A mixture containing triphenyl phosphorothionate (7.5 mmoles, 2.5677 g), α-diphenylmethanethiol-^{35}S (7.5 mmoles, 1.5023 g), and triphenyl phosphite (1.5 mmoles, 0.4654 g) was kept in a gentle stream of nitrogen for 20 hr at 60°. The mixture was then treated by the same procedure as described for nonradioactive compound and gave benzene solution containing triphenyl phosphorothionate which was free from other compound. Since crystals of the phosphorothionate did not separate for a few days and were expected to have low activity, a double-dilution method was utilized. The benzene solution was diluted with ethanol to 20 ml. To each of two aliquots (2 ml) of the solution was added a known amount (a or a', $a < a'$) of the nonactive triphenyl phosphorothionate. The added crystals dissolved on heating. White crystals of triphenyl phosphorothionate which were isolated by cooling from each aliquot were collected, recrystallized from ethanol, and assayed for radioactivities. The specific activity (S) of the phosphorothionate to be determined is given by the equation

$$S = \frac{bb'(a' - a)}{a'b' - ab}$$

where b and b' represent specific activities resulted from dilution. The results are indicated in Table III.

Table III showed that, under the condition mentioned above, sulfur atom of triphenyl phosphorothionate exchanges with that of α-diphenolmethanethiol-^{35}S to a minor extent (0.8%).

Procedure for Aralkyl Hydrodisulfides-^{35}S, $(C_6H_5)_2CH^{35}SSH$ $C_6H_5CH_2{}^{35}SSH$, with Triphenyl Phosphite.—Benzyl and benzhydryl hydrodisulfides-^{35}S (10 mmoles) were allowed to react with triphenyl phosphite (12 mmoles) under the same conditions as described for the nonactive compounds. Radioactive thiols (after conversion to the corresponding disulfides) and triphenyl phosphorothionate were isolated and identified by the procedures described for the nonactive compounds. The radioactive compounds were recrystallized to constant activities and subjected to counting analysis. The specific activity of triphenyl phosphorothionate was determined also by the double-dilution method because of its low radioactivity (see Table II).

Table III

Isotopic Exchange of Triphenyl Phosphorothionate with α-Diphenylmethanethiol-^{35}S in the Presence of Triphenyl Phosphite

$(C_6H_5O)_3PS$ added as a diluent, mg	383.8 (a'), 152.8 (a)
Specific activity of diluted $(C_6H_5O)_3PS$, cpm/mg	18 (b'), 26 (b)
Specific activity (S) of $(C_6H_5O)_3PS$, cpm/mg	37
Specific activity (A) of standard $(C_6H_5O)_3PS$, cpm/mg	4557
$S/A \times 100$, %	0.8

Counting Analysis of the Active Products.—Activities were counted with a Packard Tri-Carb liquid scintillation spectrometer Model 314 using POPOP as a scintillator and toluene as a solvent.

The Synthesis of *cis*- and *trans*-δ-Pinenes *via* Hydroboration of Verbenene

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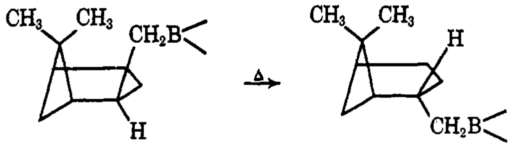
Bromination of β-pinene with N-bromosuccinimide produces myrtenyl bromide as the major product. α-Pinene reacts under similar conditions to give verbenyl bromide, contaminated with some myrtenyl bromide. Dehydrobromination of either myrtenyl bromide or verbenyl bromide gives verbenene in high yield. The hydroboration of verbenene with bis(3-methyl-2-butyl)borane proceeds selectively at the *exo*-cyclic double bond. Protonolysis of the intermediate organoborane with propionic acid yields *cis*-δ-pinene. Alternatively, hydroboration of verbenene with dicyclohexylborane followed by isomerization and protonolysis affords *trans*-δ-pinene.

In connection with a study on elimination reactions in the pinane series, the *cis*- and *trans*-δ-pinenes were required as reference compounds. *cis*-δ-Pinene has been previously synthesized by thermal decomposition of the xanthates derived from iso- and neoisoverbanol.[1] These alcohols, however, are not readily accessible. The *trans* olefin has been isolated by repeated distillations from a mixture of α-pinene and *trans*-δ-pinene obtained by elimination from pinocampheyl tosylate with sodium ethoxide.[1] It appeared to us, however, that the selective hydroboration of verbenene followed by protonolysis might offer a convenient synthesis of the *cis*- and *trans*-δ-pinenes.

