

Our results agree with those of Dewar,⁹ who also found the syn migration to be favored over the anti migration. In contrast, the triplet-triplet conversion was found to be slightly preferred by least motion considerations.⁷ It seems therefore that the rearrangement is non-least-motion-controlled.

Conclusions

Our results were arrived at by a limited optimization procedure regarding the geometries of the various C_2H_4 species under consideration. A complete optimization of these and in particular the transition-state geometries could change the relative energies by several kcal/mol. This is not expected to influence the overall stereochemical consequences of the rearrangement which involves the *relative ordering* of the energies of the individual species. On the other hand, since optimization generally lowers the energy, it is likely that the barriers to the migrations would decrease substantially. Consequently, the barrier to the preferred syn mode should be regarded as an upper limit, bearing in mind that the reaction is known to be extremely facile.

As for methylcarbene, it was shown that increasing the basis set results in the decrease of the singlet-triplet separation from 21.6 kcal/mol to approximately zero. A very recent, and probably one of the most refined, theoretical studies of methylene, by Bender, *et al.*,¹⁶ resulted in similar conclusions. In our case this decrease warrants caution in the assignment of the ground electronic state. It is suggested that methylcarbene

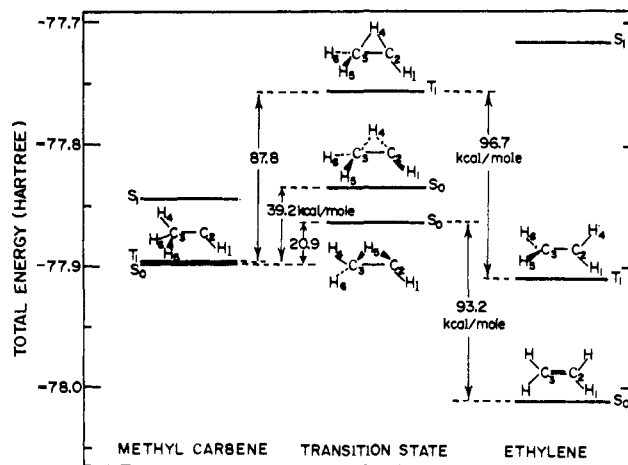


Figure 6. A summary of thermodynamic and kinetic stabilities of selected low-lying states of various C_2H_4 species.

most probably has a singlet ground state, with the reservation that for a better understanding of the (S_0 - T_1) spacing a complete study of the energy surface is necessary.

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Stereochemistry of the Thermal Addition of β -Pinene to Maleic Anhydride

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Abstract: Two stereochemical aspects of the thermal ene reaction between β -pinene and maleic anhydride have been investigated, the configuration of the allylic hydrogen transferred in the reaction and the preference for endo *vs.* exo orientation. Two routes are described to a stereospecifically labeled β -pinene in which the C-3 hydrogen trans to the *gem*-dimethyl bridge is replaced by deuterium. Use of this material in ene reactions with maleic anhydride and dimethyl acetylenedicarboxylate showed that $95 \pm 5\%$ of the deuterium is transferred. Determination of the absolute configuration at the new asymmetric center in the adduct as *R*, by degradation to (*S*)-(+)-3-methylpentanoic acid, revealed that the major adduct is **2b**, formed by endo addition. Of four possible transition-state orientations A-D, C is established as the preferred pathway.

The thermal addition of an alkene to another olefin possessing an allylic hydrogen, the so-called "ene" reaction, is one of the simplest reactions of organic chemistry.¹ Though radical² and other mechanisms³ have been advanced, the addition is usually considered to proceed in a symmetry-allowed concerted process^{4,5}

(1) For reviews, see (a) H. M. R. Hoffmann, *Angew. Chem.*, **81**, 597 (1969); (b) E. C. Keung and H. Alper, *J. Chem. Educ.*, **49**, 97 (1972).

(2) H. A. Chia, B. E. Kirk, and D. R. Taylor, *Chem. Commun.*, 1144 (1971).

(3) C. Agami, M. Andrac-Taussig, and C. Prevost, *Bull. Soc. Chim. Fr.*, 173 (1966); C. Agami, M. Andrac-Taussig, C. Justin, and C. Prevost, *ibid.*, 1195 (1966).

via a six-membered cyclic transition state (eq 1), unless prohibited by steric factors.⁶ Consistent with the concerted mechanism are two important stereochemical observations: (a) the new C-C and C-H bonds are formed *cis*,⁷ and (b) asymmetric induction occurs in the adduct

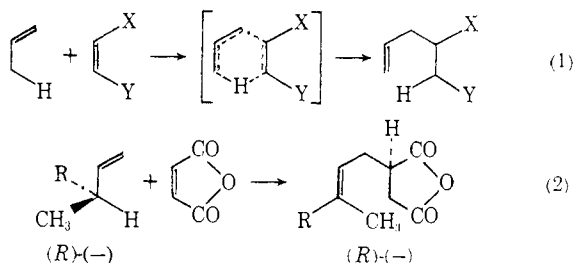
(4) R. T. Arnold and J. F. Dowdall, *J. Amer. Chem. Soc.*, **70**, 2590 (1948).

(5) S. Dai and W. R. Dolbier, Jr., *J. Amer. Chem. Soc.*, **94**, 3953 (1972).

(6) J. Lambert and J. J. Napoli, *J. Amer. Chem. Soc.*, **95**, 294 (1973).

