Unusual Reactivity in a Highly Substituted Olefin. The 2,2,8,8,10-Pentamethyl-1(9)-octalin System

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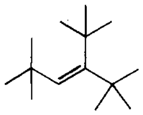
Epoxidation of the highly hindered octalin **2** afforded the corresponding epoxide mixture **3** and **4** in a 70:30 ratio. Attempted oxidation of the double bond with sodium dichromate or potassium permanganate gave only the cis epoxide **4**, as did ozonolysis. Hydroboration afforded the crystalline dialkyldiborane **11**, which failed to undergo normal oxidation with basic hydrogen peroxide. Borane **11** reacted smoothly in solution with molecular oxygen, affording directly the trans fused decalone **12**. High-temperature hydroboration of **2** proceeded normally to afford an 88:12 mixture of diols **9** and **10**. These experimental results are largely explicable in terms of severe steric hindrance of the double bond in **2**, and a direct comparison with the reactivity of the closely related acyclic olefin **1** is made.

Steric effects on the properties and reactivities of appropriately substituted olefins have been the subject of a number of recent investigations.[1] Syntheses of sterically hindered olefins are generally difficult to achieve, and it is only recently that a synthesis of the highly hindered olefin tri-*tert*-butylethylene (**1**) has been effected by Abruscato and Tidwell.[2] These authors have also reported on the effect of such steric hindrance on the Raman,[2] ultraviolet,[3] and ^{13}C NMR spectra,[4] and on the chemical reactivity of the double bond in **1**.[5]



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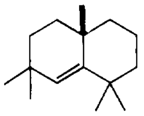


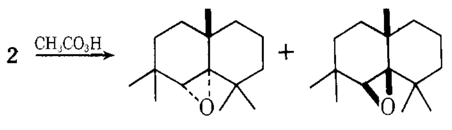
2

The influence of steric effects on the reactivity of the double bond in **1** stems both from hindrance to attack by the *tert*-butyl groups and from torsional strain at the double bond induced by relief of steric compression.[6] Separation of these two effects is not possible in such acyclic systems such as **1** but they can be largely separated if the double bond is incorporated into an appropriately substituted ring system.

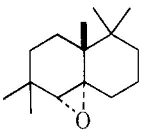
During the course of a systematic investigation of the chemistry of the sesquiterpene hydrocarbon (−)-thujopsene we had previously reported the conversion of (−)-thujopsene to the optically active olefin **2**.[8] Olefin **2** possesses the same substitution pattern as **1** but differs from **1** in several important ways. The torsional angle of **1** has been calculated[7] to be 16°, which is considerably larger than the 0.5–5° reported[6a] for a number of cyclohexene skeletons. The torsional angle should be considerably less in **2**, since the nonbonded interactions giving rise to torsional strain in **1** have now become bonded interactions by incorporation into the octalin skeleton; consequently the effect on reactivity of the double bond in **2** should be principally steric hindrance alone. The octalin system also is considerably more rigid with no free rotation of the σ bonds directly attached to the double bond. Finally, the octalin system affords an analysis of the stereochemistry of the attack on the double bond since the two sides are now nonequivalent.

Hydrogenation of 2. Treatment of **2** with 55 psi of hydrogen over PtO_2 at 75° afforded no uptake of hydrogen and the starting material was recovered unchanged, whereas less stringent conditions were shown to effect the reduction of **1**.[5]

Epoxidation. Treatment of **2** with buffered peracetic acid proceeded normally and at a reasonable rate to afford epoxide mixture **3** (70%) and **4** (30%) in high yield. These two isomers were not separable by GLC and the isomer ratio was determined by the integration of the respective epoxide proton singlets occurring at δ 2.68 for the major trans epoxide **3** and at δ 2.78 for the minor cis epoxide **4**. These stereochemical assignments can be unequivocally made from this chemical shift difference. Earlier studies have shown that in steroidal systems not containing any unsaturated functionality in proximity to the epoxide, the α-epoxide proton in $5\beta,6\beta$-epoxy steroids always occurs at lower field than the β-epoxide proton in the corresponding $5\alpha,6\alpha$-epoxy steroids.[9,10] The same chemical shift order has also been shown[8] to occur in the closely related epoxides **5** and **6**, where the trans epoxide **5** showed a one-proton singlet at δ 2.31 and the cis epoxide **6** the corresponding singlet at δ 2.60.



3 4



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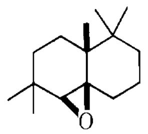


6

Oxidation. Attempts at oxidation of the double bond employing refluxing basic aqueous potassium permanganate[11] gave only recovered starting material. Assuming that lack of mutual solubility precluded reaction, the oxidation was then carried out with potassium permanganate in acetic acid at 25°.[12] Under these conditions no olefin **2** was recovered and a 67% yield of cis epoxide **4** was obtained. Similar results (79% yield) were also obtained when sodium dichromate in acetic acid–acetic anhydride was employed as the oxidizing agent. Within the limits of the NMR analytical method (2%) no trans epoxide **3** could be detected employing either oxidizing agent. No evidence was obtained for any rearranged products under either of the above conditions.