Recent investigations on the hydroboration of β-pinene with diborane revealed that the *cis* addition of the boron–hydrogen bond moiety proceeds from the side away of the *gem*-dimethyl group to produce the less stable of the two possible myrtanylboranes.[2,3] The product, when heated *in situ* with propionic acid, a reaction which proceeds with retention of configuration, was converted into *cis*-pinene.[3] Under the influence of heat, the initially formed organoborane isomerized to the *trans* derivative,[2] which gave *trans*-pinane on protonolysis.[3]



Provided that the *exo*-cyclic double bond of verbenene could be selectively converted into the organoborane, the combination of a hydroboration–protonolysis or a hydroboration–isomerization–protonolysis sequence would result in the formation of *cis*- and *trans*-δ-pinenes, respectively.

Verbenene has previously been synthesized by dehydration of verbenol, obtained from the autooxidation of α-pinene.[4,5] This route, however, gives low yields of the diene and involves tedious isolation procedures. Allylic brominations of olefins with N-bromosuccinimide (NBS) followed by dehydrobromination have been widely used for the preparation of dienes.[6] Thus, the readily accessible pinenes appeared to offer the logical substrates for the preparation of verbenene. Treatment of (−)-β-pinene (100% excess) with NBS in carbon tetrachloride yielded, among the higher boiling components, a monobromide (51%), which by gas

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(1) H. Schmidt, *Chem. Ber.*, **80**, 520 (1947).

(2) J. C. Braun and G. S. Fisher, *Tetrahedron Letters*, 9 (1960).

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

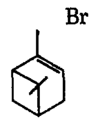
(4) A. Blumann and O. Zeitschel, *Chem. Ber.*, **54**, 887 (1921).

(5) N. R. Moore and G. S. Fisher, *J. Am. Chem. Soc.*, **78**, 4362 (1956).

(6) F. L. Greenwood and J. A. Sealak, *J. Org. Chem.*, **22**, 776 (1957).

chromatographic examination was found to be 90% pure.[7] Its nmr spectrum was consistent with that expected for myrtenyl bromide. Moreover, displacement of the bromide with sodium acetate in acetic anhydride yielded an acetate, which on reduction with lithium aluminum hydride gave the known myrtenol.[8]

The preferred formation of myrtenyl bromide (**1**) over pinocarvenyl bromide (**2**) is not unexpected as rearrangements in NBS brominations are well known.[9,10]



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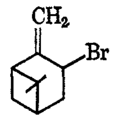
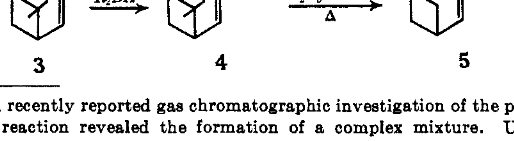


2

The myrtenyl bromide thus obtained was then dehydrobrominated with γ-collidine. Vpc examination of the reaction mixture revealed a 64% yield of verbenene, which was isolated by preparative vpc and identified through its ultraviolet and nmr spectra.

Alternatively α-pinene can serve as a convenient precursor for verbenene. Thus bromination of the olefin (100% excess) with NBS yielded besides a high-boiling residue, 52% of a monobromide previously reported as verbenyl bromide.[11] Gas chromatographic examination of this product resulted in extensive decomposition, but did reveal the presence of a small amount of myrtenyl bromide. In contrast to the displacement reaction observed when myrtenyl bromide reacted with sodium acetate in acetic anhydride, the monobromo product from α-pinene underwent mainly elimination. Examination of the reaction mixture by vpc using an internal standard as reference revealed 62% verbenene and 27% myrtenyl acetate. This indicates that verbenyl bromide is the major monobromo derivative obtained by NBS bromination of α-pinene. Verbenene was also produced when the verbenyl bromide product was heated in the presence of γ-collidine.