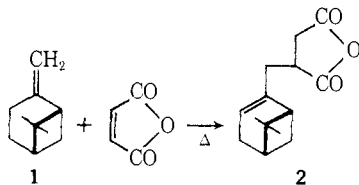
(7) (a) K. Alder and H. von Brachel, *Justus Liebigs Ann. Chem.*, **651**, 141 (1962); (b) L. E. Friedrich, J. A. Kampmeier, and M. Good, *Tetrahedron Lett.*, 2783 (1971).

when the hydrogen transferred is initially attached to a chiral center⁸ (eq 2); the configuration of the products



indicates that the reactants are oriented so as to minimize steric repulsions in the transition state. Moreover, endo addition has been shown to predominate over exo in several cases investigated,⁹ though sometimes by only a small factor.

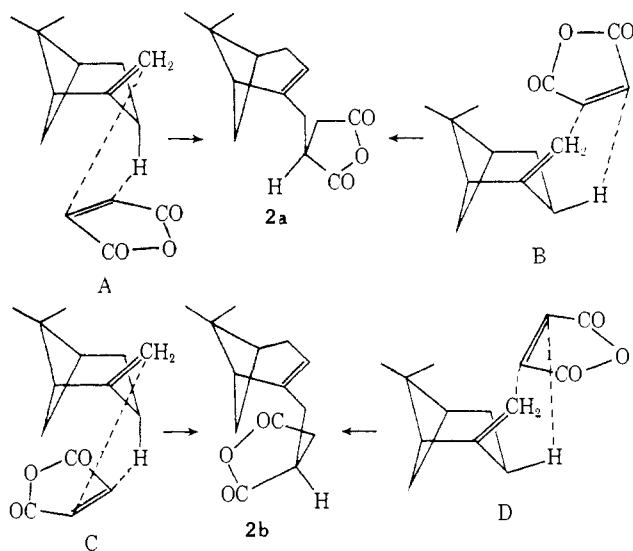
β -Pinene (**1**) is a particularly reactive olefin in ene reactions;¹⁰ the fact that it forms adducts without skeletal rearrangement was taken as evidence against the intervention of cationic or radical intermediates. Arnold and Showell reported¹⁰ that the thermal reaction between β -pinene and maleic anhydride yielded a 3:1 mixture of diastereomeric adducts of structure **2**;



the major adduct could be isolated in pure form by recrystallization.

Four basic stereochemical orientations are possible for the transition state in a concerted addition leading to **2** (Scheme I). Transition states A and C involve the

Scheme I



transfer of the allylic hydrogen trans to the *gem*-dimethyl bridge, while in B and D the hydrogen cis to the bulkier bridge is transferred. A and D represent exo

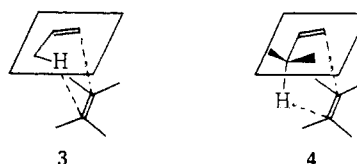
(8) R. K. Hill and M. Rabinovitz, *J. Amer. Chem. Soc.*, **86**, 965 (1964).

(9) J. A. Berson, R. G. Wall, and H. D. Perlmutter, *J. Amer. Chem. Soc.*, **88**, 187 (1966).

(10) R. T. Arnold and J. S. Showell, *J. Amer. Chem. Soc.*, **79**, 419 (1957).

addition while B and C involve endo orientation of the addends. It will be noted that using (1*S*,5*S*)-1-(-)- β -pinene (depicted), transition states A and B lead to adduct **2a**, in which the new asymmetric center on the anhydride ring has the *S* configuration, while C and D would afford the diastereomer **2b**, with the new asymmetric center *R*.

We undertook to sort out which of these four possible transition states are involved in the formation of the two adducts and which represents the major pathway. The answers to these questions might illuminate two stereochemical aspects of the ene addition: (a) they would provide an independent test of the preference for endo *vs.* exo orientation, and (b) they might answer the more subtle question of the preferred conformation of the allylic C-H bond. Is there a preference for this bond to lie parallel with the double bond, as in **3**, analogous to the cisoid diene conformation in the Diels-Alder addition, or conversely as in **4**, per-



pendicular to the double bond, so that the p orbital which develops as the C-H bond is broken is generated parallel to the existing π orbitals?

Most authors who have considered this question favor **4** on theoretical grounds,^{11,6,12} but there is so far no experimental evidence available.¹³ The difficulty in providing an experimental test is, of course, that of finding an alkene in which the allylic hydrogens are rigidly fixed as in **3** or **4** and which still takes part in ene reactions. β -Pinene is almost such a molecule. In its most stable chair conformation (shown in Scheme I), the allylic C-H bond at C-3 cis to the *gem*-dimethyl bridge is equatorial and consequently roughly parallel to the double bond, while the other C-H bond at C-3 is axial and approximately perpendicular to the double bond. Thus transition states A and C have the chair-like perpendicular conformation **4**, while transition states B and D have the boat-like parallel conformation **3**. It is obvious that this experiment would not provide a rigorous argument, first because β -pinene is not a rigid molecule and may not necessarily react in the most stable conformation, and secondly because transition states B and D are hindered by the bulky *gem*-dimethyl bridge which blocks the top face of the double bond. Nevertheless, a strong stereoelectronic preference for conformation **3** might be detected despite steric hindrance, and it appeared worthwhile to ascertain unambiguously which hydrogen is transferred.

Experimentally, then, the distinction among transition states A-D can be made by determining (1) whether the equatorial or axial hydrogen at C-3 of β -pinene is transferred to maleic anhydride and (2) the absolute configuration at the new asymmetric center in the adduct.

(11) J. H. Brewster, *J. Amer. Chem. Soc.*, **81**, 5491 (1959).