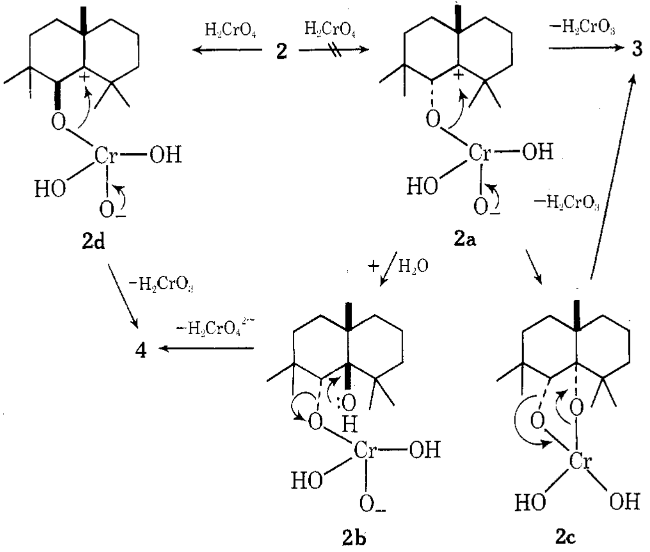
Epoxide formation under such conditions is not new. The tetraarylethylenes have been shown to form good yields of the corresponding epoxide with either reagent,[12,13] with stereoisomeric epoxides formed from unsymmetrically substituted tetraarylethylenes.[13] In the present case only one stereoisomer is found with either reagent.

Irrespective of the exact mechanistic nature of peracid epoxidations, whether via a concerted mechanism[14] or via a

1,3-dipolar addition reaction,[15] in molecules containing no other functionality peracids preferentially attack olefinic double bonds from the least hindered side. In the case of olefin **2** this least hindered side must be the α face, since the major epoxide **3** possesses the trans ring fusion.

Little is known concerning the detailed mechanism of the oxidation of alkenes.[13] Allylic oxidation[16] cannot occur on olefin **2**, since no allylic hydrogens are available for abstraction. Direct attack of the chromium(VI) species from the apparently least hindered α face of olefin **2** would lead to an intermediate species such as structure **2a** in Scheme I. Although β-face addition of water to give **2b** followed by internal nucleophilic displacement[13] of the chromium(IV) species would afford the observed cis epoxide **4**, this mechanism cannot be operative here, since similar results were obtained with anhydrous sodium chromate and with potassium permanganate in an anhydrous reaction mixture. Alternate decomposition of intermediate **2a** directly or via cyclic intermediate **2c** would lead to the trans epoxide **3**, which is not observed, as the product. Consequently, the preferred attack of the oxidizing agent must be from the apparently more hindered β face via the intermediate **2d** (or its cyclic five-membered ring counterpart) with the oxidizing agent cis to the angular methyl group. Decomposition of this intermediate then leads to the observed cis epoxide **4**.

Scheme I

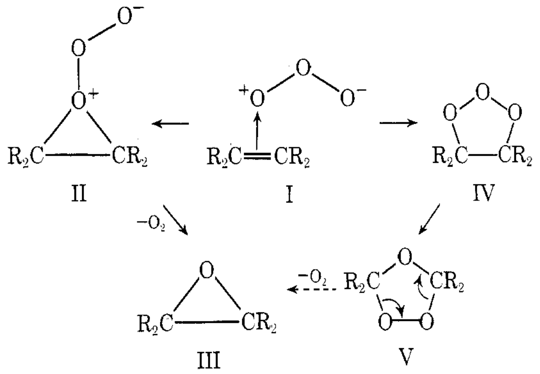


A similar mechanism can also be advanced to explain the identical stereochemical outcome when potassium permanganate in acetic acid is employed.

The nature of the transition state for epoxide formation under these conditions is unknown. Clearly this transition state does not resemble the reactant-like transition state of the peracid epoxidation or a predominance of the trans epoxide **3** would have been found.

Ozonolysis. Ozonolysis of **2** at 0° in ethylene dichloride afforded the cis epoxide **4** in 70% isolated yield. Detailed analysis of the NMR spectrum showed that only 3% of the trans epoxide **3** was present.

Numerous examples are found in the literature of the formation of epoxides during the ozonolysis of olefins.[17] These epoxides, termed partial cleavage products,[18] generally are found when there is considerable steric hindrance to the double bond. Recent work has indicated that in the ozonolysis reaction an initial π complex I is formed.[19] As the bulk of the R groups increases, 1,3-dipolar cycloaddition to give the normal initial ozonide (1,2,3-trioxalane IV) becomes unfavorable and collapse to the σ complex II occurs instead.[18,20] Loss of molecular oxygen from II then affords the partial cleavage product, epoxide III.



The above mechanism, although accounting for epoxide formation from hindered olefins, is difficult to reconcile with the observed cis ring fusion of the major epoxide **4** obtained by ozonolysis of **2** unless the attack of ozone is exclusively from the apparent more hindered β face of olefin **2**. Decomposition of σ complex II would not be expected to alter the stereochemistry of initial attack on the double bond.