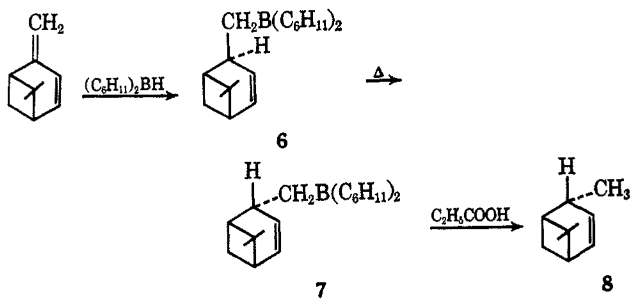
The reaction of diborane with dienes is essentially nonselective.[12] However, the selective hydroboration of the *exo*-cyclic double bonds of vinylcyclohexene and limonene has been achieved with bis(3-methyl-2-butyl)borane. Consequently, treatment of verbenene (**3**) with this hydroborating agent should result in the formation of the *cis*-δ-pinene boro derivative (**4**). Protonolysis of the intermediate organoborane with a carboxylic acid[13] should then result in the cleavage of the pinene–boron bond to give *cis*-δ-pinene (**5**).



3 4 5

(+)-Verbenene readily underwent hydroboration with bis(3-methyl-2-butyl)borane in diglyme solution. The intermediate **4** when heated *in situ* with propionic acid gave essentially pure (−)-*cis*-δ-pinene, which could be hydrogenated over platinum or carbon[14] to *cis*-pinane. The physical constants of the olefin are nearly identical with those reported for *cis*-δ-pinene by Schmidt.[1]

As mentioned previously, *cis*-myrtanylborane isomerized under the influence of heat to give the thermodynamically more stable *trans* isomer. Similarly, the organoborane (**4**) derived from verbenene should undergo isomerization to the corresponding *trans* derivative. However, as the isomerization proceeds by a succession of elimination–addition reactions, then organoborane (**4**) might produce bis(3-methyl-2-butyl)borane in the elimination step. This is known to isomerize very readily to the corresponding less hindered primary organoboranes,[15] and these reagents would discriminate less between the *exo*- and *endo*-cyclic double bond in the addition step than the bis(3-methyl-2-butyl)borane. In order to circumvent this difficulty, verbenene was hydroborated with dicyclohexylborane in diglyme.[16] The organoborane formed (**6**) was heated for 2 hr at 125–130° to achieve isomerization to the *trans*-organoborane (**7**). The reaction mixture was diluted with propionic acid, and then heated at 140°. The olefin obtained, when hydrogenated over platinum on carbon,[14] gave a compound which had a vpc retention time identical with a known sample of *trans*-pinane. The physical constants for the olefin agree with those reported for *trans*-δ-pinene (**8**).[1]



6 7 8

Experimental Section[17]

Myrtenyl Bromide.—β-Pinene (54.2 g, 0.40 mole, $[\alpha]_D$ −21°) and 35.6 g of N-bromosuccinimide (0.20 mole) were heated under reflux for 1 hr in dry carbon tetrachloride. After removal of the succinimide by filtration, the carbon tetrachloride was removed at 0° under reduced pressure. The resulting residue was dissolved in cold *n*-pentane (40 ml) and filtered, and the solvent was evaporated. Excess β-pinene was recovered by distillation at 20 mm, and the product distilled at 46–48° (0.1 mm) to give 21.8 g of myrtenyl bromide (51%): $n^{27}D$ 1.5205, $\alpha^{25}D$ −28.4° (1 dm) [lit.[11] bp 102° (12 mm), $n^{15}D$ 1.5240, $[\alpha]_D$ −35° ($CHCl_3$)]. Gas chromatographic examination on a SE-30 column revealed that this material was approximately 90% pure. The nmr spec-

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[7] A recently reported gas chromatographic investigation of the products of this reaction revealed the formation of a complex mixture. Unfortunately, neither the reaction conditions nor the nature of the products was given: E. S. Huyser and D. N. DeMott, *Chem. Ind.* (London), 1954 (1963).

[8] H. Schmidt, *Ber. Schimmel and Co.*, 79 (1941); *Chem. Zentr.*, **1**, 2531 (1942).

[9] M. S. Kharasch, E. T. Margolis, and F. R. Mayo, *J. Org. Chem.*, **1**, 393 (1936); D. R. Howton and E. R. Buchman, *J. Am. Chem. Soc.*, **70**, 5396 (1953).

[10] It is reported that methylenecyclohexane undergoes bromination with NBS to yield 2-bromomethylenecyclohexane. However, we have recently observed that treatment of an excess of methylenecyclohexane with NBS in carbon tetrachloride gives a 45% yield of 1-(bromomethyl)cyclohexene: unpublished work with C. C. Whitney.

[11] Buu-Hoi, Hiong-Ki-Wei, J. Lecomte, and R. Roger, *Bull. Soc. Chim. France*, 148 (1946).

