(23) Recent unpublished results indicate that the photochemically generated nitrile ylide does not undergo reclosure to starting azirine.
(24) P. J. Wagner, *Accounts Chem. Res.*, **4**, 168 (1971).
(25) E. F. Ullman and B. Singh, *J. Amer. Chem. Soc.*, **88**, 1844 (1966); **89**, 6911 (1967).
(26) B. Singh, A. Zweig, and J. B. Gallivan, *J. Amer. Chem. Soc.*, **94**, 1199 (1972).
(27) P. J. Wagner, A. E. Kemppainen, and H. N. Schott, *J. Amer. Chem. Soc.*, **95**, 5604 (1973).
(28) All melting points are corrected and boiling points uncorrected. Elemental analyses were performed by Scandinavian Microanalytical Laboratory, Herlev, Denmark, and Alfred Bernhardt Laboratories, Hohenweg, Germany. The infrared absorption spectra were determined on a Perkin-Elmer Infracord spectrophotometer, Model 137. The ultraviolet absorption spectra were measured with a Cary recording spectrophotometer, using 1-cm matched cells. The nuclear magnetic resonance spectra were determined at 60 MHz with the Varian Associate high-resolution spectrometer and at 100 MHz using a Jeol-MH-100 spectrometer.
(29) G. A. R. Kon and R. G. W. Spickett, *J. Chem. Soc.*, 2725 (1949).
(30) A. Barbot, *Bull. Soc. Chim. Fr.*, **47**, 1314 (1930).

# Acid-Catalyzed Angular Methyl Migration in a Substituted Octalin[1]

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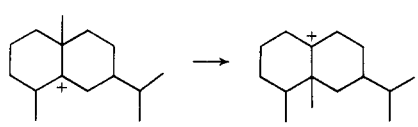
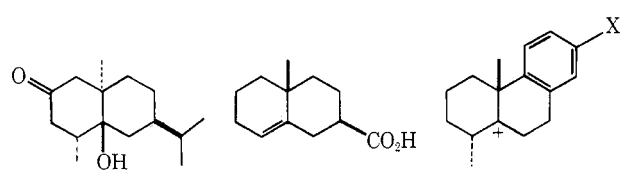
The acid-catalyzed isomerization of optically active 2,2,8,8,10-pentamethyl-1(9)-octalin (12) of known absolute configuration affords two major olefin products, 13 and 14, whose gross structure was determined by a combination of spectral data and chemical transformations of each product to the common derivative, alcohol 17. The absolute configuration at the chiral angular methyl center in 13 and 14 was determined by the ORD curves of the corresponding trans-fused 1-decalone derivatives 25 and 20. The isomerization pathway of 12 to 13 and 14 therefore involves a specific spiro[4.5]decalyl cation to key intermediate 29a which undergoes angular methyl migration. Intermediate 29a was generated independently and shown to undergo rapid conversion to octalins 13 and 14.

A vast amount of literature has appeared over the years dealing with the solvolytic and acid-catalyzed rearrangements of a wide variety of organic molecules found in nature.[2] Backbone rearrangements and angular methyl migrations have been well documented in the biosynthetic pathways leading to the multicyclic triterpenes.[3] Similarly, angular methyl migration has long been considered for the derivation of the eremophilane-type sesquiterpenes from the eudesmane skeleton (1 → 2).[4]

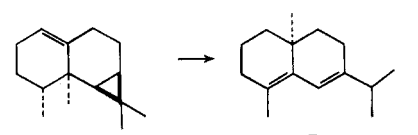


1 2

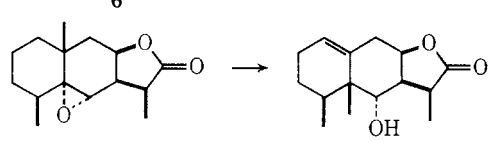
Angular methyl migrations of the above type, however, have been difficult to achieve in decalin systems under laboratory conditions. Attempts to dehydrate ketol 3 with concomitant angular methyl migration failed to afford any methyl-migrated products.[5] The apparent methyl migration observed[6] in the rearrangement of 4 has subsequently been shown to proceed *via* spiro intermediates.[7] Some angular methyl migration has been observed in the rearrangement products arising from cation 5 generated by appropriate solvolysis conditions, although the same cation generated by acid from the corresponding olefin gave only small amounts of such products.[8] Formic acid treatment of 6 has, however, been reported to afford the angular methyl migrated product, diene 7.[9] Likewise, a recent communication[10] shows that formic acid–acetone treatment of epoxydihydroalantolactone (8) gives reasonable yields of the angular methyl migrated product 9.



3 4 5

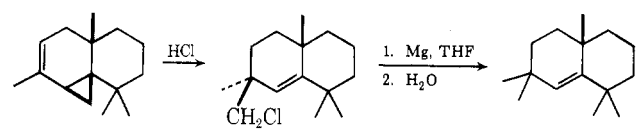


6 7



8 9

**Scheme I**




10 11 12

Both of the latter two examples which give rise to angular methyl migration products contain more than simple double-bond functionality. We wish to report now a substituted simple octalin system whose acid-catalyzed rearrangement proceeds *via* both a spiro[4.5]decalyl cation system and an angular methyl migration.

## Results

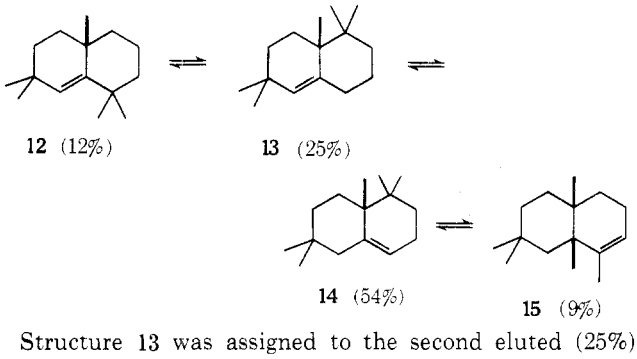
**Synthesis of (+)-(*S*)-2,2,8,8,10-Pentamethyl-1(9)-octalin (12).** The octalin employed in this study was readily obtained from (−)-thujopsene (10) *via* the two-step sequence outlined in Scheme I. Treatment of 10 with hydrogen chloride eventually formed the most stable addition product, neopentyl chloride 11.[11] Reduction of 11 to the desired octalin 12 was conveniently effected by aqueous treatment of the corresponding Grignard complex. The nmr spectrum of 12 showed five methyl singlets and a sharp vinyl proton singlet at $\delta$ 5.13, in full agreement with the assigned structure.

It is important to note that the pentamethyloctalin 12 thus obtained is optically active and possesses the absolute configuration depicted. The absolute stereochemistry

of (−)-thujopsene has previously been established[12] as shown in structure **10**. Since the chemical transformations of **10** to **12** have not involved the chiral center at C-10, the absolute configuration at that center in **12** remains unchanged.