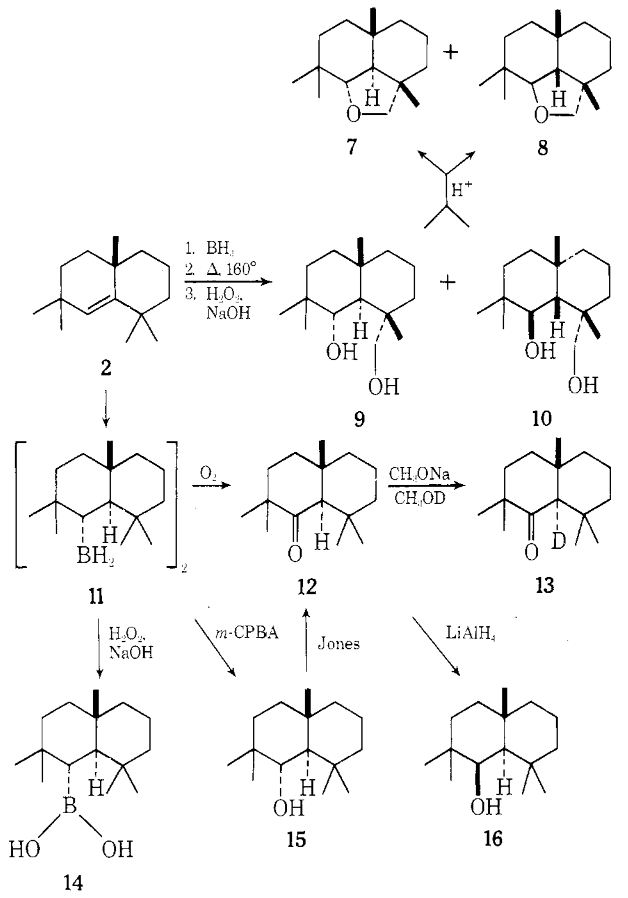
An alternate explanation would involve formation of the 1,2,4-trioxalane V from the initial ozonide IV, with the single oxygen on the more hindered face cis to the angular methyl group of **4** and the peroxy bridge on the less hindered trans face. Loss of oxygen from the peroxy bridge would then afford the observed cis stereochemistry of **4**. This explanation is unlikely for two reasons. First, steric considerations argue against the initial formation of the ozonide IV from either face. Second, no loss of oxygen to give epoxides has ever been observed from ozonide structures such as V.[18]

Epoxide **4** cannot be produced in the course of the ozonolysis reaction by some peroxidic ozonolysis product. This peroxidic product presumably would afford the same stereochemical outcome as the peracetic acid epoxidation which affords principally the trans epoxide **3**.

No information is available on the nature of the transition state which leads to epoxides upon ozonolysis of hindered olefins. If this transition state appears reactant-like the product distribution should reflect that found in the peracetic acid epoxidation. If the transition state appears product-like then no particular distribution can be predicted, since the relative stabilities of epoxides **3** and **4** are not known. On the basis of present evidence we cannot assign a mechanistic rationale completely consonant with these ozonolysis results.

Our results differ significantly from those reported for the ozonolysis products of tri-*tert*-butylethylene (**1**), where normal cleavage products were obtained and no epoxide formation was noted.[5] Analysis of our crude ozonolysis mixture by VPC showed only traces of three minor components at the retention time expected for the keto aldehyde normal ozonolysis product.

Hydroboration. In contrast to the relative ease of epoxidation of **2**, hydroboration proceeded quite slowly so that extended reaction times were necessary to avoid recovery of sizable amounts of starting material. Reactions run at room temperature for 20 hr generally afforded 85–90% reaction. In all cases a white precipitate was found in the reaction mixture and in one case was carefully filtered under nitrogen from the tetrahydrofuran solvent. Spectral data clearly showed a simple B–H stretching frequency at 2495 cm^{-1} and a strong band at 1570 cm^{-1} for the diborane



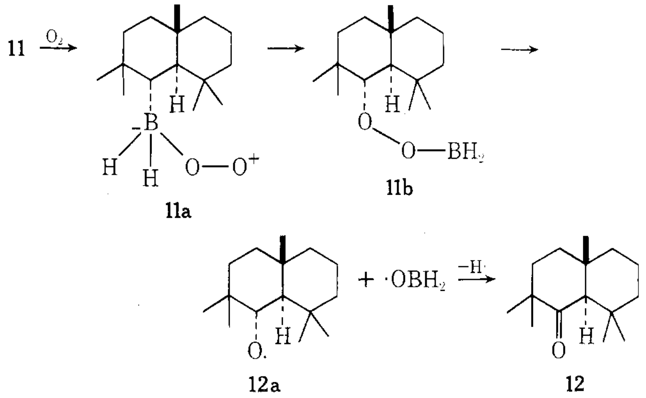
hydrogen bridge.[21] These data indicate that the precipitate is the *sym*-dialkyldiborane **11**. We will discuss later the trans ring fusion stereochemistry assigned to the dimer **11**.

Normal alkaline hydrogen peroxide oxidation[22] of the hydroboration mixture containing **11** afforded no expected secondary alcohol **15** but rather the alkyl boronic acid **14**, the simple hydrolysis product of dialkyldiborane **11**. To our knowledge this is the first report of an alkylborane obtained in a hydroboration reaction which fails to oxidize under the above conditions. The failure must be due to excessive steric hindrance to attack of the hydroperoxide anion on the boron atom to afford the necessary tetrahedral boron intermediate. Attempts at direct oxidation of **11** to ketone **12** with aqueous chromic acid[23] also failed; the sole product obtained was again the boronic acid **14**.

Oxidation to the desired alcohol **15** was finally achieved by the use of the more effective oxidizing agent *m*-chloroperbenzoic acid.[24] The trans ring fusion was assigned from the NMR spectrum, which showed a coupling constant of 11 Hz for the α hydrogen, as expected for the trans diaxial coupling of decalol **15**. Jones oxidation of decalol **15** afforded the corresponding trans ketone **12**.

Ketone **12** was also formed directly from borane **11** by direct oxidation with molecular oxygen; no evidence was obtained for the formation of decalol **15** or of the corresponding hydroperoxide.[25] The mechanism of formation of ketone **12** is not entirely clear. We have already noted that borane **11** does not undergo the normal rearrangement reactions with alkaline hydrogen peroxide, thus rendering tenable the proposal[26] that, in systems where ionic attack may not be favored, radical reactions become more important. Although we fail to observe any ketone **12** or decalol **15** under the alkaline hydrogen peroxide oxidation conditions, radical reactions may indeed be the mode of formation of **12** in the reaction with molecular oxygen. In the present case this reaction may proceed by coordination of the oxygen molecule to the boron atom of the highly hindered borane **11**, followed by a migration of the alkyl group from boron to oxygen[27] as outlined in Scheme II. Radical

Scheme II



decomposition of the intermediate peroxide **11b** would generate radical **12a**, which by loss of a hydrogen radical would afford the observed ketone **12**.[28] Borane **11** must be the precursor of the intermediate peroxide **11b**; subjection of pure boronic acid **14** under the reaction conditions afforded no ketone **12** and **14** was recovered unchanged.