[12] G. Zweifel, K. Nagase, and H. C. Brown, *J. Am. Chem. Soc.*, **84**, 183 (1962).

[13] H. C. Brown and K. J. Murray, *ibid.*, **81**, 4108 (1959); *J. Org. Chem.*, **26**, 631 (1961).

[14] C. A. Brown and H. C. Brown, *J. Am. Chem. Soc.*, **84**, 2829 (1962).

[15] H. C. Brown and G. Zweifel, *ibid.*, **88**, 1433 (1966).

[16] G. Zweifel, N. R. Ayyanger, and H. C. Brown, *ibid.*, **85**, 2072 (1963).

[17] The nmr spectra were taken in carbon tetrachloride on a Varian A-60A spectrometer, using tetramethylsilane as an external standard.

trum had the following signals: τ 4.37 (1 H, multiplet, vinyl H), 6.11 (2 H, quartet, CH_2Br).

To 10 g of myrtenyl bromide (47 mmoles) was added 8.2 g (0.10 mole) of anhydrous sodium acetate and 20 ml of acetic anhydride. The reaction mixture was then heated for 2 hr at 140–145°, cooled, diluted with *n*-pentane, and neutralized with sodium hydroxide followed by sodium bicarbonate. The pentane layer was separated, and the aqueous phase was extracted twice with ether. After drying over anhydrous magnesium sulfate, the combined extracts were concentrated to dryness. The residue obtained was purified by gas chromatography on an ethylene glycol adipate column to give 5.3 g of myrtenyl acetate (58%): n^{27}D 1.4730, α^{25}D $-40°$ (1 cm) (lit.[18] n^{25}D 1.4784). The nmr spectrum had signals at τ 4.50 (1 H, multiplet, vinyl H) and 5.26 (2 H, quartet, CH_2OAc).

To a solution of myrtenyl acetate (4.8 g, 25 mmoles) in 10 ml of tetrahydrofuran was added at room temperature 35 ml of a 0.8 *M* solution of lithium aluminum hydride in tetrahydrofuran. After stirring the mixture for 1 hr, the excess hydride was decomposed with wet tetrahydrofuran, and the precipitate formed was brought in solution by adding a saturated solution of Rochelle salt. The mixture was then extracted with ether, and the combined extracts were dried over anhydrous magnesium sulfate. The residue obtained after evaporation of the solvents was purified by gas chromatography to obtain 2.3 g of myrtenol (61%): n^{25}D 1.4950; d^{20} 0.976; $[\alpha]$D $-48.5°$; hydrogen phthalate mp 112–113°; nmr τ 4.67 (1 H, multiplet, vinyl H), 6.20 (2 H, quartet, CH_2OH (lit.[8] *n*D 1.4968, $[\alpha]$D $-46°$, hydrogen phthalate mp 114–115°).

Verbenene from Myrtenyl Bromide.—To 12.0 g. of myrtenyl bromide (56.5 mmoles) was added 40 ml of γ-collidine. The reaction mixture was then heated for 4 hr at 140°, diluted with *n*-pentane, and washed with cold 2 *N* hydrochloric acid. Vpc examination of the resulting pentane solution indicated a 64% yield of verbenene. The residue remaining after evaporation of the solvent was purified by vpc on a Carbowax 20M (alkaline) column. The verbenene obtained had n^{26}D 1.4970; d^{20} 0.880; $[\alpha]$D $+86°$; $\lambda_{\max}^{\text{EtOH}}$ 246 mμ (ϵ 11,230); nmr τ 3.97 (2 H, quintet, olefinic H), 5.5 (2 H, singlet, vinylic H) [lit.[5] n^{20}D 1.4997; $[\alpha]$D $+94°$; $\lambda_{\max}^{\text{EtOH}}$ 245 mμ (ϵ 10,550)].

Verbenyl Bromide.—A mixture of $(-)$-α-pinene (54.4 g, 0.40 mole, $[\alpha]$D $-46°$) and 35.6 g (0.20 mole) of NBS in 150 ml of dry carbon tetrachloride was stirred and heated under reflux for 30 min. Since the reaction was very exothermic once it had started, occasional cooling was necessary. The succinimide formed was removed by filtration. The solvent was then evaporated at 20° under reduced pressure, and the residue obtained was distilled at 0.1 mm to give a mixture of α-pinene and the bromo derivative. After removing the crystalline material which formed on cooling, redistillation gave 22.2 g of bromopinene (52%): bp 56–58° (0.1 mm), n^{27}D 1.5190, α^{25}D $+104°$ (1 dm). Vpc examination on a SE-30 column revealed that the verbenyl bromide was contaminated with some myrtenyl bromide: lit.[11] n^{14}D 1.5220, $[\alpha]$D $-73°$ ($CHCl_3$).