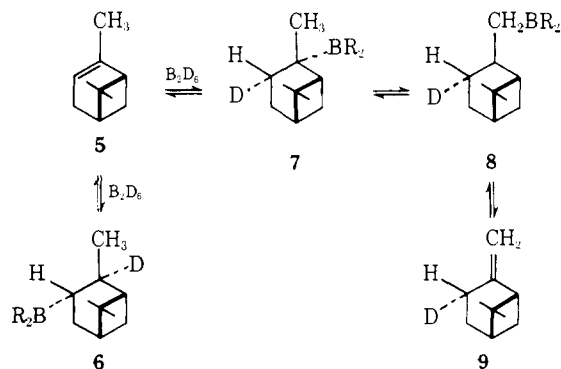
(12) T. C. Gilchrist and R. C. Storr, "Organic Reactions and Orbital Symmetry," Cambridge University Press, Cambridge, 1972, pp 241-243.

(13) For evidence that allylic C-C bond cleavage favors the "perpendicular" conformation, see J. A. Berson and R. S. Wood, *J. Amer. Chem. Soc.*, **89**, 1043 (1967).

Which Allylic Hydrogen Is Transferred? Stereo-specific labeling at C-3 is required to answer this question. Two methods were found to introduce a deuterium specifically trans to the *gem*-dimethyl bridge.

(i) Brown and coworkers¹⁴ have shown that the reversibility of the hydroboration reaction may be used to isomerize olefins to the terminal isomer; among many examples reported was the isomerization of α -pinene to β -pinene. The use of B_2D_6 in this reaction leads to a specifically deuterated β -pinene, as shown in Scheme II.

Scheme II

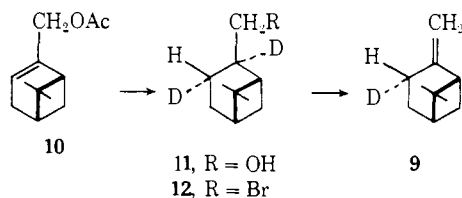


Since the normal addition of diborane to α -pinene (**5**) takes place *cis* from the less hindered face of the double bond¹⁵ to give **6**, so should addition in the reverse direction, affording **7**. Isomerization to **8** and exchange to **9** leave the deuterium trans to the bulkier bridge.

Specifically deuterated β -pinene was successfully prepared by this method, though the maximum amount of deuterium introduced was 55%. Since all reagents were carefully dried, the low deuterium content is probably due, not to adventitious water, but to the fact that the exchange of **7** with **8** and of **6** with δ -pinene generates diborane containing B-H bonds which then competes with B_2D_6 . This would seem to constitute an inherent limitation to the use of this method for deuterium labeling.

(ii) A route which gave higher deuterium content began with reduction of myrtenyl acetate (**10**) with deuterated diimide, followed by hydrolysis to a dideuterated *cis*-myrtenol (**11**) (Scheme III). Diimide is

Scheme III



known to deliver hydrogen *cis* to α -pinene from the less hindered face of the double bond,¹⁶ so this fixes the configuration of the deuterium atoms in **11** as shown. Conversion to bromide **12** and dehydrobromination gave labeled β -pinene **9**, this time containing 81% d_1 by mass spectroscopy. When reduction with D_2 over Adams' catalyst was substituted for diimide reduction,

(14) H. C. Brown, M. V. Bhatt, T. Munekata, and G. Zweifel, *J. Amer. Chem. Soc.*, **89**, 567 (1967).

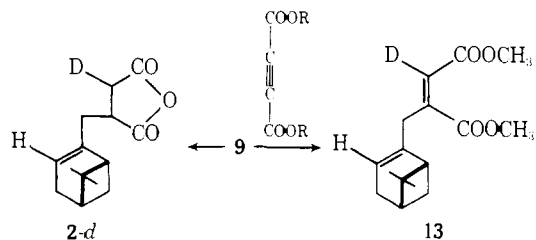
(15) G. Zweifel and H. C. Brown, *J. Amer. Chem. Soc.*, **86**, 393 (1964).

(16) E. E. van Tamelen and R. J. Timmons, *J. Amer. Chem. Soc.*, **84**, 1067 (1962).

extensive exchange occurred, leading to β -pinene containing 14% d_0 , 43% d_1 , 34% d_2 , and 9% d_3 .

Determination of whether hydrogen or deuterium is transferred in the reaction of **9** with maleic anhydride was easily accomplished by nmr analysis of the crystalline adduct **2**. The vinyl hydrogen appearing in the spectrum of the unlabeled adduct as a multiplet at δ 5.4 was still present in the adduct from **9**. Integration showed that $95 \pm 5\%$ of the deuterium present in **9** was transferred to the anhydride.

It is difficult to detect the deuterium transferred to the anhydride ring in the multiplet region between δ 2.0 and 3.4, because of the subsequent exchange (see ref 7b and below). Consequently, a second adduct was investigated, that formed with dimethyl acetylenedicarboxylate, in which only a single isomer can be formed and the hydrogen transferred is nonexchangeable. The nmr spectrum of adduct **13**, formed from 81% deu-



terated β -pinene, showed 0.95 ± 0.05 vinyl proton at δ 5.4 (pinene double bond) and 0.24 ± 0.05 vinyl proton at δ 5.8 (maleate double bond), proving again that $94 \pm 6\%$ of the deuterium is transferred to the enophile.