The trans ring fusion stereochemistry of optically active decalone **12** was unambiguously determined by analysis of the ORD curve, which showed a strong negative Cotton effect. The absolute sterochemistry at the chiral angular methyl center in octalin **2** is known[8] to be as shown and none of the reactions leading to decalone **12** have involved that center. Application of the octant rule[29] in the present case clearly predicts a negative Cotton effect for the trans-fused decalone **12**, whereas a positive Cotton effect would be predicted for the corresponding cis-fused isomer, whether in the steroid or the nonsteroid conformation.

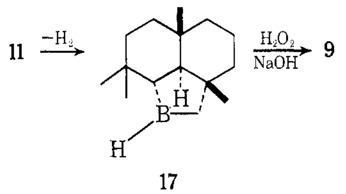
Additional confirmation for the trans ring fusion of **12** was provided by equilibration experiments. Ketone **12** was recovered unchanged upon basic treatment. The possibility that no enolization had occurred was disproved by the incorporation of one deuterium atom upon equilibration in basic CH_3OD solution, and the loss of the one-proton singlet at δ 2.33 in the NMR spectrum of the deuterated ketone **13**.

Lithium aluminum hydride reduction of **12** afforded a secondary alcohol **16** different from the hydroboration–oxidation alcohol **15**, as expected from reduction of the least hindered α face of the carbonyl group. The NMR spectrum showed a doublet for the α proton with a coupling constant of 4 Hz, as expected for the axial–equatorial relationship of the C-1 and C-9 protons in **16**.

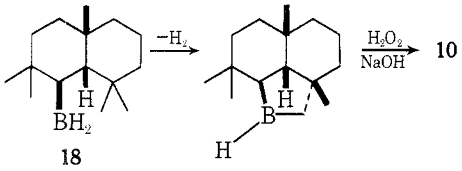
No evidence had been obtained thus far on the presence of any products obtainable from initial hydroboration of **2** from the β face leading to the cis ring fusion. Inspection of molecular models revealed a close proximity of the boron atom in **11** to the α-methyl group at C-8, and the same proximity in the steroid conformation of the corresponding alkylborane derived from β-face attack. Heating of the hydroboration mixture to 160° in diglyme, followed by normal alkaline hydrogen peroxide treatment, afforded in good yield the crystalline diol **9** as the major product. All attempts at isolation and purification of the minor diol **10** failed.

Evidence for the presence of diol **10** was obtained by acid-catalyzed cyclization of the crude diol mixture above to an 88:12 mixture of isomeric ethers. These were separated by column chromatography and afforded spectral data consistent with the assigned structures of **7** for the major ether and **8** for the minor ether.

Diol **9** thus arises from oxidation of internal dialkylborane **17**, in turn formed by loss of the elements of hydrogen from **11**. Similarly, diol **10** is formed by oxidation of **19**[31] derived from **18**. Such cyclizations of alkylboranes have been well documented[5,30] in other systems where a δ hydrogen is appropriately oriented with respect to the boron atom.



17



18

19

It is interesting to note that no difficulty was encountered in the alkaline hydrogen peroxide oxidation of the dialkylborane mixture **17** and **19** to the respective diols **9** and **10**, whereas alkylborane **11** fails to oxidize under these conditions. This result is reasonably explained by the reduced steric interactions to attack at the boron atom in **17** and **19**, since the former nonbonded interaction from the α-methyl group at C-8 in **11** now has been minimized by bond formation to the boron atom.

In the case of olefin **2** we have already shown that epoxidation occurs principally (70%) from the less hindered α face. The hydroboration results also indicate that the α face is preferred (88%) in that reaction to an even greater extent. These observations are in general agreement with earlier studies showing only slight differences in the stereochemical outcome of epoxidation as compared to hydroboration on the same molecule.[32]

Finally, our results differ from the reported[5] hydroboration–oxidation of tri-*tert*-butylethylene (**1**). For olefin **1** no crystalline alkylborane could be isolated, and normal alkaline hydrogen peroxide treatment of the alkylborane gave a mixture of the corresponding secondary alcohol, the ketone derived from this alcohol, and the corresponding tetrahydrofuran ether. The ether may arise from cyclization of the diol derived from the internal dialkylborane, which in the case of **1** is formed at 25°. For olefin **2**, however, this low temperature is not sufficient to form intermediates **17** and **19**, which are only obtained by refluxing in diglyme (160°). In the case of olefin **2** diol **9** could readily be isolated, whereas no diol could be isolated from olefin **1** owing to facile cyclization to the tetrahydrofuran ether.

