-8.



II

Alkaloids which contain a hydroxyl group in the α position to the heterocyclic nitrogen are not uncommon, but have not been found previously among the hydrophenanthrenes. Thebaine is a very reactive molecule, and one cannot exclude the possibility that 16-hydroxythebaine may be an artifact produced during the drying or storage of opium or during the isolation and purification of the alkaloids. So far, extensive studies of the chemical reactions of thebaine have not revealed a product of this nature. *In vitro* oxidation of codeine introduces a hydroxyl function in the 10 position.[12] On the other hand, the biosynthesis postulated for several opium alkaloids involve oxidation at a carbon atom adjacent to the nitrogen, *e.g.*, biosynthesis of chelidonine, narcotine, porphyroxine, or protopine. It is, therefore, conceivable that the hydroxyl group is introduced at the reticuline stage and that 3-hydroxyreticuline may undergo biotransformation in the normal way to 16-hydroxythebaine. This view gains support from the fact that (+)-reticuline produced in the biosynthetic sequence is racemized in the opium poppy by an oxidation–reduction system.[13]

(10) Japan Electronic Optics Laboratory Model JNM 4H-100.

(11) R. W. King, C. F. Murphy, and W. C. Wildman, *J. Amer. Chem. Soc.*, **87**, 4912 (1965).

(12) H. Rapoport and G. W. Stevenson, *ibid.*, **76**, 1796 (1954).

Experimental Section

Isolation.—Four pounds of powdered opium of Indian origin were extracted and a preliminary separation of alkaloid groups was carried out as described in a previous communication.[14] A chloroform solution of the nonphenolic fraction was concentrated under reduced pressure. Addition of methanol gave a heavy precipitate containing mainly codeine and cryptopine. The filtrate was evaporated to dryness and the residue was extracted with ether. The ether solution was concentrated and subjected to preparative tlc on silica gel with chloroform–methanol (9:1) (double development). The alkaloid band having the lowest R_f value (*ca.* 0.05) was scraped off and extracted with methanol. The methanol solution, which contained several alkaloids as indicated by glc and analytical tlc, was concentrated and chromatographed on a column of neutral alumina (Woelm, activity IV) with benzene and ethanol. The polarity of the eluent was increased gradually during the elution by increasing the concentration of ethanol from 0 to 50%. The progress of the elution was monitored by glc and micro tlc. After the elution of 13-oxycryptopine[15] a new alkaloid appeared in the eluate. The fractions containing this alkaloid were combined and evaporated to dryness under reduced pressure. The yellowish-brown residue (29 mg) was crystallized from a mixture of acetone and petroleum ether (bp 30–60°), yielding pale yellow crystalline prisms which melted at 126–128° (capillary) and 118–119° (micro mp, K.). The crystalline compound exhibited single, well-defined spots in three different tlc systems, *e.g.*, silica gel with chloroform–methanol (9:1) and benzene–ethanol (4:1), alumina with benzene–ethanol (4:1).

Registry No.—II, 34388-67-5.

(13) A. R. Battersby, D. M. Foulkes, and R. Binks, *J. Chem. Soc.*, 3323 (1965).

(14) E. Brochmann-Hanssen, B. Nielsen, and K. Hirai, *J. Pharm. Sci.*, **56**, 754 (1967).

(15) E. Brochmann-Hanssen, A. Y. Leung, K. Hirai, and G. Zanati, *Planta Med.*, **18**, 366 (9970).

The Hydroboration of Dihydrothujopsene

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The hydroboration of dihydrothujopsene (**2**) at room temperature affords as the major component the abnormal hydroboration addition product, tertiary alcohol **7**, and a minor product, diol **8**, derived from the normal hydroboration addition orientation.

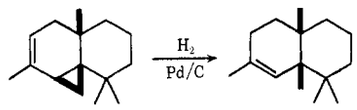
Although a number[1] of recent publications have dealt with the intriguing chemistry of the sesquiterpene hydrocarbon (−)-thujopsene (**1**) there has appeared no chemistry pertaining to dihydrothujopsene[2] (**2**), derived from **1** by catalytic 1,4 reduction.