**Acid-Catalyzed Isomerization of 12.** Treatment of octalin **12** with 20% sulfuric acid in acetic acid at 40° slowly gave an equilibrium mixture of four components in a ratio of 12:25:54:9 in the order of their elution on a Carbowax 20M gas chromatography column. Subjection of pure major (54%) product to the same isomerization conditions afforded a nearly identical mixture of the above four components, thus showing that a true equilibrium had been established. Isomerizations starting from **12** interrupted at partial conversion showed a much higher ratio of the last eluted component with respect to the other two major products than found under equilibrium conditions.

These components were separated *via* spinning-band distillation. The first eluted component was identical with starting octalin **12**. The last eluted component clearly showed four upfield methyl singlets, a vinyl methyl, and a broad vinyl hydrogen absorption in the nmr spectrum. Consideration of the structure of the products of closely related isomerizations,[13,14] in combination with our spectral data, allows us to assign structure **15** for this initial isomerization product.



**12** (12%) **13** (25%) **14** (54%) **15** (9%)

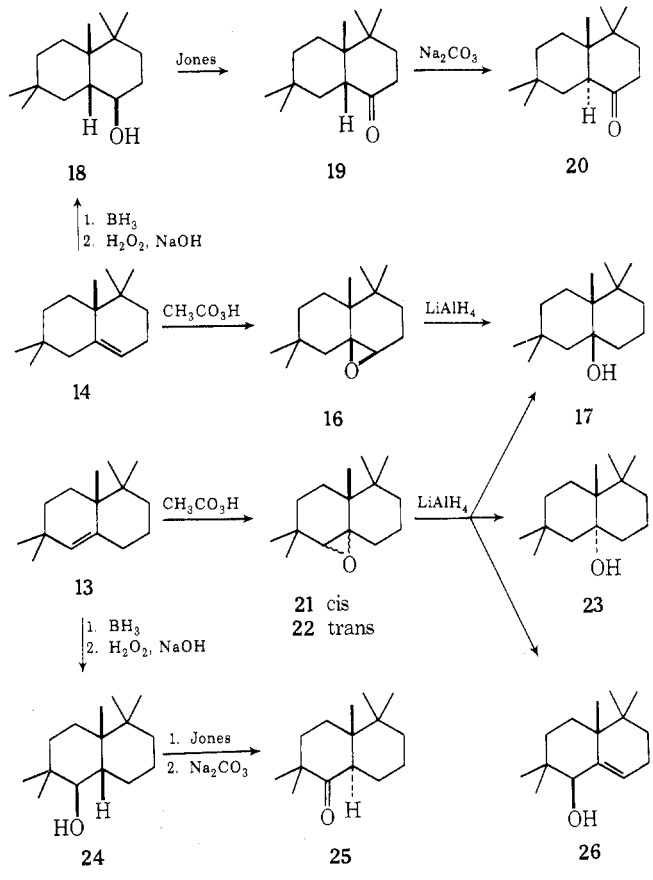
Structure **13** was assigned to the second eluted (25%) component on the basis of its nmr spectrum, which showed five methyl singlets and a vinyl hydrogen singlet only slightly broadened by allylic coupling. Suspicion that the major equilibrium component was the double bond positional isomer **14** of octalin **13** was confirmed *via* conversion of each pure olefin isomer to a common derivative, tertiary alcohol **17**.

**Structure Proof of Octalins 13 and 14.** As shown in Scheme II, treatment of octalin **14** with peracetic acid afforded a single epoxide isomer **16**. Inspection of molecular models clearly shows that the $\alpha$ face is badly hindered by the $\alpha$-methyl group at C-7 and therefore $\beta$-face epoxidation leading to **16** is expected. Similar results have also been reported for the closely related olefin 7,7,10-trimethyl-1(9)-octalin.[15] Reduction of epoxide **16** with lithium aluminum hydride then gave the tertiary decalol **17**.

In similar fashion the epoxide mixture **21** and **22** was obtained from octalin **13** in an 82:18 ratio as determined directly by gas chromatography and by integration of the proton singlets $\alpha$ to the epoxide in the two isomers. The cis stereochemistry of the major product **21** is again assigned from a consideration of molecular models where $\beta$-face attack is less hindered than $\alpha$-face attack. Reduction of this epoxide mixture with lithium aluminum hydride afforded three products, **17** (44%), **23** (14%), and **26** (42%), which were separated by column chromatography.

Alcohol **17** was identical in all respects with the tertiary alcohol obtained from reduction of epoxide **16** and thereby proves the isomeric relationship between precursor octalins **13** and **14**. Spectral data indicated that the minor

**Scheme II**




(14%) reduction product was the trans decalol **23** derived from reduction of minor trans epoxide **22**. The remaining product was assigned the allylic alcohol structure **26** from the nmr spectrum. This alcohol presumably arises *via* lithium aluminum alkoxide rearrangement[16] of hindered epoxide **21** in competition with the normal hydride reduction leading to tertiary alcohol **17**.

Since all three product olefins **13**, **14**, and **15** were optically active, we next sought to establish the absolute stereochemistry of the chiral angular methyl center at C-10 in both octalins **13** and **14**. Hydroboration–oxidation[17] of octalin **14** gave the crystalline secondary alcohol **18** as the sole product. The cis stereochemistry arising from $\beta$-face attack is again assigned from consideration of molecular models and by analogy to a closely related octalin system.[15] Jones oxidation[18] of **18** gave the cis-fused decalone **19**, which was readily equilibrated in base to the more stable trans-fused decalone **20**.

A similar sequence was followed starting from octalin **13**. A 77:23 mixture of secondary alcohols was obtained. The major isomer in this mixture is assigned structure **24**, again based upon attack from the least hindered $\beta$ face. This crude decalol mixture was directly oxidized with Jones[18] reagent and the crude ketone mixture thereby obtained was treated with base to give the more stable trans-fused decalone **25**.

With both the gross structure and the relative (trans ring fusion) stereochemistry of both decalones **20** and **25** now established, we next sought to determine their absolute configuration *via* their optical rotatory dispersion curves. Decalone **20** was found to have a strong positive Cotton effect and decalone **25** a strong negative Cotton effect. Since the trans ring fusion avoids the conformational mobility inherent in the cis-fused decalones, the octant rule[19] can be unambiguously applied to decalones **20**

and **25**. Application of the octant rule in the present case clearly predicts the experimentally determined sign of the Cotton effect for both decalones **20** and **25** with the absolute configuration as shown in Scheme II. These findings are also in agreement with the results of related decalone systems studied earlier by Djerassi and coworkers.[20]

Since none of the reactions leading from octalins **13** and **14** to decalones **20** and **25** have involved the chiral center at C-10, the absolute configuration at the angular methyl center for these olefins must also be as shown in Scheme II.

## Discussion

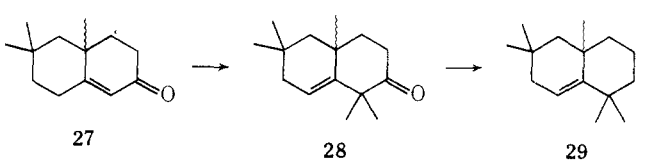
Octalin **12** presents an interesting case for the study of the isomerization pathways available in the 9-decalyl cation system. Scheme III outlines the four isomerization pathways possible from initially formed cation **12a**.