Experimental Section[33]

(*S*)-2,2,8,8,10-Pentamethyl-1(9)-octalin (2). This octalin was prepared as previously described from (−)-thujopsene.[8]

Epoxidation of 2. To a mixture of octalin **2** (15.0 g, 73 mmol), ethylene dichloride (30 ml), and sodium carbonate (7 g) was added 40% peracetic acid (25 g, 131 mmol) at 30° over 10 min. After an additional 3 hr at 40°, water (60 ml) was added and the layers were separated. The organic phase was washed once with sodium carbonate solution and the solvent was removed under reduced pressure. Distillation afforded 14.2 g (88%) of a colorless oil: bp 74–76° (0.5 mm); $n^{20}\text{D}$ 1.4784; $[\alpha]^{25}\text{D}$ +37.5° (neat); ir (liquid film) 1028, 1020, 960, 31, 919, 830 cm^{-1}; NMR ($CDCl_3$) δ 0.73, 1.01, 1.04, 1.11, 1.18, (s, 3 each), 2.68 (s, 1, from major isomer **3**), 2.78 (s, 1, from minor isomer **4**); mass spectrum *m/e* (rel intensity) 222 (M^+, 14), 207 (13), 140 (52), 123 (53), 95 (41), 81 (73), 69 (66), 55 (55), 43 (63), 41 (100). No separation could be achieved by gas chromatography. Integration of the proton singlets at δ 2.78 and 2.68 showed a mixture of 30% epoxide **4** and 70% of *trans*-1(*R*),9(*S*)-epoxy-2,2,8,8,10(*S*)-pentamethyldecalin (**3**).

Anal. Calcd for $C_{15}H_{26}O$: C, 81.02; H, 11.79. Found: C, 81.10; H, 11.84.

Oxidation of 2. A. Aqueous Potassium Permanganate. A mixture of olefin **2** (10.3 g, 50 mmol), water (200 ml), potassium hydroxide (1 g), and potassium permanganate (37 g) was heated at reflux for 6 hr.[11] The mixture was cooled, filtered, and extracted with hexane. The solvent was removed under reduced pressure, affording 10.0 of material with an ir spectrum identical with that of starting olefin **2**.

B. Potassium Permanganate–Acetic Acid. A mixture of olefin **2** (10.3 g, 50 mmol), acetic acid (250 ml), and potassium permanganate (27 g) was stirred at 25° with slight cooling for 4 hr.[12] The mixture was then filtered and water (750 ml) was added. The mixture was extracted with hexane and the solvent was removed under reduced pressure. Distillation afforded 7.4 g (67%) of *cis*-1(*S*),9(*R*)-epoxy-2,2,8,8,10(*S*)-pentamethyldecalin (**4**); bp 71–72° (0.5 mm); $n^{20}\text{D}$ 1.4785; $[\alpha]^{25}\text{D}$ +25° (neat); ir (liquid film) 1018, 958, 930, 918, 852, 649 cm^{-1}; NMR ($CDCl_3$) δ 0.80, 1.10 (s, 3 each), 1.00 (s, 9), 2.78 (s, 1); mass spectrum *m/e* (rel intensity) 222 (M^+, 8), 140 (28), 125 (31), 123 (45), 95 (33), 81 (57), 69 (57), 67 (26), 55 (49), 43 (64), 43 (64), 41 (100). No absorption at δ 2.68 in the NMR spectrum for the one-proton singlet of epoxide **3** was detectable.

Anal. Calcd for $C_{15}H_{26}O$: C, 81.02; H, 11.79. Found: C, 81.11; H, 11.70.

C. Sodium Dichromate. To a solution of olefin **2** (9.0 g, 43.7 mmol), acetic acid (20 ml), and acetic anhydride (60 ml) was added sodium dichromate dihydrate (26 g) portionwise at 30° over 0.5 hr. After stirring at 40° for 3 hr, the solution was poured into water (150 ml) and extracted with benzene. The combined organic extracts were washed with sodium carbonate solution and the solvent was removed under reduced pressure. Distillation afforded 7.6 g (79%) of epoxide **4** which exhibited spectral data identical with those of the epoxide obtained in part B above.

Similar results, although at a slower rate, were obtained when anhydrous sodium chromate was employed.

Ozonolysis of 2. A solution of olefin **2** (10.3 g, 50 mmol) in ethylene dichloride (100 ml) was ozonized at 0° for 4 hr. The ozonolysis mixture was then added to a suspension of zinc dust (10 g) in 10% aqueous acetic acid (100 ml) and heated to 75° for 1 hr. The mixture was cooled and extracted with ethylene dichloride. After removal of the solvent under reduced pressure, the residue was analyzed by VPC and found to contain no olefin **2**, epoxide **4** (92%), and three minor components (total of 8%) at much longer retention times. Distillation of this residue afforded 7.8 g (71%) of epoxide **4** which exhibited spectral characteristics identical with those of the epoxide **4** obtained from the oxidation above. Detailed analysis of the NMR spectrum showed the presence of 3% of the isomeric epoxide **3**.

Hydroboration of 2. A. Dialkyldiborane 11. A solution of olefin **2** (5.1 g, 25 mmol) and 25 ml (25 mmol) of 1 *M* diborane in tetrahydrofuran solution was allowed to stir under nitrogen at 25° for 20 hr. The resultant precipitate was carefully filtered under nitrogen, affording 1.6 g (34%) of dialkyldiborane **11** which exhibited the following properties: mp 120–122° dec; ir (KBr) 2495 (B–H), 1570 (BH_2B bridge), 1186, 1074, 777 cm^{-1}; NMR ($CDCl_3$) δ 0.80, 0.85 (s, 3 each), 0.96 (s, 9); mass spectrum *m/e* (rel intensity) 221 (1), 206 (7), 191 (32), 121 (18), 95 (37), 69 (19), 58 (27), 43 (100), 41 (29).

Anal. Calcd for $C_{30}H_{58}B_2$: C, 81.79; H, 13.30; B, 4.91. Found: C, 79.66; H, 13.16; B, 5.02.

A satisfactory carbon analysis could not be obtained. These crystals proved to be stable in air, but reacted rapidly with molecular oxygen in solution (see part D below).