During the course of some systematic investigations on the chemistry of thujopsene-derived hydrocarbons, we examined the hydroboration of dihydrothujopsene (**2**), expecting to obtain the secondary alcohol mixture **3** and **4** for eventual oxidation to the corresponding ketones. Although two products in a 77:23 ratio were indeed isolated in an overall yield of 84%, neither of these afforded the spectral or chemical characteristics compatible with secondary alcohols **3** and **4**.

The major component of the hydroboration reaction

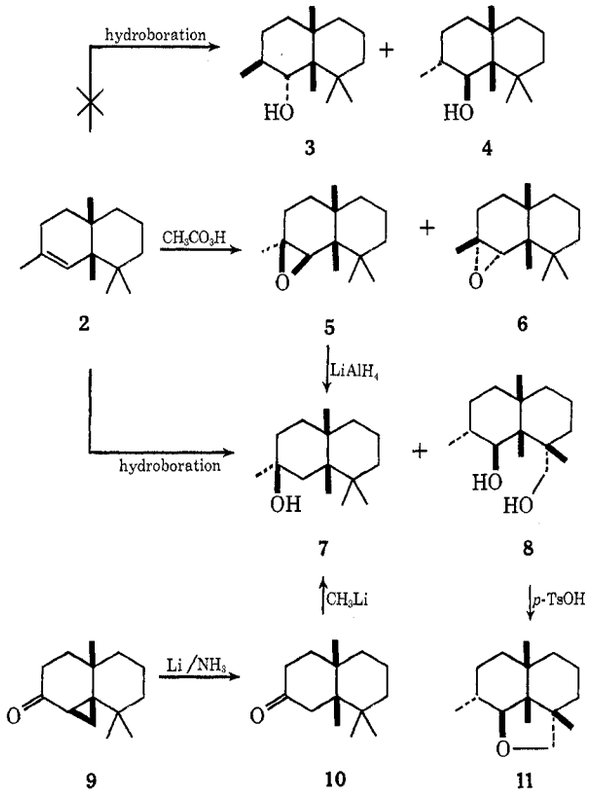
(1) See H. U. Daeniker, A. R. Hochstetler, K. Kaiser, and G. C. Kitchens, *J. Org. Chem.*, **37**, 1 (1972), and references cited therein.

(2) T. Norin, *Acta Chem. Scand.*, **15**, 1676 (1961).



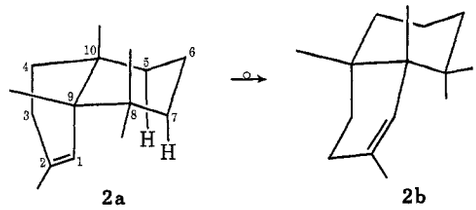
1 2

clearly was a tertiary alcohol, as evidenced by five methyl singlets in the nmr spectrum and by its inertness toward standard Jones reagent. Furthermore, this alcohol **7** was found to be identical with the tertiary alcohol obtained by reduction of epoxide **5** and with the tertiary alcohol derived from ketone **10** by treatment with methyllithium. The structure of ketone **10** is well established, since it is easily obtained *via* Birch reduction of the known ketone dihydromayurone (**9**).[3]



3 4 2 5 6 7 8 9 10 11

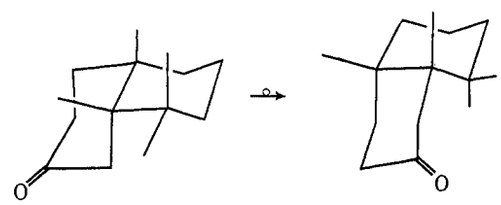
The conversion of epoxide **5** to tertiary alcohol **7** shows that both epoxidation and hydroboration occur predominantly from the same face of the precursor dihydrothujopsene molecule. Although the cis ring fusion in **2** forces us to consider both steroid (**2a**) and nonsteroid (**2b**) cis decalin forms, conformational



2a 2b

analysis indicates that the steroid form **2a** should be favored. Attack of an external reagent on the least hindered β face of the double bond (the α face is badly hindered by the axial hydrogens at C-5 and C-7) affords the stereochemistry indicated for the major epoxide **5** and the major hydroboration product **7**. The same conclusion, β-face attack for hydroboration, has been published for the structurally and conformationally closely related (−)-thujopsene (**1**) molecule,[4] and for the epoxidation of 5β-Δ^3-cholestene, reported[5] to favor β-face over α-face attack by a 9:1 ratio.

