Reductive elimination of (+)-6 using the same protocol provided unnatural (+)-2 with $[\alpha]^{25}_D$ +62.5° (c 1.33, $CHCl_3$).

X-ray Structural Determination of (-)-6. The compound crystallizes in the monoclinic space group C2 with a = 22.648 (6) Å, b = 6.619 (2) Å, c = 12.638 (5) Å, β = 104.92 (3), V = 1816 (1), Z = 4, density = 1.12 (1) (obs), 1.124 (calcd). Data were collected with Mo K radiation, scan rate = 2.0°/min, scan width = 2.0° plus dispersion, background counts = 30 s, θ-2θ technique. Of the 1358 data examined from 0°-45°, 918 were considered observed. The structure was solved by a combination of MULTAN 78 and Fourier analyses. Full-matrix anisotropic refinement (without hydrogen atoms) led to discrepancy factors of R = 0.079 and w_R = 0.095. Analysis of thermal parameters, bond distances, hydrogen bonding, and alternate refinements led to unambiguous assignment of the methyl and hydroxide groups. Details on the programs and techniques used are available.[8]

Acknowledgment. This work was supported by a grant from the National Science Foundation.

Registry No. (-)-2, 80082-35-5; (+)-2, 90580-44-2; (-)-3, 80482-67-3; (+)-3, 33993-53-2; 4, 16647-04-4; (-)-5, 90433-70-8; (+)-5, 90433-71-9; (-)-6, 90433-72-0; (+)-6, 90528-05-5.

Supplementary Material Available: Bond angles, bond distances, and final atomic parameters (3 pages). Ordering information is given on any current masthead page.

(8) Corey, E. R.; Corey, J. Y.; Glick, M. D. *J. Organomet. Chem.* **1977**, *129*, 17.

Essential Oil Constituents of *Artemisia tridentata rothrockii*. The Isolation and Characterization of Two New Irregular Monoterpenes[1]

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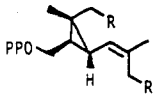
The neutral pentane extract of the leaves and flower heads of *Artemisia tridentata rothrockii* was found to contain two new non-head-to-tail monoterpenes, rothrockene (8) and neolyratol (19), in addition to several previously characterized monoterpenes. The absolute stereochemical structures of these compounds have been established by chemical and spectral means.

We have been interested in the biosynthesis of non-head-to-tail monoterpenes primarily as a model for the study of the formation of the biologically important steroid precursor squalene in mammals.[2] The biogenesis of these irregular terpenes presumably involves ionization and subsequent rearrangement of the structurally analogous cyclopropyl intermediates, chrysanthemyl pyrophosphate (**1a**) and presqualene pyrophosphate (**1b**).[2,3] As a result



1a: R=H
2b: R=geranyl

of this analogy, three additional irregular C_{10} skeketal systems **2**, **3**, and **4**, might occur in addition to the known artemisyl **5**, chrysanthemyl **6**, and santolinyl **7** systems (Scheme I). The isolation of monoterpenes possessing these carbons skeletons would provide support for the proposed biosynthetic sequence and for the idea that plant enzyme systems might act as simple models of mammalian squalene synthetase. Furthermore, since irregular monoterpenes with artemisyl, chrysanthemyl, and santolinyl skeletons have thus far been identified only in plants of the Anthemideae tribe of the Asteraceae family, this class of compounds may function as a useful taxonomic tool as well.

To these ends, we have been screening plants of the Asteraceae for non-head-to-tail monoterpenes. In a recent communication we described the isolation and structure elucidation of a novel irregular monoterpene hydrocarbon possessing a heretofore unknown skeletal system from the sagebrush, *Artemisia tridentata rothrockii*.[4,5] We now