B. Alkylboronic Acid 14. A solution of olefin **2** (10.3 g, 50 mmol) and 50 ml (50 mmol) of 1 *M* diborane in tetrahydrofuran solution was stirred under nitrogen at 25° for 20 hr. The mixture was cooled and carefully treated with water (5 ml), followed by 10% aqueous sodium hydroxide (30 ml) and 35% hydrogen peroxide (25 ml). The mixture was allowed to stir at 40° for 4 hr and then was thoroughly extracted with hexane. The solvent was removed under reduced pressure, affording 12 g of crude solid, mp 126–130°. This solid was recrystallized from hexane, affording 9.1 g (72%) of boronic acid **14**: mp 145–146°; $[\alpha]^{25}\text{D}$ +18° (*c* 0.05, $CHCl_3$); ir (KBr) 3300 (OH), 1315, 1020, 765 cm^{-1}; NMR ($CDCl_3$) δ 0.88, 0.92, 1.08 (s, 3 each), 0.96 (s, 6), 4.52 (s, 2); mass spectrum *m/e* (rel intensity) 252 (M^+, 31), 237 (62), 153 (44), 123 (29), 109 (30), 95 (68), 81 (54), 69 (93), 55 (80), 43 (43), 41 (100).

Anal. Calcd for $C_{15}H_{29}BO_2$: C, 71.44; H, 11.59; B, 4.29. Found: C, 71.16; H, 11.60; B, 4.53.

An attempt to oxidize the crude hydroboration mixture with an acid solution of sodium dichromate[22] again afforded only the boronic acid **14**.

These crystals of boronic acid **14** were stable to oxygen in ether solvents.

C. 2,2,8,8,10(*S*)-Pentamethyl-*trans*-decal-*trans*-1(*S*)-ol (15). A solution of olefin **2** (10.3 g, 50 mmol) and 50 ml (50 mmol) of 1 *M* diborane in tetrahydrofuran solution was stirred under nitrogen at 25° for 22 hr. To this mixture was added a solution of 85% *m*-chloroperbenzoic acid (31 g, 150 mmol) in chloroform (175 ml) at 35° over 0.5 hr. After an additional 1 hr at 35° the mixture was cooled and treated with 30% aqueous sodium hydroxide (50 ml). The organic phase was washed neutral with water and the solvent was removed under reduced pressure. Distillation afforded 6.8 g (61%) of an 11:89 mixture of two peaks by vpc. The minor peak was identical with a 70:30 mixture of epoxides **3** and **4** (by epoxidation of unreacted **2**). A sample of the major isomer (**15**) was purified by preparative gas chromatography and exhibited the following characteristics: mp 42–44°; $[\alpha]^{25}D$ +2.5° (*c* 20%, $CHCl_3$); ir (liquid film) 3570 (OH), 1075, 1020, 977 cm^{-1}; NMR ($CDCl_3$) δ 0.91, 0.96, 1.13 (s, 3 each), 1.02 (s, 6), 3.61 (d, *J* = 11 Hz, 1).

Anal. Calcd for $C_{15}H_{28}O$: C, 80.29; H, 12.58. Found: C, 79.94; H, 12.59.

D. (*S*)-2,2,8,8,10-Pentamethyl-*trans*-1-decalone (12). A solution of olefin **2** (15.3 g, 75 mmol) and 75 ml (75 mmol) of 1 *M* diborane in tetrahydrofuran solution was stirred under nitrogen at 25° for 17 hr. The nitrogen purge line was removed and connected to an oxygen tank and a slow stream of oxygen was passed into the solution. The temperature rose to 45° in 0.5 hr, at which point the precipitate (alkylborane **11**) initially present had all dissolved. After an additional 1.5 hr the temperature began to drop and the solution cooled to room temperature. Oxygen feed was continued for an additional 1.0 hr. Water (80 ml) was then added and the mixture was extracted with hexane. The solvent was removed under reduced pressure and afforded 16 g of residue. The ir spectrum showed a sizable carbonyl absorption. This residue was chromatographed on 200 g of silica. Elution with hexane afforded 3.4 g of recovered unreacted olefin **2**. Continued elution with 0.5% ether in hexane gave 5.1 g (40%) of decalone **12** which exhibited the following characteristics: bp 72–74° (0.5 mm); mp 29–30°; $n^{20}D$ 1.4840; $[\alpha]^{25}D$ −63° (neat); ir (liquid film) 1703 (C=O), 1081, 970, 951, 843 cm^{-1}; NMR ($CDCl_3$) δ 0.87, 0.92, 1.01, 1.17, 1.21 (s, 3 each), 2.33 (s, 1); NMR (C_6H_6) δ 0.68, 1.00, 1.02, 1.05, 1.32 (s, 3 each), 2.20 (s, 1); mass spectrum *m/e* (rel intensity) 222 (M^+, 3), 207 (11), 151 (100), 123 (18), 82 (15), 69 (15), 67 (15), 55 (14), 43 (14), 41 (27); CD (*c* 0.0140, dioxane) θ_{337} 0, θ_{310} −10,690, θ_{306} −10,120, θ_{301} −10,477, θ_{235} 0; ORD ϕ_{326} −6557°, ϕ_{319} −4561°, ϕ_{315} −4707°, ϕ_{305} 0°, ϕ_{280} +6058°.

Anal. Calcd for $C_{15}H_{26}O$: C, 81.02; H, 11.79. Found: C, 81.24; H, 11.79.

Elution with 10% ether in hexane afforded 3.9 g (27%) of alkylbornic acid **14** which was identical with the same material isolated in part B above.

Oxidation of 2,2,8,8,10(*S*)-Pentamethyl-*trans*-decal-*trans*-1(*S*)-ol (15). The standard Jones oxidation procedure[34] was employed on 2.8 g (12.5 mmol) of decalol **15**. Short-path distillation afforded 2.4 g (86%) of decalone **12** which was identical with the same material isolated in part D above.