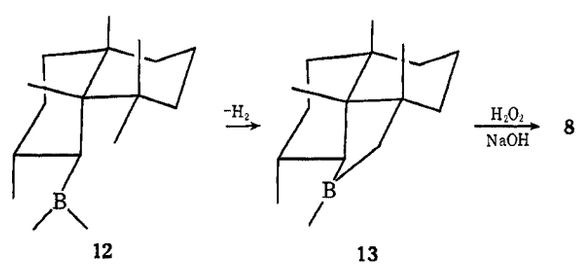
Additional proof for the stereochemical assignment is afforded by the conversion of ketone **10** to tertiary alcohol **7**. Steroid conformation **10a**, again the most



10a 10b

favored, predicts attack from the less hindered α face to afford alcohol **7**, as found, whereas the less favored conformation **10b** predicts β-face attack with formation of the epimeric tertiary alcohol. Previous reports in 3-keto steroids with a cis A–B ring fusion, where the steroid conformation for rings A and B must hold due to the trans B-C ring fusion, show that the major alcohol product from Grignard reactions is indeed that obtained *via* attack from the α face.[6]

The minor hydroboration product showed a one-proton doublet at δ 3.64 and a two-proton AB pattern centered at δ 2.30 consistent with diol structure **8**. Treatment of diol **8** with *p*-toluenesulfonic acid in benzene afforded a quantitative conversion into the corresponding cyclic ether **11**. Diol **8** must arise in the hydroboration reaction from the internal dialkylborane intermediate **13** derived from the initial monoalkylborane **12** by loss of the elements of hydrogen.[7]



12 13

Molecular models clearly indicate the close proximity of the hydrogens on the α methyl at C-8 with the β-alkylborane substituent at C-1 obtained from β-face attack with the expected orientation of the borane addition. Unfortunately, the same arguments can be advanced from α-face attack of the borane followed by ring inversions and loss of the elements of hydrogen from the β methyl at C-8. Both diol **14** and subsequent ether product **15** would exhibit nmr spectra virtually identical with those of diol **8** and ether **11**, respectively.

Regarding the stereochemistry of diol **8**, we must compare the 92:8 ratio of epoxides **5** and **6** to the 77:23 ratio of hydroboration products **7** and **8**. We have earlier proved that both epoxide **5** and alcohol **7** derive

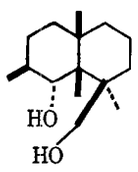
(3) (a) T. Nozoe, H. Takeshita, S. Ito, T. Ozeki, and S. Seto, *Chem. Pharm. Bull.*, **8**, 936 (1960); (b) W. G. Dauben and A. C. Ashcraft, *J. Amer. Chem. Soc.*, **85**, 3673 (1963).

(4) S. P. Acharya and H. C. Brown, *J. Org. Chem.*, **35**, 3874 (1970).

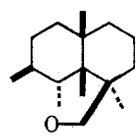
(5) V. Sanda and J. Fajkos, *Collect. Czech. Chem. Commun.*, **32**, 3726 (1967).

(6) R. J. Gritter and R. J. Albers, *J. Org. Chem.*, **29**, 728 (1964).

(7) H. C. Brown, K. J. Murray, H. Müller, and G. Zweifel, *J. Amer. Chem. Soc.*, **88**, 1443 (1966).



14



15

from β-face attack on **2**. Since only two epoxides are possible from **2**, the minor epoxide must possess structure **6** derived from α-face attack. If the steric requirements in the transition state for hydroboration are similar to or greater than that for epoxidation, one would then expect that β-face attack indeed holds for the minor hydroboration product and structure **8** is correct. Conversely, if the steric requirements for hydroboration are less than that for epoxidation, one might expect α-face attack to afford structure **14** for the diol product.