These results establish conclusively that in ene reactions of β -pinene with at least these two enophiles, the allylic hydrogen trans to the *gem*-dimethyl bridge is transferred exclusively, within experimental error. Arnold has recently found the same result for the addition of β -pinene to benzyne and to α -keto esters.¹⁷ This result is consistent both with the expectation⁸ that orientation should minimize steric repulsions in the transition state and with a preference for breaking that C-H bond perpendicular to the double bond, and it will require further experiments to differentiate between these two factors.

Configuration at the New Asymmetric Center. The results above rule out transition states B and D for the β -pinene-maleic anhydride addition. To distinguish between the remaining two possibilities A and C it is necessary to elucidate the absolute configuration at the new asymmetric center in the anhydride ring.

The major diastereomeric adduct, mp 92-94°, was first reduced with lithium aluminum hydride to diol **14** (Scheme IV) to eliminate immediately any possibility of epimerization during subsequent reactions. Conversion to the tosylate **15** and another hydride reduction gave hydrocarbon **16**.

The aim now was to destroy the two asymmetric centers in the pinenyl portion of **16**, leaving only the side chain asymmetric center which could then be related to a simple compound of known configuration. Attempts to degrade **16** by oxidation did not afford clean products. Photolysis of **16** in toluene, however, effected the slow formation of a mixture of two isomers,

(17) (a) R. T. Arnold and V. Garsky, Abstracts, 163rd National Meeting of the American Chemical Society, Boston, Mass., Apr 9-14, 1972, ORGN-107; (b) V. Garsky, D. F. Koster, and R. T. Arnold, *J. Amer. Chem. Soc.*, **96**, 4207 (1974).

assigned structures **17** and **18**. Hydrocarbon **17** showed characteristic absorption for a vinyl group in both the nmr and ir spectra, gave an ir spectrum similar to that of ocimene (**20**), and had a uv spectrum (λ_{\max} 236 nm (ϵ 16,450)) nearly identical with that of ocimene (λ_{\max} 237 nm (ϵ 16,400)). Isomer **18** showed λ_{\max} 280 nm, comparable to the major uv absorption band of alloocimene (**21**) at 277 nm, and undoubtedly results from thermal 1,5-hydrogen transfer of **17** just as alloocimene is formed from ocimene. A close parallel to this photoisomerization may be found in the conversion of α -pinene to ocimene by sensitized or nonsensitized photolysis.¹⁸

The photochemical cleavage of the pinene ring greatly facilitated the configurational correlation, since ozonolysis of the photolysis mixture led directly to (*S*)-(+)-3-methylpentanoic acid (**19**), identified by comparison with an authentic sample. The acid showed $[\alpha]_D +5.55$ in benzene, gave a dextrorotatory amide, and was calculated to be 92% optically pure. Since (*R*)-(-)-3-methylpentanoic acid has been correlated with (*R*)-(+)-2-methyl-1-butanol¹⁹ via 2-methylbutanoic acid,²⁰ the *S* configuration of the dextrorotatory degradation product is secured. The adduct from which it is formed must then have the *R* configuration at the chiral center on the anhydride ring. This degradation establishes that the major crystalline adduct from the ene reaction is **2b**, and that the preferred transition-state geometry in adduct formation is the endo orientation C. The 3:1 ratio favoring endo addition agrees with the earlier results of Berson.⁹

Before this conclusion can be finally accepted, it is necessary to show that the 3:1 diastereomer ratio found by Arnold and Showell¹⁰ is a kinetically, not thermodynamically, controlled ratio. That the latter possibility is real is shown by previous reports of thermal isomerization of substituted succinic anhydrides, e.g., methylsuccinic anhydride is 70% racemized in 24 hr in refluxing *o*-dichlorobenzene,⁸ and a 4:1 mixture of the meso and racemic isomers of 2,3-diethylsuccinic anhydride is isomerized²¹ to a 4:10 mixture on heating to 165°. Normally the conditions of the ene addition do not bring about complete stereomutation.^{7b,8,9} We have tested this point in the present case by following the mutarotation of the pure adduct **2b** in refluxing xylene, the conditions of its formation. The results, summarized in Table I, lead to two conclusions: (i) thermal isomerization does occur, but the degree of mutarotation is fairly slight during the time of the addition reaction (about 12% decrease in optical rotation in 22 hr); (ii) the product mixture obtained after 20 hr cannot be an equilibrium mixture, since the rotation continues to decrease for 100 hr. Nmr spectra indicate that no gross structural change has occurred during this time. We conclude that the 3:1 ratio of adducts isolated after 20 hr is clearly not an equilibrium mixture,

(18) (a) R. Mayer, K. Bochow, and W. Zieger, *Z. Chem.*, **4**, 348 (1964); (b) W. F. Erman, *J. Amer. Chem. Soc.*, **89**, 3828 (1967); (c) G. Frank, *J. Chem. Soc. B*, 130 (1968); (d) P. J. Kropp, *J. Amer. Chem. Soc.*, **91**, 5783 (1969).

(19) K. Freudenberg and J. Geiger, *Justus Liebigs Ann. Chem.*, **575**, 145 (1952); K. Freudenberg and W. Hohmann, *ibid.*, **584**, 54 (1953).

(20) (a) Conversion of (-)-2-methylbutanoic acid to (-)-3-methylpentanoic acid: K. B. Wiberg and T. W. Hutton, *J. Amer. Chem. Soc.*, **78**, 1640 (1956); K. J. Sax and W. Bergmann, *ibid.*, **77**, 1910 (1955). (b) Oxidation of (-)-2-methyl-1-butanol to (+)-2-methylbutanoic acid: J. Brenner and K. Mislow, *J. Org. Chem.*, **21**, 1312 (1956).