9-Deuterio-2,2,8,8,10(*S*)-Pentamethyl-*trans*-1-decalone (13). A solution of ketone **12** (120 mg, 5.4 mmol) and 5 ml (5 mmol) of 1 *M* sodium methoxide in methanol-*O-d* was allowed to reflux under nitrogen for 18 hr. The solution was cooled and hexane (15 ml) was added. The organic layer was separated and washed neutral with water. The solvent was removed under reduced pressure and the residue was distilled, affording 110 mg (92%) of decalone **13**: bp 70–75° (0.5 mm); ir (liquid film) 2120 (C–D), 1703 (C=O), 1290, 1178, 1110, 1025, 993, 958, 912, 830 cm^{-1}; NMR ($CDCl_3$) δ 0.87, 0.91, 1.00, 1.16, 1.20 (s, 3 each; mass spectrum *m/e* (rel intensity) 223 (M^+, 8), 208 (5), 151 (100), 123 (18), 69 (17), 55 (11), 41 (19).

Identical treatment of ketone **12** with sodium methoxide in methanol gave only recovered starting material.

2,2,8,8,10(*S*)-Pentamethyl-*trans*-decal-*cis*-1(*R*)-ol (16). Under a nitrogen atmosphere was charged lithium aluminum hydride (200 mg, 5 mmol) and anhydrous ether (20 ml). Ketone **12** (1.1 g, 5 mmol) dissolved in ether (5 ml) was then added over 5 min and the mixture was allowed to reflux for 0.5 hr. The mixture was cooled and water (0.4 ml) was carefully added, followed by 10% aqueous sodium hydroxide (0.4 ml). After an additional 2 hr the mixture was filtered and the solvent was removed under reduced pressure. The residue was distilled, affording 1.05 g (94%) of decalol **16** contaminated (by VPC) with 5% of the isomeric decalol **15**: bp 80–85° (0.5 mm); $n^{20}D$ 1.4919; $[\alpha]^{25}D$ +19° (neat); ir (liquid film) 3730 (nonbonded OH), 3570 (bonded OH), 1085, 1032, 1020, 985, 968, cm^{-1}; NMR ($CDCl_3$) δ 0.92 (s, 3), 0.95, 1.23 (s, 6 each), 3.66 (d, *J* = 4 Hz, 1).

Anal. Calcd for $C_{15}H_{28}O$: C, 80.29; H, 12.58. Found: C, 80.29; H, 12.55.

8(*S*)-Hydroxymethyl-2,2,8,10(*S*)-tetramethyl-*trans*-decal-*trans*-1(*S*)-ol (9). A solution of olefin **2** (15.3 g, 75 mmol) and 75 ml (75 mmol) of a 1 *M* solution of diborane in tetrahydrofuran was stirred under nitrogen at 25° for 18 hr. Anhydrous diglyme (75 ml) was then added and the tetrahydrofuran was removed by distillation. The solution was then heated at 160° for 3 hr. The solution was cooled, and water (5 ml) was carefully added, followed by 10% aqueous sodium hydroxide (35 ml) and 35% hydrogen peroxide (35 ml). After stirring for 2 hr at 30° the mixture was filtered. Water (250 ml) was added and the mixture was well extracted with hexane. The hexane extracts were washed with water and the solvent was removed under reduced pressure. Crystallization of the residue from hexane afforded 10.6 g (59%) of diol **9**: mp 148–150°; $[\alpha]^{25}D$ +7° (*c* 0.1, $CHCl_3$); ir (KBr) 3230 (OH), 1060, 1030, 1008 cm^{-1}; ir (KBr) 3230 (OH), 1060, 1030, 1008 cm^{-1}; NMR ($CDCl_3$) δ 0.91, 1.01, 1.14, 1.26 (s, 3 each), 3.45 (d, *J* = 10.5 Hz, 1), 2.94, 3.73 (AB, *J* = 11.5 Hz, 2), 3.85 (s, 1, OH); mass spectrum *m/e* (rel intensity) 222 (M − 18, 1), 109 (35), 95 (26), 81 (38), 67 (35), 55 (60), 43 (66), 41 (100).

Anal. Calcd for $C_{15}H_{28}O_2$: C, 74.95; H, 11.74. Found: C, 75.08; H, 11.99.

Chromatography of the crystallization residue on silica did not separate the minor diol **10** from the remaining major diol **9**.

2a*β*,5a*β*,8,8-Tetramethyl-8a*βH*,8b*αH*-decahydronaphtho[1,8-*bc*]furan (7). A sample of diol **9** (5.0 g, 20.8 mmol), *p*-toluenesulfonic acid (0.8 g), and benzene (100 ml) was allowed to reflux with a water separator for 2.5 hr. The cooled solution was washed once with sodium bicarbonate solution and the solvent was removed under reduced pressure. Distillation of the residue afforded 4.2 g (91%) of ether **7**: by 70–72° (0.3 mm); $n^{20}D$ 1.4872; $[\alpha]^{25}D$ +27° (neat); ir (liquid film) 1070, 1049, 1039, 971 cm^{-1}; NMR ($CDCl_3$) δ 0.87, 1.01, 1.07, 1.14 (s, 3 each), 3.67 (d, *J* = 11.5 Hz, 1), 3.47, 3.53 (AB, *J* = 8 Hz, 2); mass spectrum *m/e* (rel intensity) 222 (M^+, 22), 208 (15), 151 (100), 123 (39), 109 (68), 95 (68), 81 (58), 67 (40), 55 (54), 43 (50), 41 (77).

Anal. Calcd for $C_{15}H_{26}O$: C, 81.02; H, 11.79. Found: C, 80.94; H, 12.05.