Previous studies[8] on selected substituted cyclohexene derivatives have indicated only very slight differences in the stereochemical outcome of epoxidation as compared to hydroboration on the same molecule. Although the generality of this conclusion has not been rigorously established, in view of the threefold difference in the amount formed of epoxide **6** *vs.* diol **8**, we feel that β-face attack indeed holds for both hydroboration products and that the diol therefore possesses structure **8** rather than **14**.

This hydroboration reaction is unique in two interesting aspects. The major product, tertiary alcohol **7**, corresponds to Markovnikov hydration of the double bond, whereas in all known examples to date the anti-Markovnikov product always predominates. For example, 1,1-dimethyl-*tert*-butylethylene affords 98% of the secondary alcohol and only 2% of the tertiary alcohol.[9] Styrene affords 80% of the expected primary alcohol and 20% of the secondary alcohol due to electronic effects of the aromatic ring.[9] In our case, trisubstituted olefin **2**, no such electronic effects can be invoked to explain the dramatic reversal of the hydroboration orientation. The steric effects of the C-8 *gem*-dimethyl group and the angular methyl group at C-9 in **2** must be so overwhelming that this consideration governs the attack of the borane rather than the usual electronic directing effects.

The second aspect of this reaction involves the facile formation of the dialkylborane intermediate **13** from the monoalkylborane **12**. Conversions of this type are well known[7] but usually occur only at elevated temperatures such as refluxing diglyme (160°). Logan and Flautt have previously[10] shown that *trans*-1,2-di-*tert*-butylethylene readily formed an internal dialkylborane upon heating with borane in refluxing diglyme, but could isolate the expected secondary alcohol product if the reaction was performed at 30°. In our case no evidence for a secondary alcohol product could be obtained at 25°, even this temperature being sufficient to form dialkylborane **13**, the precursor of diol **8**.

Experimental Section

Materials and Equipment.—(−)-Thujopsene (**1**) was readily obtained in 99% purity by careful fractional distillation of Hibawood oil through a 2-ft Goodloe column, bp 67–68° (0.5 mm), $n^{20}D$ 1.5050, $[\alpha]^{25}D$ −92.5° (neat).

Spectra were recorded using a Perkin-Elmer 457 grating ir spectrophotometer and a Varian A-60A nmr spectrometer. Gas chromatography was performed on an F & M 720 instrument employing a 2 m × 0.25 in. copper column packed with 20% Carbowax on Chromosorb G. Combustion analyses were determined by Schwartzkopf Microanalytical Laboratory, Woodside, N. Y.

Dihydrothujopsene (2).—A 250-g (1.21 mol) sample of (−)-thujopsene (**1**) was hydrogenated with 5 g of 5% palladium on carbon catalyst at 30° in a Parr shaker. The reaction was stopped when 1 molar equiv of hydrogen had been absorbed. The mixture was filtered and the filtrate was distilled, affording 238 g (94%) of colorless liquid: bp 67° (0.3 mm); $n^{20}D$ 1.5042 (lit.[3] $n^{20}D$ 1.5100); $[\alpha]^{25}D$ +49° (neat) (lit.[3] $[\alpha]D$ + 24°); ir (neat) 1675, 1090, 1061, 1022, 969, 858 cm^{-1} (lit.[3] 1675 cm^{-1}); nmr ($CDCl_3$) δ 0.92, 0.96 (s, 6 H each), 1.66 (s, 3 H), 5.30 (s, 1 H, $W_{1/2}$ = 4 Hz). Analysis by gas chromatography showed no unreacted thujopsene and a purity of 95% for the product, olefin **2**.