(21) K. Nagarajan, C. Weissmann, H. Schmid, and P. Karrer, *Helv. Chim. Acta*, **46**, 1222 (1963).

Table I. Mutarotation of **2b** in Refluxing Xylene

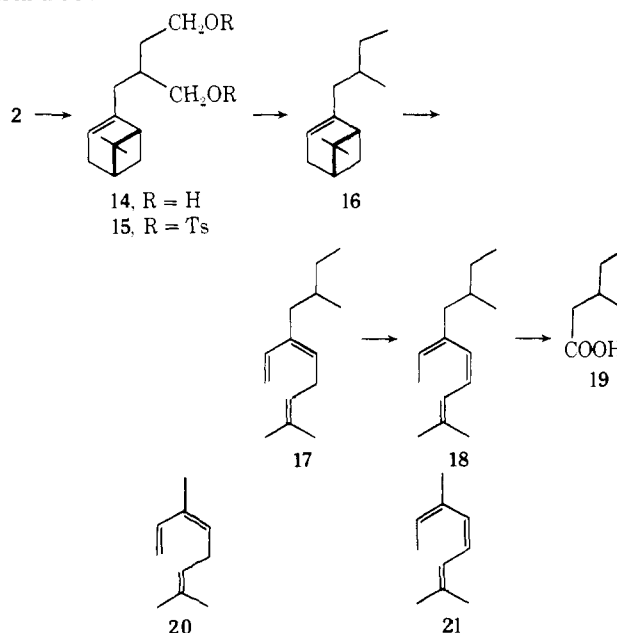
Time, hr	$[\alpha]^{25}_D$, deg
0	-59.4
5	-57.5
10	-56.1
22	-52.5
33	-51.6
48	-50.3
74	-42.7
99	-37.7

but neither is it exactly the kinetically controlled ratio; the ratio of rates of formation of endo (**2b**) and exo (**2a**) adducts is apparently somewhat greater than 3:1.

Experimental Section

Melting points were determined in a Thomas-Hoover oil immersion apparatus and are uncorrected. Ultraviolet spectra were recorded on a Cary 14 spectrophotometer. Nuclear magnetic resonance spectra were obtained on Varian A-60 and HR-100 instruments; we acknowledge the assistance of Mr. Courtney Pape. Chemical shifts are recorded in ppm (δ), with tetramethylsilane as an internal standard. Infrared spectra were recorded on a Perkin-Elmer Model 237B spectrophotometer. Specific rotations were obtained on Perkin-Elmer Model 141 and Rudolph polarimeters using a 1-dm cell; chloroform was the solvent unless otherwise specified. Elemental analyses were performed by Galbraith Micro-analytical Laboratories, Knoxville, Tenn., and Spang Micro-analytical Laboratories, Ann Arbor, Mich.

Scheme IV



Hydroboration-Isomerization of α -Pinene. The reaction was carried out according to the general procedure of Brown.¹⁴ In a 100-ml flask fitted with a distillation column were placed 6.8 g (50 mmol) of α -pinene, $[\alpha]^{25}_D +28.8^\circ$ (*c* 2.08), 570 mg of lithium aluminum deuteride (99%), and 15 ml of triglyme. The flask and the apparatus were flushed with nitrogen and a static nitrogen pressure was maintained throughout the reaction. Hydroboration was achieved by adding 5.5 ml of a 3.65 *M* solution of boron trifluoride triglymate²² to the well-stirred reaction mixture at room temperature. The reaction mixture was heated to 155–160° and maintained at this temperature for 3 hr. After completion of the isomerization, 17 g (100 mmol) of 1-dodecene was added and the heating continued at 160°. The displaced β -pinene (**9**) was removed by distillation under reduced pressure over 7 hr. Gas chromatography

(22) H. C. Brown and G. Zweifel, *J. Amer. Chem. Soc.*, **83**, 1241 (1961).

graphic analysis of the distillate (3.5 g) showed 86% β -pinene and 14% α -pinene. Preparative gas chromatography was utilized to separate the β -pinene from the mixture; ir (film) 2167 cm^{-1} (C-D); m/e 137, 55% d_1 .

β -Pinene Oxide. To a mixture of 42.5 g (0.31 mol) of β -pinene and 100 g of powdered, anhydrous sodium carbonate in 400 ml of methylene chloride, kept stirred in an ice-water bath, was added dropwise 65.3 ml (0.34 mol) of 40% peracetic acid containing a small amount of sodium acetate. The mixture was stirred at room temperature until the solution gave a negative test with starch-iodide paper. The solid salts were removed by suction filtration and washed well with additional methylene chloride. The solvent was removed on a rotary evaporator and the residue was distilled under vacuum: bp 64–66° (4.2 mm), lit.²³ bp 98–99° (33 mm); yield 37.1 g (78%); $[\alpha]_D^{25} +4.8^\circ$ (c 1.9), lit.²³ $[\alpha]_D^{16} +2.9^\circ$; ir (film) 1200, 900, 815, 770 cm^{-1} ; nmr (CDCl_3) δ 2.71–2.49 (q, 2 H, $J = 11.5$ and 5 Hz), 2.44–1.40 (m, 8 H), 1.27 (s, 3 H), 0.94 (s, 3 H).