2a*β*,5a*β*,8,8,-Tetramethyl-8a*αH*,8b*βH*-decahydronaphtho[1,8-*bc*]furan (8). A sample (4.5 g) of the mother liquors from crystallization of diol **9** was treated as above with *p*-toluenesulfonic acid (0.7 g) in benzene (90 ml). The isolated crude mixture (4 g) was chromatographed on 60 g of silica. Early fractions eluted with 5% ether in hexane afforded a pure sample of the ether **7** described above. Continued elution with 5% ether in hexane afforded a pure sample of ether **8**. After recrystallization from hexane at 0°, ether **8** exhibited the following properties: mp 84–86°; $[\alpha]^{25}D$ +2.5° (*c* 0.1, $CHCl_3$); ir (KBr) 1030, 995, 933, 923, 852, 800 cm^{-1}; NMR ($CDCl_3$) δ 0.89, 0.92 (s, 3), 1.05 (s, 6), 3.28, 3.48 (AB, *J* = 7.5 Hz, 2), 3.61 (d, *J* = 9 Hz, 1); mass spectrum *m/e* (rel intensity) 222 (M^+, 10), 207 (12), 177 (29), 151 (100), 109 (22), 95 (33), 81 (23), 55 (26), 41 (36).

Anal. Calcd for $C_{15}H_{26}O$: C, 81.02; H, 11.79. Found: C, 80.98; H, 12.01.

Determination of the Ratio of Ethers 7 and 8 from the High-Temperature Hydroboration of 2. The hydroboration procedure outlined above for the isolation of diol **9** was run on one-tenth the scale. The crude product was then treated with *p*-toluenesulfonic acid (0.1 g) in benzene (25 ml) at reflux with a water separator for 3.0 hr. The cooled solution was washed with sodium bicarbonate solution and the solvent was removed under reduced pressure. Distillation of the residue afforded 1.40 g of mobile oil, bp 70–75° (0.3 mm). Analysis by VPC showed two components, identified as ether **7** (88%) and ether **8** (12%). The hydroboration reaction thus occurs principally from the α face of olefin **2**.

Reduction of 2. A sample of olefin **2** (20.6 g, 0.1 mol), acetic acid (90 g), and platinum oxide (200 mg) was charged into a Parr shaker and heated at 75° under 55 lb of hydrogen pressure for 3 hr. No hydrogen uptake was observed during this time. The mixture was cooled and filtered, then added to water (200 ml) and well extracted with hexane. The organic extracts were washed with sodium bicarbonate solution and the solvent was removed under reduced pressure, affording 20.5 g of recovered olefin **2**.

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Registry No.—**2**, 32540-36-6; **3**, 54689-00-8; **4**, 54713-02-9; **7**, 54689-01-9; **8**, 54713-03-0; **9**, 54689-02-0; **11**, 54724-65-1; **12**, 54689-03-1; **13**, 54713-04-1; **14**, 54689-04-2; **15**, 54689-05-3; **16**, 54689-06-4; peracetic acid, 79-21-0; potassium permanganate, 7722-64-7; sodium dichromate, 10588-01-9; diborane, 19287-45-7; *m*-chloroperbenzoic acid, 937-14-4.

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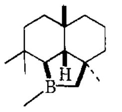

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Addition of Aryl Nitrenes to Olefins[1]

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Pentafluoronitrosobenzene undergoes an "ene"-type reaction with a variety of olefins. When triethyl phosphite is added to the olefin *before* the addition of the nitroso compound (inverse addition), pentafluorophenylnitrene is formed which adds stereospecifically to a number of olefins to give the corresponding aziridines. The possibility of a 1,3-dipolar addition of the nitrene precursor followed by elimination of triethyl phosphate has been discounted. Pentafluorophenylnitrene, generated photochemically from the azide, behaves analogously, but thermal decomposition of the azide in the presence of olefins gives products arising from an initial 1,3-dipolar adduct. 4-Azidotetrachloropyridine behaves similarly but the derived nitrene is less electrophilic.

Authenticated examples of the addition of thermally generated discrete nitrenes to olefinic bonds to give aziridines have appeared infrequently in the literature, since azides, the usual nitrene precursors, themselves react with aliphatic multiple bonds at temperatures generally lower than those required to generate the corresponding free nitrene.[2] The issue is further complicated by the fact that the 1,2,3-triazolines thus produced may subsequently lose nitrogen to give the same aziridines as would be expected from nitrene addition.[3]

The addition of ethoxycarbonylnitrene, generated by photolysis of ethyl azidoformate at ambient temperature, to olefins to give *N*-carbethoxyaziridines has been studied extensively.[4] It was shown that both singlet and triplet nitrene added to the olefin but that only the singlet species added stereospecifically.[5] Addition of triplet nitrene occurred via a 1,3-diradical intermediate which resulted in stereochemical scrambling. Addition to conjugated dienes is usually in the 1,2 manner,[5] rather than 1,4 manner,[6] except in certain cases such as the additions to pyrroles or to thiophenes, e.g., the additions of *N*-carbethoxynitrene to pyrroles or to thiophenes,[7a] or those which proceed via a triplet diradical, e.g., the addition of cyanonitrene to cyclooctatetraene.[7b]

Evidence for the direct addition of aryl nitrenes to olefins is scanty, there being only one clear-cut example, that of aziridine formation during the photolysis of ferrocenyl azide in cyclohexene.[8] Formation of 1,2,3-triazolines in the thermal reaction of aryl azides with olefins or acetylenes is well known,[3,9] as is the reaction with certain other unsaturated species, such as enol ethers[10] and enamines.[11] With highly polarized double bonds such as these, the addition is usually regiospecific.

We have previously shown that pentafluorophenylni-