1α,2α-Epoxy-2β,8,8,9β,10β-pentamethyldecalin (6).—To a vigorously stirred mixture of 206 g (1 mol) of dihydrothujopsene (**2**), 400 ml of hexane, and 75 g of anhydrous sodium acetate was added 270 g (1.42 mol) of 40% peracetic acid over 1 hr. After heating at 40° for 18 hr, an additional 100 g of 40% peracetic acid was added and allowed to agitate for an additional 24 hr. Water (400 ml) was added and the mixture was extracted with hexane. The combined organic phases were washed basic with 10% sodium carbonate solution and once with aqueous sodium thiosulfate solution. Gas chromatography showed three components, unreacted **2** (1.5%), epoxide **6** (8.0%), and epoxide **5** (90.5%). Distillation through a 37-cm column packed with glass helices afforded 208 g (94%) of the epoxide mixture **5** and **6**, bp 78–82° (0.5 mm). Spinning band redistillation of this material afforded in the early fractions a pure sample of the minor epoxide **6** which exhibited the following characteristics: bp 72° (0.4 mm); $n^{20}D$ 1.4945; ir (neat) 1245, 1210, 1110, 1020, 918, 885, 815, 583 cm^{-1}; nmr ($CDCl_3$) δ 0.91, 0.98, 1.26 (s, 3 H each), 1.04 (s, 6 H), 2.67 (s, 1 H); $[\alpha]^{25}D$ +41° (neat).

Anal. Calcd for $C_{15}H_{26}O$: C, 81.02; H, 11.79. Found: C, 80.83; H, 11.76.

Identical epoxide product ratios were obtained when the epoxidation was performed employing tetrahydrofuran as the solvent.

1β,2β-Epoxy-2α,8,8,9β,10β-pentamethyldecalin (5).—Continued spinning band distillation from the preceding experiment afforded pure major epoxide **5** which exhibited the following characteristics: bp 75° (0.4 mm); $n^{20}D$ 1.4958; $[\alpha]^{25}D$ +19° (neat); ir (neat) 1079, 1037, 1008, 948, 862, 820 cm^{-1}; nmr ($CDCl_3$) δ 0.97, 1.06 (s, 6 H each), 1.29 (s, 3 H), 2.84 (s, 1 H).

Anal. Calcd for $C_{15}H_{26}O$: C, 81.02; H, 11.79. Found: C, 81.21; H, 11.74.

2α,8,8,9β,10β-Pentamethyl-2β-decalol (7). A. From the Hydroboration of Dihydrothujopsene (2).—A solution (125 ml, 0.125 mol) of 1 *M* borane in tetrahydrofuran was placed under nitrogen and cooled to 5°. Dihydrothujopsene (**2**) (25 g, 0.121 mol) was added and the mixture was stirred at 25° for 18 hr. The solution was cooled to 0° and water (10 ml) was carefully added, followed by 10% aqueous sodium hydroxide (100 ml) and 30% hydrogen peroxide (100 ml). After stirring at 40° for 3 hr, hexane (100 ml) was added and the layers were separated after filtration from an insoluble precipitate. The aqueous phase was extracted with hexane. The combined organic extracts were washed with 10% sodium thiosulfate solution and dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure, affording 27 g of a viscous oil. Hexane (25 ml) was added and the solution was refrigerated overnight. Filtration afforded 7.4 g of crystalline alcohol **7**: mp 93–94°; $[\alpha]^{25}D$ +34° (*c* 20%, $CHCl_3$); ir (KBr) 3430, 1291, 1211, 1182, 1162, 1115, 1080, 925, 908, 881 cm^{-1}; nmr ($CDCl_3$) δ 0.78, 1.03, 1.06, 1.12, 1.19 (s, 3 H each).

Anal. Calcd for $C_{15}H_{28}O$: C, 80.29; H, 12.58. Found: C, 80.31; H, 12.65.

The mother liquors from the above crystallization were chromatographed on 250 g of silica gel. Elution with hexane gave 0.8 g (3%) of unreacted dihydrothujopsene (**2**). Further elution with 5% ether in hexane afforded 10.8 g of additional crystalline alcohol **7** (total isolated yield 18.2 g, 67%).