Myrtenol. To a solution of 36.6 g (0.5 mol) of diethylamine in 500 ml of anhydrous ether, cooled in an ice-water bath, was added 270 ml (0.5 mol; 1.85 M solution in ether) of methylithium under a nitrogen atmosphere. After 10 min a solution of 30.4 g (0.2 mol) of β -pinene oxide and 1500 ml of anhydrous ether was added and the mixture was heated to reflux for 2 days.²⁴ The reaction mixture was cooled and poured into water, and the organic layer separated. The aqueous layer was extracted with ether and the combined organic layers were washed with 1 N hydrochloric acid, saturated sodium bicarbonate solution, and water. After drying over anhydrous magnesium sulfate the solvent was removed on a rotary evaporator and the residue was fractionated under vacuum: bp 62–64° (0.4 mm), lit.²⁵ bp 95–97° (11 mm); yield 24.7 g (81%); $[\alpha]_D^{25} -50.6^\circ$ (c 1.5), lit.²⁵ $[\alpha]_D^{20} -45.8^\circ$ (c 2.0); ir (film) 3330, 1660, 800 cm^{-1} ; nmr (CDCl_3) δ 5.48–5.32 (m, 1 H), 3.9 (s, finely split, 2 H), 3.26 (s, 1 H), 2.5–2.0 (m, 5 H), 1.31 (s, 3 H), 1.16 (d, 1 H, $J = 8.5$ Hz), 0.86 (s, 3 H).

Myrtenyl Acetate (10). A solution of 7 g of myrtenol in 50 ml of acetic anhydride and 100 ml of pyridine was heated to reflux for 24 hr. Excess acetic anhydride and pyridine were removed by distillation. The residue was diluted with water and extracted with ether. The ether extract was washed with water and dried over anhydrous magnesium sulfate. The solvent was removed on a rotary evaporator and the residue was distilled under vacuum: bp 50–51° (0.15 mm), lit.²⁶ bp 110–112° (10 mm); $[\alpha]_D^{25} -54^\circ$ (c 2.97); yield 8.4 g (94%); ir (film) 1745, 1660, 800 cm^{-1} ; nmr (CDCl_3) δ 5.62–5.46 (m, 1 H), 4.44 (s, 2 H), 2.54–2.04 (m, 5 H), 2.03 (s, 3 H), 1.30 (s, 3 H), 1.18 (d, 1 H, $J = 8.5$ Hz), 0.84 (s, 3 H).

$2\alpha,3\alpha$ -Dideuterio-*cis*-myrtenol (11). To a solution of 2.328 g (0.012 mol) of myrtenyl acetate (10) and 46.56 g (0.24 mol) of dipotassium azodicarboxylate²⁷ in 70 ml of ethanol- d_1 was added 20 g of acetic acid- d_1 in 20 ml of ethanol- d_1 over a period of 1.5 hr. After the mixture was stirred at room temperature for 12 hr, 10.5 g of acetic acid- d_1 in 10 ml of ethanol- d_1 was added dropwise in 1 hr. The reaction mixture was stirred at room temperature for 20 hr. After removing most of the ethanol by distillation, the residue was diluted with water and extracted with ether. The ether extract was washed successively with sodium bicarbonate solution and water and dried over anhydrous magnesium sulfate. The solvent was removed on a rotary evaporator and the residue (2.4 g) was hydrolyzed by refluxing in 150 ml of 1 N methanolic potassium hydroxide solution for 4 hr. The reaction mixture was then diluted with water and extracted with ether. The ether extract was washed with water and dried over anhydrous magnesium sulfate. The solvent was removed on a rotary evaporator. Gas chromatographic analysis of the product showed 20% *cis*-myrtenol and 80% myrtenol. Preparative gas chromatography was utilized to separate the *cis*-myrtenol from the unreacted myrtenol. The *cis*-myrtenol¹⁵ isolated was identical (ir and vpc retention time) with an authentic sample: bp 89–91° (2.2 mm); $[\alpha]_D^{25} -19.5^\circ$ (c 1.68), prepared in 91% yield by hydrogenation of myrtenol over a platinum catalyst.

In a small scale (2 mmol) preparation using a large excess (60

mmol) of dipotassium azodicarboxylate 45% reduction was achieved.

$2\alpha,3\alpha$ -Dideuterio-*cis*-myrtenyl Bromide (12). To a solution of 750 mg (2.86 mmol) of triphenylphosphine in 3 ml of acetonitrile, cooled in an ice-water bath, was added 460 mg (2.56 mmol) of bromine in 2 ml of acetonitrile in 10 min. The ice-water bath was then removed and a solution of 400 mg (2.56 mmol) of $2\alpha,3\alpha$ -dideuterio-*cis*-myrtenol was added in 10 min. After the addition was complete the reaction mixture was heated to reflux for 1 hr. Acetonitrile was removed by distillation, warm pentane was added to the residue, and the mixture was filtered. The residue was washed several times with warm pentane and filtered to remove the triphenylphosphine oxide. The combined filtrate was concentrated on a rotary evaporator to give 390 mg of $2\alpha,3\alpha$ -dideuterio-*cis*-myrtenyl bromide. Gas chromatographic analysis of the product showed essentially pure bromide.

When the same procedure was applied to unlabeled *cis*-myrtenol, the bromide was obtained in 66% yield: bp 75–77° (5 mm), lit.²⁸ bp 94° (14 mm); nmr (CDCl_3) δ 3.38 (d, $J = 8$ Hz, 2 H), 1.24 (s, 3 H), 1.02 (s, 3 H).