Verbenene from Verbenyl Bromide.—The verbenyl bromide–myrtenyl bromide mixture obtained from α-pinene (20 g, 92 mmoles) was treated with 80 ml of γ-collidine, and heated for 90 min at 140°. The reaction mixture was worked up as described above and the crude product was purified by vpc on a Carbowax 20M (alkaline) column to obtain 5.6 g of pure verbenene (46%): n^{27}D 1.4967, d^{20} 0.880, $[\alpha]$D $+83°$. The ultraviolet, infrared, and nmr spectra were identical with those observed for verbenene derived from myrtenyl bromide. Alternatively, treatment of 20 g of bromide mixture (92 mmoles) with 16.4 g of anhydrous sodium acetate and 40 ml of acetic anhydride and refluxing for 2 hr yielded 62% verbenene (vpc analysis) and 27% myrtenyl acetate.

***cis*-δ-Pinene.**—To 7.7 g of 2-methyl-2-butene (0.11 mole) in 25 ml of diglyme was added 42 ml of 1 *M* sodium borohydride in diglyme. This mixture was cooled in an ice bath, and diborane was generated by adding while stirring 55 mmoles (7 ml) of boron trifluoride etherate. After maintaining the mixture for 2 hr at 0–5°, it was treated with 6.7 g (50 mmoles, $[\alpha]$D $+86°$) of verbenene at 0° and stirred for an additional 2 hr at room temperature. The reaction mixture was then diluted with 17 ml propionic acid and heated under reflux for 2.5 hr. Ether (from boron trifluoride etherate) and isobutane were lost during the heating. The reaction mixture was cooled to room temperature, and sufficient 6 *N* sodium hydroxide was added to ensure an excess. The upper phase was separated, diluted with *n*-pentane, and washed with cold water to remove diglyme. After evaporation of the solvent the residue was purified by preparative vpc on a didecylphthalate column. The *cis*-δ-pinene collected had n^{25}D 1.4670; d^{20} 0.867; $[\alpha]$D $-50°$; nmr τ 4.04 (1 H, multiplet, C_4-H) 4.60 (1 H, broad doublet, C_3-H) (lit.[1] n^{20}D 1.4696, $[\alpha]$D $-59°$).

Hydrogenation of a small sample of this material over platinum on carbon and examination of the crude reaction mixture on a squalene column revealed that essentially pure *cis*-pinane had been formed.

***trans*-δ-Pinene.**—To 9.2 g (0.11 mole) of cyclohexene in 25 ml of diglyme was added 42 ml of a 1 *M* solution of sodium borohydride in diglyme. Hydroboration was achieved by adding 55 mmoles (7 ml) boron trifluoride etherate at 0°. After 2 hr, 6.7 g (50 mmoles, $[\alpha]$D $+86°$) of verbenene was added to the resulting mixture and it was kept for 2 hr at room temperature. The organoborane formed was then isomerized at 125–130° for 2 hr. This reaction mixture was then diluted with 17 ml of propionic acid, heated for 2.5 hr at 140°, and cooled to room temperature, and sufficient 6 *N* sodium hydroxide was added to ensure an excess. The upper phase formed was separated, diluted with *n*-pentane, washed with cold water to remove diglyme, and dried over anhydrous magnesium sulfate. The residue remaining after concentration was purified by vpc on a didecylphthalate column to obtain 2.6 g of *trans*-δ-pinene: n^{25}D 1.4645; d^{20} 0.863; $[\alpha]$D $+119°$; nmr τ 4.04 (1 H, multiplet, C_4-H), 4.75 (1 H, broad doublet, C_3-H) (lit.[1] n^{20}D 1.4671; $[\alpha]$D $-112°$).

A small sample of the *trans*-δ-pinene was hydrogenated over platinum on carbon. Examination of the crude reaction mixture by vpc on a squalene column revealed that the compound had a retention time with a known sample of *trans*-pinane.

Acknowledgment.—We are greatly indebted to the Glidden Company, Jacksonville, Florida, for a gift of $(-)$-β-pinene.

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[18] F. W. Semmler and K. Bartelt, *Chem. Ber.*, **40**, 1363 (1907).