B. From Reduction of Epoxide 6.—A sample of epoxide **6** (5.0 g, 22.5 mmol) and lithium aluminum hydride (4.5 g, 115

(8) D. J. Pasto and F. M. Klein, *J. Org. Chem.*, **33**, 1468 (1968).
(9) H. C. Brown and G. Zweifel, *J. Amer. Chem. Soc.*, **82**, 4708 (1960).
(10) T. J. Logan and T. J. Flautt, *ibid.*, **82**, 3446 (1960).

mmol) in anhydrous dimethoxyethane (60 ml) was allowed to reflux for 72 hr. The mixture was cooled, and water (9 ml) was added followed by 10% aqueous sodium hydroxide (7.5 ml). After stirring at room temperature for 5 hr, the mixture was filtered and the solvent was removed at reduced pressure, affording 5.0 g of viscous oil. Analysis by gas chromatography showed three components, which were identified as dihydrothujopsene (16%), unreacted epoxide **6** (47%), and tertiary alcohol **7** (37%) on the basis of vpc retention times and by comparison of the ir and nmr spectra of the isolated components with those of authentic samples.

C. From Ketone 10.—To a sample of ketone **10** (800 mg, 3.8 mmol) dissolved in ether (12 ml) was added over 20 min a solution of 2.3 *M* methyllithium in ether (10 ml, 23 mmol). After stirring at 30° for 0.5 hr, the mixture was cooled and water (10 ml) was carefully added. The mixture was extracted with ether and the organic extracts were dried over anhydrous magnesium sulfate. The solvent was removed at reduced pressure, affording 900 mg of crude solid material. Analysis by gas chromatography gave two peaks with retention times of tertiary alcohol **7** (56%) and starting ketone **10** (44%). Separation of the two peaks by preparative gas chromatography afforded a pure sample of tertiary alcohol **7**, mp 93–94°, with an ir and nmr spectra identical with those obtained from part A above.

8α-Hydroxymethyl-2α,8β,9β,10β-tetramethyl-1β-decalol (8).—Continued elution of the chromatography column employed in the separation of the hydroboration products of dihydrothujopsene (see part A above) with 25% ether in hexane afforded 4.2 g (17%) of crystalline diol **8**, mp 104–106°. Crystallization from ether at −15° afforded the analytical sample: mp 115–116°; $[\alpha]^{25}D$ −24° (*c* 15%, $CHCl_3$); ir (KBr) 3200 (OH), 1182, 1049, 1025, 1001, 918 cm^{-1}; nmr ($CDCl_3$) δ 0.97, 1.04, 1.07 (s, 3 H each), 1.02 (d, 3 H, J = 5.5 Hz), 3.28, 3.32 (2 H AB pattern, J_{AB} = 6 Hz), 3.64 (d, 1 H, J = 9 Hz).

Anal. Calcd for $C_{15}H_{28}O_2$: C, 74.95; H, 11.74. Found: C, 75.17; H, 11.53.

8,8,9β,10β-Tetramethyl-2-decalone (10). To a mixture of freshly distilled ammonia (100 ml), anhydrous ether (40 ml), and ketone **9**[3a] (4.0 g, 19.5 mmol) was added lithium wire (300 mg, 43.5 mmol) in 50-mg portions over 15 min. The resulting deep blue mixture was stirred for 1.0 hr; then a 1:1 ethanol–ether mixture (10 ml) was added. The ammonia was allowed to evaporate and the residue was extracted with ether. The ether extracts were washed with brine and dried over magnesium sulfate. The solvent was removed at reduced pressure and the residue was crystallized from hexane (20 ml) affording 3.4 g (84%) of ketone **10**: mp 150–151°; $[\alpha]^{26}D$ +10° (*c* 15, $CHCl_3$); ir (KBr) 1700 (C=O), 1296, 1270, 1111, 1018 cm^{-1}; nmr ($CDCl_3$) δ 0.81; 0.88, 1.05, 1.10 (s, 3 H each).

Anal. Calcd for $C_{14}H_{24}O$: C, 80.71; H, 11.61. Found: C, 80.60; H, 11.47.