Dehydrobromination of $2\alpha,3\alpha$ -Dideuterio-*cis*-myrtenyl Bromide. A solution of 390 mg of $2\alpha,3\alpha$ -dideuterio-*cis*-myrtenyl bromide and 700 mg of 1,5-diazabicyclo[3.4.0]nonene-5 in 3 ml of xylene was heated under reflux for 2 days. The reaction mixture was cooled, poured into cold 1 N sulfuric acid, and extracted with ether. The ether extract was washed successively with sodium carbonate solution and water, then dried over anhydrous magnesium sulfate. The solvent was removed on a rotary evaporator, and the residual deuterated β -pinene (9) was purified by gas chromatography. Mass spectroscopy showed 81% d_1 ; $[\alpha]_D^{25} -19.4^\circ$ (c 0.475).

Reaction of β -Pinene with Maleic Anhydride. (a) Maleic anhydride (15 g, 0.15 mol) was dissolved in refluxing xylene (70 ml) and β -pinene (21.7 g, 0.16 mol) was added. The solution was heated under reflux for 20 hr and cooled, and the solvent was removed under vacuum. The warm residue was dissolved in *n*-hexane and the solution cooled overnight in a refrigerator. The white crystalline solid was twice recrystallized from *n*-hexane to give (–)-(10-pinen-2-yl)succinic anhydride (2b): mp 92–93° (lit.¹⁰ mp 92.5–93.5); yield 10.5 g (28%); $[\alpha]_D^{25} -87.8^\circ$ (c 1.61), lit.¹⁰ $[\alpha]_D^{26} -88.4^\circ$.

(b) Use of 3 α -deuterio- β -pinene (9) containing 55% d_1 led to the adduct mp 92–94°, m/e 235, 55% d_1 . The nmr spectrum showed the vinyl hydrogen at δ 5.30–5.45 integrating for 0.97 ± 0.03 H.

Reaction of β -Pinene with Dimethyl Acetylenedicarboxylate. (a) To a solution of 4.76 g (0.035 mol) of β -pinene in 150 of xylene, 10 g (0.07 mol) of dimethyl acetylenedicarboxylate was added and the mixture was heated to reflux in a nitrogen atmosphere for 20 hr. The solvent and the excess dimethyl acetylenedicarboxylate were removed under reduced pressure. The residual adduct (13) was distilled under vacuum: bp 117–118° (0.3 mm); yield 6.5 g (68%); $[\alpha]_D^{25} -35.33^\circ$ (c 2.278); $\lambda_{\text{max}}^{\text{OH}}$ 215 nm (ϵ 10,150); ir (film) 1730, 1645, 1600, 1440, 1265 cm^{-1} ; nmr (CDCl_3) δ 5.8 (s, split, 1 H), 5.45–5.3 (m, 1 H), 3.77–3.7 (two singlet, 6 H), 3.2–2.8 (m, 2 H), 2.5–1.9 (m, 5 H), 1.25 (s, 3 H), 1.16 (d, 1 H, $J = 8.5$ Hz), 0.81 (s, 3 H); m/e 278. Anal. Calcd for $\text{C}_{16}\text{H}_{22}\text{O}_4$: C, 69.04; H, 7.97. Found: C, 68.80; H, 8.02.

(b) Use of 3 α -deuterio- β -pinene (9) containing 55% d_1 in the reaction afforded adduct 13, bp 118° (0.3 mm), m/e 279, 55% d_1 . The nmr singlet at δ 5.8 integrated for 0.48 ± 0.03 H, while the signal at δ 5.30–5.45 integrated for 0.97 ± 0.03 H.

(c) A sample of 9 containing 81% d_1 led to adduct 13, m/e 279, 81% d_1 . The nmr signal at δ 5.8 integrated for 0.24 ± 0.05 H, while the signal at δ 5.30–5.45 integrated for 0.95 ± 0.05 H.

(–)-2-(10-Pinen-2-yl)butane-1,4-diol (14). A solution of 74 g of anhydride 2b in 200 ml of tetrahydrofuran was slowly added to a stirred suspension of lithium aluminum hydride (15.5 g) in 1 l. of anhydrous ether. After the addition was complete, the mixture was stirred and refluxed for 12 hr. The reaction was cooled and the excess hydride decomposed by the careful addition of 20% aqueous sodium hydroxide. The solids were filtered and washed well with ether. The combined ether solutions were dried (magnesium sulfate) and distilled to give (–)-2-(10-pinen-2-yl)butane-1,4-diol (14), 56 g (79%), bp 161° (1.5 mm), $[\alpha]_D^{25} -13.1^\circ$ (c 4.53). The ir spectrum (neat) showed broad absorption at 3300 cm^{-1} (hydroxyl) and no carbonyl absorption. The nmr spectrum showed 1 vinyl proton at δ 5.3 and 2 hydroxyl protons at 4.2.

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2-(10-Pinen-2-yl)butane 1,4-Di-*p*-toluenesulfonate (15). (–)-2-(10-Pinen-2-yl)butane-1,4-diol (14) (73 g) was dissolved in 350 ml of pyridine. This solution was stirred and cooled to -10 to -20° . To the cooled solution was added *p*-toluenesulfonyl chloride (175 g) at such a rate to keep the temperature below -5° . The mixture was kept at 0°F for 5 hr, then at 40°F for 3 days, after which it was poured into a mixture of 1 l. of ice-water and 240 ml of concentrated hydrochloric acid. The solution was extracted with ether (3 \times 500 ml) and the combined ether extracts were washed with cold water and saturated sodium bicarbonate until the washings were basic. After drying (magnesium sulfate), the ether solution was concentrated to leave the oily tosylate, 163 g (94%). Several recrystallizations from ether-petroleum ether ($60-70^{\circ}$) gave the pure tosylate (15), mp $71-74^{\circ}$. The infrared spectrum (Nujol) showed no hydroxyl absorption and no carbonyl absorption but did show sulfonate bands at 1180 and 1365 cm^{-1} . *Anal.* Calcd for $\text{C}_{25}\text{H}_{38}\text{O}_6\text{S}_2$: C, 63.13; H, 6.81; S, 12.04. Found: C, 62.91; H, 6.60; S, 12.03.