Path A involves $\beta$-methyl migration from C-2 to C-9 to afford the cis-fused cation **15a** and the corresponding olefin **15**. Such a product has literature precedent[13,14] in closely related systems and in the case of the 8,8,10-trimethyl-1(9)-octalin isomerization[13] comprises 94% of the equilibrium mixture. In the present case olefin **15** becomes a minor product owing to the additional steric effects of the *gem*-dimethyl group at C-7 with the angular methyl group at C-9. Although spectral data for olefin **15** could also be compatible with the trisubstituted spiro olefins derived from cations **12b** or **12c**, this possibility seems rather unlikely in view of the known[21,22] rapid isomerization of spiro olefins of this type to the octalin systems under mineral acid treatment, and indeed are not even found in the equilibrium mixture.

Path B involves stereospecific contraction of the B ring in cation **12a** to generate the spiro[4.5]decalyl cation **12b**. Subsequent opposite-sense rearrangement gives cation **13a′**, in turn leading to octalins **13′** and **14′**. Such a pathway, however, predicts that the configuration at the chiral angular methyl group is opposite to that experimentally found and is therefore dismissed as a viable pathway.

Path C involves stereospecific contraction of ring A in cation **12a** to generate the alternate spiro[4.5]decalyl cation **12c**. Again, opposite-sense rearrangement would generate the new cation **29a**. Two severe 1,3-diaxial methyl interactions in this cation can be readily alleviated by angular methyl migration to generate cation **13a**. Deprotonation now affords octalins **13** and **14** possessing the correct absolute configuration at C-10.

Additional evidence for the isomerization route of path C was obtained from independent generation of racemic cation **29a** from racemic octalin **29**. This octalin was synthesized by modified Wolff–Kishner reduction of ketone **28**, which in turn was obtained from alkylation of ketone

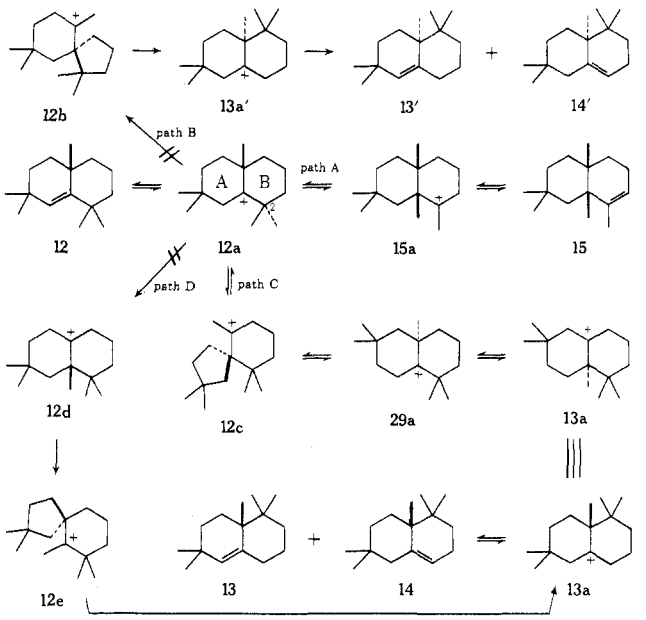


27 28 29

**27**, the Robinson annelation product of 2,4,4-trimethylcyclohexanone and methyl vinyl ketone.

Treatment of racemic octalin **29** under our standard acid isomerization conditions led to a rapid disappearance of **29** (none observed by glc after 0.5 hr) and the immediate formation of racemic octalins **13** and **14** in a 1:2 ratio. Extended reaction times slowly saw the appearance of racemic octalins **12** and **15** up to the equilibrium percentages. These results show that cation **29a**, once formed, more rapidly undergoes angular methyl migration to energetically favorable cation **13a** than reversion to spiro cation **12c**.

**Scheme III**




Path D involves initial angular methyl migration to afford cation **12d**. Subsequent formation of cation **12e** by contraction of the A ring in cation **12d** would ultimately lead to cation **13a** of the correct absolute configuration. The net difference between path C and path D is in the sequence of steps; in path C the spiro intermediate precedes angular methyl migration, whereas in path D angular methyl migration precedes the spiro intermediate.

We favor the path C route for two reasons. First, we have already described the independent generation of racemic cation **29a** and shown its ready conversion to racemic olefins **13** and **14**. Second, if path D were operative one would expect to see some evidence for the formation of the two octalins obtainable by loss of a proton from cation **12d** during the course of the isomerization. These octalins do not appear to have any more severe steric interactions than those found in octalin **15**, which is actually present in the equilibrium mixture. The absence of octalin **29** from the equilibrium mixture is, however, expected, since there are two 1,3-diaxial methyl interactions in that olefin.

The rotations of the optically pure product octalins **13**, **14**, and **15** are not known and therefore our observed rotations of these octalins give us no clue to their optical purity. Some decrease in optical activity corresponding to 20% racemization of octalin **12** recovered from the equilibrium mixture was noted. This decrease indicates that octalins **13**, **14**, and **15**, although not optically pure, do retain a high degree of optical purity. The racemization noted is most likely due to a small amount of the path B isomerization pathway affording the enantiomeric olefins **13′** and **14′**.

## Experimental Section[23]

**Materials.** (−)-Thujopsene 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).

**(+)-2(*S*)-Chloromethyl-2,8,8,10(*S*)-tetramethyl-1(9)-octalin (11).** A mixture of (−)-thujopsene (**10**, 816 g, 4 mol), acetic acid (800 ml), and anhydrous calcium chloride (444 g, 4 mol) was heated at 60° for 2 hr. After cooling, the reaction mixture was di-

luted with water (2 l.) and extracted with three 300-ml portions of benzene. The combined organic extracts were washed neutral with water and the solvent was removed under reduced pressure. The residue was fractionally distilled on a 37-cm column packed with glass helices, affording 613 g (64%) of **11**: bp 89–92° (0.5 mm); $n^{20}D$ 1.5030; $[\alpha]^{25}D$ +87° (neat). The ir and nmr spectra were identical with those described in the literature.[11]

**(+)-(*S*)-2,2,8,8,10-Pentamethyl-1(9)-octalin (12).** Into a nitrogen-purged flask was charged magnesium turnings (101 g, 4.16 mol). Two addition funnels were separately charged with dry tetrahydrofuran (900 ml) and chloride **11** (1,000 g, 4.16 mol). A small amount of tetrahydrofuran (50 ml) was added to the magnesium, followed by chloride **11** (20 ml) and ethyl bromide (2 ml). The reaction mixture was then heated at 50° until reaction began and the remainder of the tetrahydrofuran and the chloride **11** were fed in over 1 hr at 50°; then the mixture was brought to reflux for 18 hr. The reaction mixture was cooled to 5°, 20% sulfuric acid (1000 ml) was added, and the mixture was allowed to stir at 25° for 2 hr. The layers were separated and the organic phase was washed with water and saturated sodium bicarbonate solution. The solvent was removed under reduced pressure and the residue was distilled, affording 651 g (76%) of **12**: bp 52° (0.3 mm); $n^{20}D$ 1.4815; $[\alpha]^{20}D$ +81° (neat); ir (liquid film) 1021, 980, 953, 928, 869, 820, 662 $cm^{-1}$; nmr ($CDCl_3$) $\delta$ 0.93, 0.96, 1.04, 1.07, 1.14 (s, 3 each), 5.13 (s, 1); mass spectrum *m/e* (rel intensity) 206 ($M^+$, 20), 191 (100), 121 (45), 107 (47), 95 (94), 69 (40), 41 (45). The nmr spectrum agrees with that reported in the literature.[24]

*Anal.* Calcd for $C_{15}H_{26}$: C, 87.30; H, 12.70. Found: C, 87.44; H, 12.72.