Scheme I

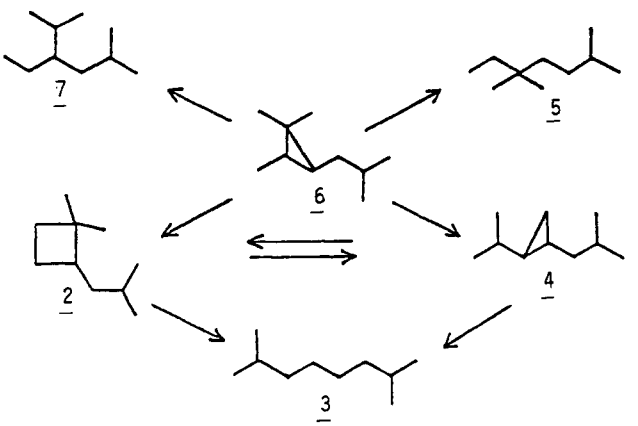


Table I. GC/MS Survey—Monoterpenes Found in *Artemisia tridentata rothrockii*[6]

compd	composition, %	compd	composition, %
artemiseole	25.2	1,8-cineole	5.3
unknown	13.8	p-cymene	5.0
santolina triene	12.8	camphor	2.9
camphene	12.1	β-pinene	1.8
α-pinene	11.2	limonene	1.5
oxidosantolina triene	7.9	artemisia alcohol	0.4

(1) Research supported by NIH Grants GM 20196 and GM 26245.
(2) Epstein, W. W.; Poulter, C. D. *Phytochemistry* **1973**, *12*, 737.
(3) Poulter, C. D.; Muscio, O. J.; Goodfellow, R. J. *Biochemistry* **1974**, *13*, 1530.
(4) Epstein, W. W.; Gaudioso, L. A. *J. Org. Chem.* **1982**, *47*, 175.

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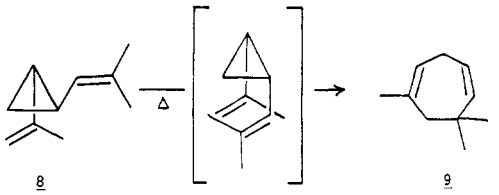
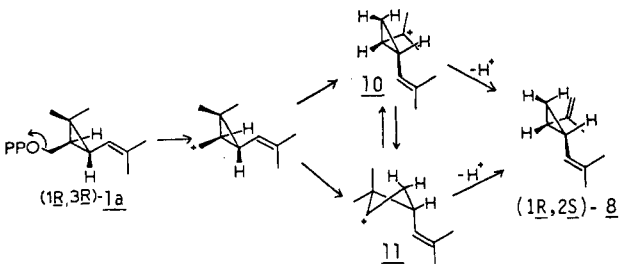
Scheme II



Scheme III



with to report the full results of our studies on this species. These investigations include, in addition to the isolation and structure of rothrockene, establishment of the absolute configuration of this molecule, determination of the absolute stereochemical structure of a new irregular monoterpenoid alcohol from the oils of this plant, as well as the identification of a number of other known monoterpenes.

Artemisia tridentata rothrockii was collected east of Ephraim, UT, at an elevation of approximately 10000 feet. The neutral pentane extract was initially analyzed by gas chromatography/mass spectroscopy (GCMS).[6] These results suggested the presence of an unknown component, as well as several previously characterized monoterpenes (Table I). Therefore, a large continuous pentane extraction was undertaken for isolation purposes.

The crude extract afforded a fragrant, colorless oil following reduced pressure distillation. The oil was concentrated with respect to the unknown by repeated silica gel chromatography. The final purification step involved preparative GLC, where some problems were initially encountered. High injector and detector temperatures (>225 °C) and prolonged retention time were condusive to rearrangement as evidenced by GLC analysis of the collected oil. These problems were circumvented by using low temperatures throughout the system (>160 °C) and by regular silylation of the column.[7] The unidentified component was isolated in pure form as a colorless oil, $[\alpha]_D$ −64.8°. A molecular formula, $C_{10}H_{16}$, was inferred from the mass spectrum molecular ion (m/e 136) and confirmed by carbon–hydrogen analysis. Analysis of the spectral data leads to the assignment of structure 8 to the unidentified volatile oil constituent of *A. tridentata rothrockii* which we have given the trivial name, rothrockene.[4]