(–)-2-(10-Pinen-2-yl)butane (16). A solution of 193 g of 2-(10-pinen-2-yl)butane 1,4-di-*p*-toluenesulfonate (15) in 180 ml of tetrahydrofuran was added slowly to a stirred suspension of 40 g of lithium aluminum hydride in 1.65 l. of ether. After the addition was complete, the mixture was stirred and refluxed for 3 days. The reaction mixture was cooled and the excess hydride decomposed by the careful addition of 10% sodium hydroxide. The solids were filtered and washed well with ether. The ether solution was concentrated and the residue distilled first through a 30-cm Vigreux column and then through a 50-cm spinning band column to give 59 g (60%) of (–)-2-(10-pinen-2-yl)butane (16), bp 95° (12 mm), $[\alpha]^{25\text{D}} -4.75^{\circ}$ (neat, 1 dm). The product was homogeneous by vpc analysis (10 ft 20% SE-30, 170° , retention time 5.5 min). The nmr spectrum showed 1 vinyl proton at δ 5.2 and 23 upfield protons. *Anal.* Calcd for $\text{C}_{14}\text{H}_{22}$: C, 87.42; H, 12.58. Found: C, 87.51; H, 12.59.

Photolysis of Hydrocarbon 16. A solution of 4 g of (–)-2-(10-pinen-2-yl)butane (16) in 150 ml of toluene was irradiated with a 450-W Hanovia lamp Vycor filter, for 20 hr. The solution was concentrated and the residue fractionated by preparative vpc (20 ft \times $\frac{3}{8}$ in. SDC 710, 210°). The first material eluted was shown to be starting material by ir and nmr comparison. The second material eluted (17) had λ_{max} 236 nm (ϵ 16,400). The ir spectrum was nearly identical with the published spectrum of ocimene,²⁹ having olefin absorption at 1635, 1605, 890, and 990 cm^{-1} . The nmr spectrum showed a pattern characteristic of a vinyl group with absorptions centered at δ 5.2 and 6.2, along with a broad triplet at 2.8. Reinjection of this material into an analytical column (5 ft 20% SE-30, 170° , retention time 3 min) showed a small amount of starting material as an impurity.

The third material eluted (18) was thermally unstable; reinjection in an analytical column (5 ft 20% SE-30, 170°) gave four peaks

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of approximately equal intensity. The uv spectrum showed λ_{max} 280 nm (ϵ 1980) (reported³⁰ for allocimine is λ_{max} 277 nm (ϵ 41,900)).

(S)-(+)-3-Methylpentanoic Acid (19). A solution of 5 g of 16 in 200 ml of toluene was irradiated under the conditions described above for 34 hr. After concentrating the toluene solution, the residue was dissolved in 150 ml of methylene chloride and cooled to Dry Ice-acetone temperature. Ozone ($\sim 4\%$ in oxygen) was bubbled through the solution for 6.5 hr. The dark blue solution was allowed to warm to room temperature and concentrated by carefully warming in a water bath while passing a stream of nitrogen over the surface. Acetic acid (40 ml) was added and this solution was added to a mixture of water (60 ml), 30% hydrogen peroxide (20 ml), and concentrated sulfuric acid (1 ml). The excess methylene chloride was distilled and the resulting solution was refluxed for 4 hr. The solution was cooled, basified with 6 *N* sodium hydroxide, and washed with ether. The aqueous phase was acidified with 6 *N* hydrochloric acid and extracted with ether. The acidic ether extracts were combined and dried (magnesium sulfate) and the solution was concentrated to leave an acidic residue which was distilled. The best distillation cuts were purified by preparative vpc (20 ft \times $\frac{3}{8}$ in. 30% SDC 710, 180°) and gave 240 mg of (S)-(+)-3-methylpentanoic acid (19), $[\alpha]^{25\text{D}} +5.55^{\circ}$ (benzene, *c* 11.7). This material was homogeneous by vpc (5 ft 20% SE-30, 150° , retention time 1.5 min). The infrared spectrum (neat) was identical with that of an authentic sample of 3-methylpentanoic acid.³¹

The acid was converted to the crystalline amide, which melted at $124-125.5^{\circ}$ after recrystallization from heptane-benzene (lit.³² mp $125.7-126^{\circ}$), $[\alpha]^{25\text{D}} +8.35$ (*c* 5.04). The ir spectrum was identical with that of an authentic sample. *Anal.* Calcd for $\text{C}_8\text{H}_{13}\text{NO}$: C, 62.57; H, 11.38; N, 12.16. Found: C, 62.67; H, 11.29; N, 12.08.

Mutarotation of Adduct 2b. A solution of 1.006 g of adduct 2b in 100 ml of xylene was divided into aliquots, sealed in glass ampoules, and heated at $153 \pm 3^{\circ}$. The optical rotations observed after varying periods of time are listed in Table I.

Another portion of the xylene solution was kept at room temperature. After 124 hr the optical rotation had changed from an initial value of -59.4 to -58.3° .

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