**Acid-Catalyzed Isomerization of 12.** A mixture of octalin **12** (350 g, 1.70 mol), 98% sulfuric acid (350 g), and acetic acid (1400 g) was agitated at 40° for 24 hr. The mixture was cooled and the organic layer was separated. The acid layer was poured into ice-cold water (3 l.) and extracted with three 200-ml portions of hexane. The combined organic extracts were washed with water and saturated sodium carbonate solution. The solvent was removed under reduced pressure and the residue was flash distilled, affording 336 g (96%) of isomerized olefin mixture, bp 70–80° (0.4 mm). Vpc analysis showed four peaks identified as **12** (12%), **13** (25%), **14** (54%), and **15** (9%) in the order of their elution with relative retention times (based on **12**) of 1:1.7:2.0:2.2. Analysis of the isomerization mixture after 5 hr gave the following: **12** (52%), **13** (6%), **14** (13%), and **15** (29%). Isomerization of a pure sample of **14** under the above conditions for 24 hr gave the following mixture: **12** (9%), **13** (27%), **14** (57%) and **15** (7%).

**(+)-(*R*)-2,2,5,5,10-Pentamethyl-1(9)-octalin (13).** Spinning-band distillation of the above equilibrium mixture afforded in the first fractions recovered octalin **12**, bp 79–80° (5 mm), $[\alpha]^{25}D$ +50° (neat). The ir and nmr spectra were identical with those of the starting octalin **12**. Continued spinning-band distillation afforded pure **13**: bp 89–90° (5 mm); $n^{20}D$ 1.4932; $[\alpha]^{20}D$ +30.5° (neat); ir (liquid film) 1655, 1160, 1058, 861, 839 $cm^{-1}$; nmr ($CDCl_3$) $\delta$ 0.86, 0.90, 1.08 (s, 3 each), 0.93 (s, 6), 5.11 (s, 1, $W_{1/2}$ = 4 Hz); mass spectrum *m/e* (rel intensity) 206 ($M^+$, 9), 150 (99), 137 (100), 107 (38), 95 (59), 81 (54), 69 (37), 41 (46).

*Anal.* Calcd for $C_{15}H_{26}$: C, 87.30; H, 12.70. Found: C, 87.38; H, 12.85.

**(−)-(*R*)-4,4,7,7,10-Pentamethyl-1(9)-octalin (14).** Continued spinning-band distillation of the above mixture afforded pure octalin **14**: bp 92–93° (5 mm); $n^{20}D$ 1.4941; $[\alpha]^{25}D$ −32° (neat); ir (liquid film) 1658, 1058, 1022, 830, 804 $cm^{-1}$; nmr ($CDCl_3$) $\delta$ 0.77, 0.86, 0.91, 0.93, 1.01 (s, 3 each), 5.25 (s, 1, $W_{1/2}$ = 8 Hz); mass spectrum *m/e* (rel intensity) 206 ($M^-$, 7), 191 (18), 150 (100), 135 (32), 107 (28), 79 (36), 41 (26).

*Anal.* Calcd for $C_{15}H_{26}$: C, 87.30; H, 12.70. Found: C, 87.13; H, 12.70.

**(−)-*cis*-1,7,7,9(*R*),10(*S*)-Pentamethyl-1-octalin (15).** Continued spinning-band distillation of the above equilibrium mixture afforded pure octalin **15**: bp 97–98° (5 mm); $n^{20}D$ 1.4980; $[\alpha]^{25}D$ −35° (neat); ir (liquid film) 1655, 1078, 1054, 1034, 811, 794, 689 $cm^{-1}$; nmr ($CDCl_3$) $\delta$ 0.90, 0.93 (s, 6 each), 2.67 (d, 3, $J$ = 1.5 Hz), 5.30 (m, 1, $W_{1/2}$ = 9 Hz); mass spectrum *m/e* (rel intensity) 206 ($M^+$, 13), 191 (100), 137 (30), 121 (38), 107 (30), 95 (78), 81 (32), 69 (37), 55 (31), 41 (42).

*Anal.* Calcd for $C_{15}H_{26}$: C, 87.30; H, 12.70. Found: C, 87.16, H, 12.60.

**(+)-*cis*-8(*R*),9(*S*)-Epoxy-2,2,5,5,10(*R*)-pentamethyldecalin (16).** To a mixture of pure octalin **14** (8.3 g, 45 mmol), ethylene dichloride (20 ml), and sodium carbonate (8 g) was added 40% peracetic acid (13 g, 70 mmol) at 30° over 10 min. After an additional 3 hr at 30–35°, water (50 ml) was added and the layers were separated. The organic phase was dried ($MgSO_4$) and the solvent was removed under reduced pressure. Distillation afforded 8.5 g (94%) of a colorless liquid: bp 87–89° (0.4 mm); $n^{20}D$ 1.4868; $[\alpha]^{25}D$ +10.5° (neat); ir (liquid film) 1165, 1098, 990, 954, 916, 844, 792, 747 $cm^{-1}$; nmr ($CDCl_3$) $\delta$ 0.76 (s, 3), 0.93 (s, 6), 1.03 (s, 6), 2.80–2.95 (m, 1); mass spectrum *m/e* (rel intensity) 222 ($M^+$, 24), 207 (36), 189 (23), 166 (30), 151 (30), 140 (45), 123 (71), 109 (58), 95 (56), 83 (47), 81 (62), 69 (61), 67 (45), 55 (81), 43 (61), 41 (100).

*Anal.* Calcd for $C_{15}H_{26}O$: C, 81.02; H, 11.79. Found: C, 80.93; H, 11.86.