2aβ,5aβ,8α,8bβ-Tetramethyldecahydronaphtho[1,8-*bc*]furan (11).—A solution containing diol **8** (1.5 g, 6.25 mmol) and *p*-toluenesulfonic acid (100 mg) in benzene (25 ml) was heated to reflux with a water separator for 1.5 hr. The solution was cooled and washed with sodium bicarbonate solution, and the solvent was removed at reduced pressure. Distillation of the residual oil afforded 1.34 g (97%) of ether **11**: bp 100° (bath temperature) (0.5 mm); $n^{20}D$ 1.5042; $[\alpha]^{25}D$ +1° (neat); ir (neat) 1075, 1026, 1000, 975 cm^{-1}; nmr ($CDCl_3$) δ 0.84, 0.97, 1.05 (s, 3 H each), 0.95 (d, 3 H, J = 5.5 Hz), 3.46, 3.49 (2 H, AB pattern, J_{AB} = 8 Hz), 3.85 (d, 1 H, J = 10.5 Hz).

Anal. Calcd for $C_{15}H_{26}O$: C, 81.02; H, 11.79. Found: C, 81.17; H, 11.76.

Attempted Oxidation of Alcohol 7.—A sample of alcohol **7** (200 mg, 0.9 mmol) was dissolved in acetone (5 ml) and cooled to 5°. Standard Jones reagent (0.25 ml, 1.1 molar equiv) was added dropwise at 5°. The mixture was stirred at 5° for 10 min and at 20° for 10 min. Isopropyl alcohol (1 ml) was then added, followed by 10 ml of water. The mixture was well extracted with hexane. The orgaic extracts were washed with water and sodium bicarbonate solution, and the solvent was removed at reduced pressure. The ir and nmr spectra of the crude crystalline residue (200 mg) were identical with those of the starting alcohol **7**.

Determination of the Product Ratios from the Hydroboration of Dihydrothujopsene (2).—The hydroboration procedure as described above was repeated employing olefin **2** (1.5 g, 7.5 mmol) and 1 *M* borane in tetrahydrofuran solution (8.5 ml) for 18 hr at 25°. The same oxidative work-up procedure afforded 1.6 g of viscous oil. This oil was treated with *p*-toluenesulfonic acid (100 mg) in benzene (20 ml) at reflux with a water separator for 2 hr. The mixture was cooled and washed with sodium bicarbonate solution and the solvent was removed under reduced pressure. The residue was distilled on a microstill head, affording 1.30 g of mobile oil, bp 80–100° (bath temperature) (0.5 mm). This mixture showed three peaks by vpc analysis identified as dihydrothujopsene (**2**, 35%), the corresponding 2,3 double bond isomer (42%), and ether **11** (23%).

Ether **11** arises solely from dehydration of diol **8** and the two olefins from dehydration of tertiary alcohol **11**. The ratio of the two hydroboration products **7** and **8** is thus shown to be 77:23, respectively.

Registry No.—**2**, 34407-70-0; **5**, 34407-71-1; **6**, 34417-83-9; **7**, 34407-72-2; **8**, 34407-73-3; **10**, 34407-74-4; **11**, 34407-75-5.

Acknowledgment.—The author wishes to thank Dr. Garry Kitchens and Dr. Gary Shaffer for their helpful discussions during the course of the above investigation.

Symmetry Considerations and the Mechanism of the Hydroboration Reaction. The Nature of π Complexes

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Received November 18, 1971

Consideration of the orbital symmetry of the species involved in the hydroboration of olefins shows that the four-center transition states usually proposed have significant symmetry barriers. An alternate pathway involving a complex between the olefin and the borane is discussed in terms of the three-center electron-deficient bonds implied by the π-complex formalism. It is concluded on the basis of the symmetry of these three-center molecular orbitals that the conversion of such π complexes to products can be a concerted process which does not involve significant charge separation or rearrangement to a σ complex.

Despite the great synthetic utility of the hydroboration reaction, there is surprisingly little known about its mechanism. This is certainly due in part to the great complexity of the hydroboration reaction mixtures and the concomitant difficulty of quantitative kinetic measurements in such systems. In our studies of the hydroboration of methylchlorosilylalkenes[1] we found that a consideration of the orbital symmetry of the reactants and products provides a useful insight into the

(1) P. R. Jones, J. K. Myers, and R. C. Rains, *J. Organometal. Chem.*, **34**, C9 (1972); 162nd National Meeting of the American Chemical Society, Washington, D. C., Sept 1971, Abstract INOR 126.