Dialkenylcyclopropanes such as 8 characteristically undergo facile homo-Cope rearrangements to the respective cycloheptadienes. This phenomenon has been well documented for both the cis[8-12] and trans isomers.[13-19] Whereas trans-dialkenylcyclopropanes are resistant to rearrangement below temperatures of 160 °C,[16] the corresponding cis isomers readily rearrange between −20 and +90 °C depending upon the structure. With this information in hand it is reasonable to assume that rothrockene most likely exists as the trans isomer,[17] and that it should thermally isomerize to a cycloheptadienyl system if the proposed structure is indeed correct (Scheme II). Therefore, a sample of rothrockene was sealed in a capillary tube and heated at 200 °C for 4.5 hours. Spectral analysis of the resulting material revealed that a rearrangement process had transpired.

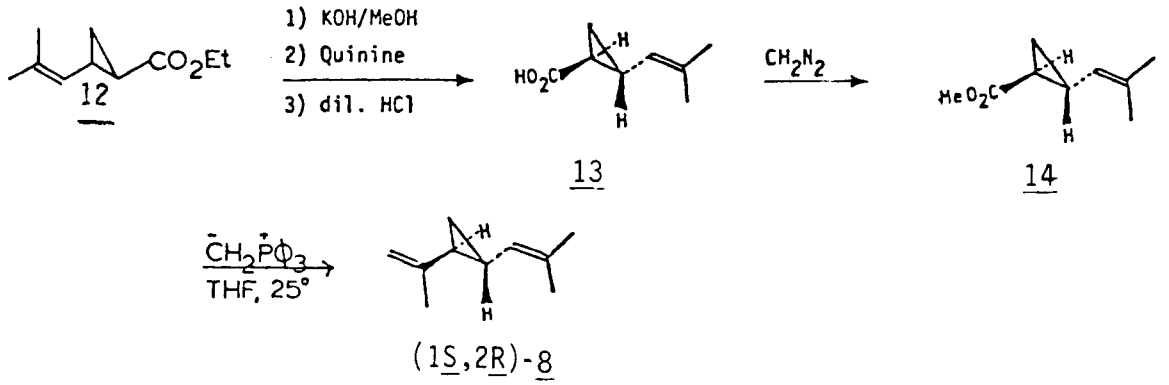
The IR spectrum clearly shows carbon–carbon bond unsaturation at 3010 and 1675 cm^{-1}, and furthermore, the band at 685 cm^{-1} is typical of a cis-disubstituted double bond system. Three methyl signals are evident in the ^1H NMR spectrum of the rearrangement product, a 6-H singlet at 1.01 ppm and a three proton singlet at 1.75 ppm, both displaying long-range coupling. These resonances are characteristic of methyl groups attached to saturated and unsaturated carbon atoms, respectively. The 2-H singlet at 2.22 ppm can be assigned to an allylic system (C=CC-H_2C), while the chemical shift and splitting pattern of the 2-H resonance at 2.67 ppm are consistent with the doubly allylic protons of C=CHCH_2CH=C. Irradiation of the latter signal collapsed the 1-H olefinic absorptions at 5.39 and 5.60 ppm to a doublet (J = 11.6 Hz) and a singlet, respectively, while the one proton doublet (J = 11.6 Hz) at 5.31 ppm remained unchanged. The ^{13}C NMR spectrum provides additional evidence that a skeletal transformation had occurred. The olefinic region is most noticeably different containing three doublets at 125.2, 125.8, and 141.6 ppm and a singlet at 138.9 ppm in place of a doublet, triplet, and two singlets.

According to these data, only structure 9 can be drawn for the thermolysis product of rothrockene. These results are completely consistent with those predicted as an outcome of the homo-Cope rearrangement process, and therefore support the structure assigned to rothrockene. Furthermore, the rearrangement also explains the difficulties encountered during the initial GC isolation of this material.