**(−)-*cis*-2,2,5,5,10(*R*)-Pentamethyl-9(*S*)-decalol (17).** A mixture of epoxide **16** (3.0 g, 13.5 mmol) and lithium aluminum hydride (1.0 g, 26 mmol) in tetrahydrofuran (20 ml) was refluxed under nitrogen for 42 hr. The mixture was cooled, carefully treated with water (2 ml) and 10% aqueous sodium hydroxide (1.6 ml), and stirred for an additional 2 hr. The mixture was filtered and the solvent was removed under reduced pressure. Short-path distillation afforded 2.6 g (86%) of a colorless oil: bp 85–90° (0.5 mm); $n^{20}D$ 1.4975; $[\alpha]^{25}D$ −9° (neat); ir (liquid film) 3500 (OH), 1070, 1007, 1000, 959, 912, 850 $cm^{-1}$; nmr ($CDCl_3$) $\delta$ 0.79, 0.91, 0.93, 0.99, 1.18 (s, 3 each); mass spectrum *m/e* (rel intensity) 224 ($M^+$, 1), 191 (12), 150 (68), 140 (66), 111 (31), 95 (61), 69 (88), 55 (72), 43 (71), 41 (100).

Vpc analysis showed the presence of 3% of unreacted **16** and no components other than **17**.

*Anal.* Calcd for $C_{15}H_{28}O$: C, 80.29; H, 12.58. Found: C, 80.05; H, 12.49.

**(−)-*cis*-4,4,7,7,10(*S*)-Pentamethyl-*cis*-decal-1(*R*)-ol (18).** The hydroboration procedure of Brown and coworkers[25] was employed on octalin **14** (9.3 g, 45 mmol) and 60 ml (60 mmol) of 1 *M* diborane in tetrahydrofuran solution at 25° for 4 hr. The mixture was cooled and carefully treated with 10% aqueous sodium hydroxide (30 ml) and 35% hydrogen peroxide (30 ml). The mixture was allowed to stir at 35° for 2 hr, then thoroughly extracted with hexane. The solvent was removed under reduced pressure to give 10 g (99%) of crude decalol **18**, mp 99–103°. A sample was recrystallized from hexane and exhibited the following characteristics: mp 111–112°; $[\alpha]^{25}D$ −2° (*c* 0.2, $CHCl_3$); ir (KBr pellet) 3310 (OH), 1059, 1030, 1014, 981 $cm^{-1}$; nmr ($CDCl_3$) $\delta$ 0.82, 0.88, 1.06 (s, 3 each), 0.94 (s, 6), 3.65–4.05 (m, 1); mass spectrum *m/e* (rel intensity) 224 ($M^-$, 1), 124 (32), 70 (100), 57 (37), 55 (35), 41 (50).

*Anal.* Calcd for $C_{15}H_{28}O$: C, 80.29; H, 12.58. Found: C, 80.40; H, 12.68.

**(+)-(*S*)-4,4,7,7,10-Pentamethyl-*cis*-1-decalone (19).** The standard Jones oxidation procedure[18] was employed on 5.0 g (22.3 mmol) of crude hydroboration decalol **18**. Short-path distillation afforded 4.5 g (91%) of colorless ketone **19**: bp 90–95° (0.7 mm); $n^{20}D$ 1.4959; $[\alpha]^{25}D$ +7° (neat); ir (liquid film) 1700 (C=O), 1208, 1120, 1020 $cm^{-1}$; nmr ($CDCl_3$) $\delta$ 0.69, 0.92, 0.96, 1.01, 1.07 (s, 3 each); mass spectrum *m/e* (rel intensity) 222 ($M^+$, 8), 207 (16), 70 (59), 55 (71), 41 (100). Vpc analysis showed only a single peak.

*Anal.* Calcd for $C_{15}H_{26}O$: C, 81.02; H, 11.79. Found: C, 80.70; H, 11.68.

**(−)-(*S*)-4,4,7,7,10-Pentamethyl-*trans*-1-decalone (20).** A sample of decalone **19** (6.0 g, 27 mmol), sodium carbonate (2 g), methanol (200 ml), and water (40 ml) was allowed to reflux under nitrogen for 18 hr. The mixture was cooled, diluted with water (50 ml), and thoroughly extracted with hexane. The solvent was removed under reduced pressure and the residue was distilled, affording 5.8 g (97%) of colorless ketone **20**: bp 95–98° (0.7 mm); $n^{20}D$ 1.4971; $[\alpha]^{25}D$ −1.5° (neat); ir (liquid film) 1710 (C=O), 1280, 1184, 1148, 1008, 580 $cm^{-1}$; nmr ($CDCl_3$) $\delta$ 0.77, 0.86, 0.92, 0.96, 1.27 (s, 3 each); mass spectrum *m/e* (rel intensity) 222 ($M^+$, 25), 208 (35), 151 (48), 124 (39), 123 (40), 109 (38), 70 (85), 69 (50), 56 (55), 55 (69), 41 (100); CD (*c* 0.0108, dioxane) $\theta_{320}$ 0, $\theta_{313}$ +139, $\theta_{298}$ +231, $\theta_{255}$ 0, $\theta_{244}$ −46, $\theta_{220}$ 0; ORD $\phi_{380}$ +111°, $\phi_{307}$ +76°, $\phi_{300}$ 0°, $\phi_{265}$ −245°, $\phi_{222}$ −208°. This ketone had the same vpc retention time as the cis-fused ketone **19**, but analysis of the nmr spectra of the two ketones showed that at equilibrium >98% of the mixture was the trans ketone **20**.

*Anal.* Calcd for $C_{15}H_{26}O$: C, 81.02; H, 11.79. Found: C, 81.08; H, 11.98.

**(−)-*cis*-1(*S*),9(*R*)-Epoxy-2,2,5,5,10(*R*)-pentamethyldecalin (21).** The procedure for the epoxidation of octalin **14** was employed with pure octalin **13** (4.1 g, 20 mmol), 40% peracetic acid (8.0 g, 42 mmol), sodium carbonate (5 g), and ethylene dichloride (15 ml). The product was isolated in the same manner and distilled, affording 3.7 g (84%) of colorless oil, bp 80–85° (0.5 mm). The gas chromatogram showed two peaks in an 18:82 ratio. These

peaks were separated by preparative gas chromatography. The major isomer, epoxide **21**, exhibited the following characteristics: $n^{20}D$ 1.4871; $[\alpha]^{25}D$ −1° (neat); ir (liquid film) 1085, 936, 916, 830, 819 $cm^{-1}$; nmr ($CDCl_3$) $\delta$ 0.89, 1.00, 1.02 (s, 3 each), 1.04 (s, 6), 2.60 (s, 1); mass spectrum *m/e* (rel intensity) 222 ($M^+$, 16), 165 (10), 153 (15), 135 (21), 125 (32), 123 (36), 109 (36), 95 (52), 81 (35), 69 (71), 67 (30), 55 (51), 43 (61), 41 (100).

*Anal.* Calcd for $C_{15}H_{26}O$: C, 81.02; H, 11.79. Found: C, 80.98; H, 11.84.

***trans*-1(*R*),9(*S*)-Epoxy-2,2,5,5,10(*R*)-pentamethyldecalin (22).** The minor epoxide isomer obtained above exhibited the following characteristics: $n^{20}D$ 1.4864; ir (liquid film) 961, 920, 854, 820 $cm^{-1}$; nmr ($CDCl_3$) $\delta$ 0.80 (s, 3), 1.02, 1.04 (s, 6 each), 2.31 (s, 1); mass spectrum *m/e* (rel intensity) 222 ($M^+$, 15), 189 (16), 153 (19), 135 (28), 125 (34), 123 (42), 109 (35), 95 (56), 81 (44), 69 (72), 53 (54), 43 (64), 41 (100).

*Anal.* Calcd for $C_{15}H_{26}O$: C, 81.02; H, 11.79. Found: C, 80.87; H, 11.86.

**Reduction of Epoxide Mixture 21 and 22.** Under a nitrogen atmosphere was charged lithium aluminum hydride (1.5 g, 39 mmol) and anhydrous 1,2-dimethoxyethane (25 ml). Epoxide mixture **21** (82%) and **22** (18%) (2.5 g, 11.2 mmol) was then added and the mixture was allowed to reflux for 24 hr. The mixture was cooled and ether (50 ml) was added followed by the careful addition of water (3 ml) and 10% aqueous sodium hydroxide (2.5 ml). After an additional 2 hr of stirring the mixture was filtered and the solvent was removed under reduced pressure. Analysis of the residue (2.6 g) by gas chromatography showed three products in a 14:44:42 ratio. These components were separated by chromatography on silica gel.

***trans*-2,2,5,5,10(*R*)-Pentamethyl-9(*R*)-decalol (23).** The early fractions above eluted with 1% ether in hexane afforded a pure sample of the minor (14%) component **23**, which exhibited the following characteristics: $n^{20}D$ 1.4935; ir (liquid film) 3610 (nonbonded OH), 3500 (bonded OH), 981, 950, 920, 841 $cm^{-1}$; nmr ($CDCl_3$) $\delta$ 0.79, 0.89, 0.92, 1.14, 1.19 (s, 3 each); mass spectrum *m/e* (rel intensity) 224 ($M^+$, 2), 191 (8), 150 (49), 140 (63), 111 (34), 95 (59), 69 (83), 55 (68), 43 (74), 41 (100).

*Anal.* Calcd for $C_{15}H_{28}O$: C, 80.29; H, 12.58. Found: C, 80.42; H, 12.38.

Later 1% ether in hexane fractions afforded a pure sample of the second (44%) component. This component was identical in all respects with the tertiary alcohol **17** previously obtained from reduction of epoxide **16**.

***cis*-2,2,5,5,10(*R*)-Pentamethyl-8-octal-1(*S*)-ol (26).** Fractions of the above chromatography eluted with 2% ether in hexane afforded pure third (42%) component **26**, which exhibited the following characteristics: $n^{20}D$ 1.4960; ir (liquid film) 3620 (nonbonded OH), 3490 (bonded OH), 1650 (C=C), 1185, 1024, 995, 975, 923, 849, 809 $cm^{-1}$; nmr ($CDCl_3$) $\delta$ 0.76, 0.85, 0.91, 0.98, 1.23 (s, 3 each), 3.58 (s, 1), 5.57 (dd, $J$ = 4, 2.5 Hz); mass spectrum *m/e* (rel intensity) 222 ($M^+$, 1), 204 (16), 189 (30), 153 (43), 110 (41), 95 (73), 81 (45), 69 (47), 55 (55), 43 (82), 41 (100).

*Anal.* Calcd for $C_{15}H_{26}O$: C, 81.02; H, 11.79. Found: C, 79.77; H, 12.01.

**(−)-*cis*-2,2,5,5,10(*S*)-Pentamethyl-*cis*-decal-1(*R*)-ol (24).** A sample of pure octalin **13** (4.1 g, 20 mmol) was treated with 1 *M* diborane in tetrahydrofuran solution (25 ml, 25 mmol) under nitrogen for 18 hr at 25°. The mixture was cooled to 0° and 10% aqueous sodium hydroxide (15 ml) was added, followed by 35% hydrogen peroxide (15 ml). After stirring for 2 hr at 35° the mixture was thoroughly extracted with hexane. The solvent was removed under reduced pressure to afford 4.4 g (98%) of crude crystalline product, mp 85–92°. Integration of the areas of the $\alpha$ to the hydroxyl proton resonances gave a 77:23 ratio of isomers. A sample was recrystallized from hexane at 0° and exhibited the following characteristics: mp 108–109°; $[\alpha]^{25}D$ −3° (*c* 0.2, $CHCl_3$); ir (KBr pellet) 3260 (OH), 1075, 1005, 990, 925 $cm^{-1}$; nmr ($CDCl_3$) $\delta$ 0.78, 0.98, 1.00 (s, 3 each), 0.87 (s, 6), 3.17 (d, 1, $J$ = 10 Hz); mass spectrum *m/e* (rel intensity) 224 ($M^+$, 16), 209 (12), 206 (7), 139 (57), 109 (21), 95 (35), 82 (100), 69 (50), 55 (44), 43 (70), 41 (56).

*Anal.* Calcd for $C_{15}H_{28}O$: C, 80.29; H, 12.58. Found: C, 80.01; C, 12.67.

**(−)-(*S*)-2,2,5,5,10-Pentamethyl-*trans*-1-decalone (25).** A sample of crude decalol mixture containing 77% of decalol **24** from the preceding hydroboration reaction was subjected to the standard Jones[18] oxidation procedure. The crude ketone mixture (2.5 g) thus obtained was then treated with methanol (75 ml), water (15 ml), and sodium carbonate (0.7 g) at reflux under nitrogen for 20 hr. The mixture was cooled, water (100 ml) was added, and the mixture was thoroughly extracted with hexane. The solvent was removed under reduced pressure and the residue was distilled, affording 2.1 g (84%) of decalone **25**: bp 85–90° (0.5 mm); $n^{20}D$ 1.4916; $[\alpha]^{25}D$ −20° (neat); ir (liquid film) 1698 (C=O), 1110, 932, 827 $cm^{-1}$; nmr ($CDCl_3$) $\delta$ 0.73, 0.82, 1.02, 1.08, 1.15 (s, 3 each), 2.70 (dd, 1, $J$ = 9, 4.5 Hz); mass spectrum *m/e* (rel intensity) 222 ($M^+$, 17), 207 (16), 153 (39), 126 (43), 120 (40), 82 (81), 69 (53), 55 (57), 41 (100); CD (*c* 0.0107, dioxane) $\theta_{328}$ 0, $\theta_{312}$ −2340, $\theta_{303}$ −4024, $\theta_{299}$ −3463, $\theta_{295}$ −4024, $\theta_{270}$ −1029, $\theta_{240}$ 0; ORD $\phi_{317}$ −2375°, $\phi_{310}$ −1671°, $\phi_{307}$ −1818°, $\phi_{297}$ 0°, $\phi_{273}$ +2276°.

*Anal.* Calcd for $C_{15}H_{26}O$: C, 81.02; H, 11.79. Found: C, 81.20; H, 12.06.

**(±)-6,6,10-Trimethyl-1(9)-octal-2-one (27).** The general procedure of Ross and Levine[26] was employed. To a mixture of potassium hydroxide (6 g), ethanol (35 ml), ether (250 ml), and 2,4,4-trimethylcyclohexanone[27] (87 g, 0.62 mol) under nitrogen at 0° was added a solution of methyl vinyl ketone (25 g, 0.35 mol) in ether (50 ml) over 1.5 hr. The mixture was allowed to agitate at 0° for 1 hr, then at 25° for 3 hr. Water (100 ml) was added and the mixture was extracted with ether. The organic phase was washed neutral with brine and the residue was distilled, affording 50 g of recovered 2,4,4-trimethylcyclohexanone, bp 65–68° (10 mm), and 36.5 g (54%) of desired octalone **27**: bp 100–103° (0.5 mm); $n^{20}D$ 1.5152; ir (liquid film) 1662 (C=O), 1615 (C=C), 1238, 1190, 863 $cm^{-1}$; nmr ($CDCl_3$) $\delta$ 0.94, 1.17, 1.31 (s, 3 each), 5.76 (d, 1, $J$ = 1.5 Hz); mass spectrum *m/e* (rel intensity) 192 ($M^-$, 49), 177 (44), 164 (33), 150 (89), 135 (100), 121 (39), 108 (94), 107 (44), 93 (45), 91 (37), 80 (36), 79 (66), 77 (34), 55 (44), 41 (65). The gas chromatogram showed a single peak.

*Anal.* Calcd for $C_{13}H_{20}O$: C, 81.20; H, 10.48. Found: C, 81.30; H, 10.36.

**(±)-1,1,6,6,10-Pentamethyl-8-octal-2-one (28).** To a suspension of 57% sodium hydride in mineral oil (14 g, 0.332 mol) in dry toluene (210 ml) under nitrogen was added *tert*-butyl alcohol (24.6 g, 0.332 mol) at 50° over 0.5 hr. The mixture was held at 50° for 1 hr, then cooled to 35°; octalone **27** (30.5 g, 0.158 mol) was added and the mixture was stirred at 35° for 1.5 hr. Methyl iodide (50 g, 0.352 mol) was then added over 5 min, and the temperature of the exothermic reaction was held to 45° with ice-bath cooling. After heat evolution ceased (0.5 hr), water (50 ml) was added. The layers were separated and the organic phase was washed once with brine (50 ml). The solvent was removed under reduced pressure and the residue was distilled, affording 31.4 g (90%) of distillate, bp 92–105° (0.5 mm). Analysis by gas chromatography showed the presence of four components in the ratio of 25:53:12:8. A sample of the major component, octalone **28**, was obtained pure by preparative gas chromatography and exhibited the following characteristics: $n^{20}D$ 1.4975; ir (liquid film) 1710 (C=O), 1653 (C=C), 1244, 1109, 1024, 822 $cm^{-1}$; nmr ($CDCl_3$) $\delta$ 0.97, 1.01, 1.04 (s, 3 each), 1.26 (s, 6), 1.41 (s, 2), 1.87 (d, 2, $J$ = 4.5 Hz), 1.70–1.95 (m, 2), 2.40–2.65 (m, 2), 5.60 (t, 1, $J$ = 4.5 Hz); mass spectrum *m/e* (rel intensity) 220 ($M^+$, 53), 205 (59), 164 (53), 149 (40), 121 (100), 109 (43), 107 (66), 93 (40), 91 (41), 55 (48), 43 (49), 41 (81).

*Anal.* Calcd for $C_{15}H_{24}O$: C, 81.76, H, 10.98. Found: C, 81.48; H, 10.98.

Nmr and mass spectral analysis of the 25% component in the above mixture indicated the introduction of three methyl groups in the alkylation process.

**(±)-3,3,8,8,10-Pentamethyl-1(9)-octalin (29).** The Wolff–Kishner procedure as modified by Nagata[28] was employed. A mixture of octalone **28** (22 g, 0.1 mol, 60% pure by vpc), 85% hydrazine hydrate (12 g, 0.2 mol), hydrazine dihydrochloride (1 g), and triethylene glycol (105 ml) was heated under nitrogen at 125° for 2 hr. Solid potassium hydroxide (18.5 g, 0.33 mol) was then cautiously added at 125°. The temperature was then raised to 225° over 1.0 hr and the excess hydrazine hydrate was removed by a Dean-Stark trap. Nitrogen evolution began when the temperature reached 175°. The reaction mixture was heated for an additional 10 min at 225° after gas evolution ceased. The mixture was cooled, poured into water (300 ml), and extracted three times with hexane (75 ml). The organic extracts were washed neutral with water and the solvent was removed under reduced pressure. Analysis by gas chromatography showed three components. The two minor components (35%) still retained a carbonyl group and were identical with the minor ketones in the starting material. The major component, octalin **29**, was purified by distillation, affording 11.4 g (55%) of colorless oil: bp 62–64° (0.5 mm); $n^{20}D$ 1.4910; ir (liquid film) 1640, 1148, 1068, 1030, 968, 815, 663 $cm^{-1}$; nmr ($CDCl_3$) $\delta$ 0.91, 0.99, 1.08, 1.12, 1.23 (s, 3 each), 1.32 (s, 2),

**Table I**

| Olefin | $T_R$[b] | 0[a] | 0.5[a] | 2.0[a] | 5.0[a] | 18[a] |
|---|---|---|---|---|---|---|
| **12** | 1.0 | 0 | 1.3 | 4.6 | 6.8 | 9.0 |
| **29** | 1.5 | 100 | 0 | 0 | 0 | 0 |
| **13** | 1.7 | 0 | 32.9 | 30.1 | 29.4 | 27.1 |
| **14** | 2.0 | 0 | 65.8 | 59.9 | 58.6 | 56.8 |
| **15** | 2.2 | 0 | 1.0 | 3.4 | 5.2 | 7.1 |

[a] Time in hours. [b] Retention time.

1.86 (d, 2, $J$ = 4.5 Hz), 5.45 (t, 1, $J$ = 4.5 Hz); mass spectrum $m/e$ (rel intensity) 206 ($M^+$, 33), 191 (100), 150 (20), 136 (28), 135 (66), 121 (62), 107 (50), 95 (47), 93 (38), 82 (38), 81 (35), 69 (48), 55 (47), 43 (34), 41 (63).

*Anal.* Calcd for $C_{15}H_{26}$: C, 87.30; H, 12.70. Found: C, 87.23; H, 12.87.

**Acid-Catalyzed Isomerization of Octalin 29.** A pure sample of octalin **29** (0.5 g, 2.5 mmol) was treated with acetic acid (4 g) containing sulfuric acid (1 g) at 40°. Samples were removed periodically for analysis by gas chromatography. Table I summarizes the results. The products were separated by preparative gas chromatography and gave ir, nmr, and mass spectra identical with those of the products previously isolated from the equilibration of olefin **12**. The octalins isolated in this experiment were optically inactive, since a racemic octalin (**29**) had been employed as the starting material.

**Registry No.**—**10**, 470-40-6; **11**, 50562-26-0; **12**, 32540-36-6; **13**, 50562-28-2; **14**, 50562-29-3; **15**, 50512-32-8; **16**, 50562-30-6; **17**, 50562-31-7; **18**, 50562-32-8; **19**, 50562-33-9; **20**, 50562-34-0; **21**, 50562-35-1; **22**, 51096-44-7; **23**, 51096-43-6; **24**, 50562-38-4; **25**, 50562-39-5; **26**, 50562-40-8; **27**, 50562-41-9; **28**, 50562-42-0; **29**, 50562-43-1.

## References and Notes


(1) Presented at the 166th National Meeting of the American Chemical Society, Chicago, Ill., Aug 1973.
(2) A comprehensive review of such rearrangements is found in J. F. King and P. de Mayo in "Molecular Rearrangements," Part 2, P. de Mayo, Ed., Interscience, New York, N. Y., 1964.
(3) R. B. Clayton, *Quart. Rev., Chem. Soc.*, **19**, 168, 201 (1965).
(4) R. Robinson, "The Structural Relations of Natural Products," Clarendon, Oxford, 1955.
(5) J. W. Huffman, *J. Org. Chem.*, **37**, 2736 (1972).
(6) C. H. Heathcock and T. R. Kelley, *Tetrahedron*, **24**, 3753 (1968).
(7) D. T. Dunham and R. G. Lawton, *J. Amer. Chem. Soc.*, **93**, 2075 (1971).
(8) H. W. Whitlock and L. E. Overman, *J. Amer. Chem. Soc.*, **93**, 2247 (1971).
(9) G. Büchi, F. Greuter, and T. Tokoryama, *Tetrahedron Lett.*, 827 (1962).
(10) I. Kitagawa, Y. Yamazoe, R. Takeda, and I. Yosioka, *Tetrahedron Lett.*, 4843 (1972).
(11) A. R. Hochstetler and G. C. Kitchens, *J. Org. Chem.*, **37**, 2750 (1972); L. E. Friedrich, Dissertation 67-8559, University Microfilms, Ann Arbor, Mich.
(12) W. G. Dauben and P. Oberhansli, *J. Org. Chem.*, **30**, 3947 (1965).
(13) J. A. Marshall and A. R. Hochstetler, *J. Amer. Chem. Soc.*, **91**, 648 (1969).
(14) G. Saucy, R. E. Ireland, J. Bordner, and R. E. Dickerson, *J. Org. Chem.*, **36**, 1195 (1971).
(15) F. Sondheimer and S. Wolfe, *Can. J. Chem.*, **37**, 1870 (1959).
(16) *Cf.* R. P. Thummel and B. Rickborn, *J. Amer. Chem. Soc.*, **92**, 2064 (1970).
(17) H. C. Brown and G. Zweifel, *J. Amer. Chem. Soc.*, **81**, 247 (1959).
(18) K. Bowden, I. M. Heilbron, E. H. R. Jones, and B. C. L. Weedon, *J. Chem. Soc.*, 39 (1946).
(19) W. Moffitt, R. B. Woodward, A. Moscowitz, W. Klyne, and C. Djerassi, *J. Amer. Chem. Soc.*, **83**, 4013 (1961).
(20) C. Djerassi, J. Burakevich, J. W. Chamberlin, D. Elad, T. Toda, and G. Stork, *J. Amer. Chem. Soc.*, **86**, 465 (1964).
(21) H. Christol and R. Vanel, *Bull. Soc. Chim. Fr.*, 1398 (1968).
(22) C. Christol, H. Christol, and R. Vanel, *Bull. Soc. Chim. Fr.*, 3685 (1970).
(23) Melting points were determined on a Hoover capillary melting point apparatus and are uncorrected. Spectra were recorded on a Perkin-Elmer 457 grating ir spectrophotometer, a Varian A-60A nmr spectrometer, and a Perkin-Elmer 270 double-focusing mass spectrometer at 70 eV. ORD and CD measurements were performed using a Jasco ORD/UV-5 spectropolarimeter with CD attachemployed for optical rotation measurements. Spinning-band separations were accomplished with a Nester-Faust NFA-100 autoannular Teflon spinning-band column. Gas chromatography was carried out on an F and M 720 instrument equipped with a 2 m × 0.25 in. copper column packed with 15% Carbowax 20M on Chromosorb P with helium as the carrier gas. Combustion analyses were determined by Schwartzkopf Microanalytical Laboratory, Woodside, N. Y.
(24) S. Itô, M. Yatagai, and K. Endo, *Tetrahedron Lett.*, 1149 (1971).
(25) H. C. Brown, K. J. Murray, L. J. Murray, J. A. Snover, and G. Zweifel, *J. Amer. Chem. Soc.*, **82**, 4233 (1960).
(26) N. C. Ross and R. Levine, *J. Org. Chem.*, **29**, 2341 (1964).
(27) Obtained by catalytic reduction of 4,4,6-trimethyl-2-cyclohexenone, the condensation product of isobutyraldehyde with methyl isopropenyl ketone.
(28) W. Nagata, M. Narisada, T. Wakabayashi, and T. Sugasawo, *J. Amer. Chem. Soc.*, **89**, 1499 (1967).


# Synthesis of *cis*-1,2-Dihydroxy-1,2-dihydronaphthalene and *cis*-1,4-Dihydroxy-1,4-dihydronaphthalene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Both of title compounds were prepared from the readily accessible *cis,cis*-1,4-dihydroxy-2,3-epoxy-1,2,3,4-tetrahydronaphthalene. The 1,2-dihydrodiol, a bacterial metabolite of naphthalene, was obtained through the action of sodium iodide and zinc dust in acetic acid on the epoxide. Conversion of the epoxide to the thioepoxide and desulfurization with triphenylphosphine provided the 1,4-dihydrodiol, which was also obtained by direct reduction of *p*-naphthoquinone with diisobutylaluminum hydride.


Although *cis*- and *trans*-1,2-dihydroxy-1,2-dihydroarenes have been known as oxidative metabolites of the aromatic ring for many years,[1] relatively little has been reported on the synthesis of this important class of metabolites. Both *cis*- and *trans*-1,2-dihydroxy-1,2-dihydrobenzene have been prepared by dehalogenation of the corresponding tetrachlorocyclohexanediols.[2] While *cis*-1,2-dihydrodiols at the K regions of polycyclic aromatic hydrocarbons are available through the action of osmium tetroxide,[3] the procedure fails with naphthalene. *trans*-1,2-Dihydrodiols have been prepared by reduction of K region *o*-quinones with lithium aluminum hydride.[4,5] The hydride reduction produces only pyrocatechol from *o*-benzoquinone[4] and a mixture of cis and trans isomers is formed from 7,12-dimethylbenz[*a*]anthracene-5,6-quinone.[5] Reduction of certain *p*-quinones such as 1,4-naphthoquinone results in conjugate addition of hydride.[6] The only 1,4-dihydrodiols without substitution at the carbinol position prepared thus far have been by lead tetraacetate oxidation[7] of the 9,10 positions of anthracene and by the lithium aluminum