The relative stereochemical structure of rothrockene was unambiguously determined to be 8 by synthetic means.[4] Based on the putatively analogous squalene synthetase reaction the biogenesis of the "rothrockyl" skeleton can be explained and the absolute stereochemistry of (−)-rothrockene predicted (Scheme III). The presumed C_{10} precursor of 8 in *A. tridentata rothrockii* is *trans*-(1*R*,3*R*)-chrysanthemyl pyrophosphate (1a) for reasons which will be discussed later. Ionization and rearrangement of this labile molecule can generate the rothrockyl system 10 directly, or indirectly via cyclobutyl intermediate 11. In either case, loss of a proton would be expected to yield rothrockene with the 1*R*,2*S* absolute configuration.

(5) The plant material collected at this site is of indeterminate nomenclature status as of this time. It has previously been referred to as *A. tridentata rothrockii*, but is tentatively assigned to *A. tridentata vaseyana*.
(6) Pearson, M. Y. M.S. Dissertation, University of Utah, 1977.
(7) The silyation reagent employed here was Rejuv-8, Supelco, Inc.
(8) Vogel, E. *Angew. Chem.* **1960**, *72*, 4.
(9) Vogel, E.; Ott, K. H.; Gatek, K. *Liebigs Ann. Chem.* **1961**, *644*, 172.
(10) Sasaki, T.; Eguchi, S.; Ohno, M. *Tetrahedron Lett.* **1969**, 3459.
(11) Schneider, M. P.; Rau, A. *J. Am. Chem. Soc.* **1979**, *101*, 4426.
(12) Brown, J. M.; Golding, B. T.; Stofko, J. *J. Chem. Commun.* **1973**, 319.
(13) Vogel, E.; Elb, R. *Angew. Chem., Int. Ed. Engl.* **1962**, *1*, 53.
(14) Ullenius, C.; Ford, P. W.; Baldwin, J. E. *J. Am. Chem. Soc.* **1972**, *94*, 5910.
(15) Jaenicke, L.; Akintobi, T.; Marrer, F. *Liebigs Ann. Chem.* **1973**, 1252.
(16) Baldwin, J. E.; Ullenius, C. *J. Am. Chem. Soc.* **1974**, *96*, 1542.
(17) Preparative GLC isolation conditions would have been expected to cause some degree of rearrangement if *cis*-8 was involved; injector temperature 135 °C, column temperature = 140 C, detector temperature = 75 °C, and retention time = 30 min.
(18) Moore, R. E.; Pettus, J. A.; Mistysyn, J. *J. Org. Chem.* **1974**, *39*, 2201.
(19) Moore, R. E. *Acc. Chem. Res.* **1977**, *10*, 40.
(20) Bertele, E.; Schudel, P. *Helv. Chim. Acta* **1967**, *50*, 2445.
(21) Robinson, W. Ph.D. Thesis, University of Illinois, 1972.
(22) Coates, R. M.; Robinson, W. *J. Am. Chem. Soc.* **1971**, *93*, 1785.

Scheme IV



12 13 14 (1S,2R)-8

The absolute stereochemistry of (−)-rothrockene was established, and found to be in accord with that predicted, by synthesis of the 1*S*,2*R* enantiomer (Scheme IV). Trans ester **12** was prepared as previously described[4] and hydrolyzed to the corresponding acid. Optically active trans acid **13** was resolved by using quinine[23] and converted to (+)-*trans*-methyl ester **14** with diazomethane. The absolute configuration of **14** has been established as 1*S*,2*R* by Poulter et al.[23] Reaction of **14** with the "salt free" ylide and subsequent purification gave a colorless oil whose properties were identical to natural rothrockene, but of opposite rotation, $[\alpha]_D$ +62.7°. Comparison of this value with that obtained for naturally occurring (−)-rothrockene indicates that synthetic (+)-rothrockene is 96.7% optically pure and that (−)-**8** has the predicted 1*R*,2*S* absolute configuration. Johnson et al.[27] have independently determined the absolute stereochemistry of **8** and concur with the designation.

Several known monoterpenes were isolated from two LC fractions of the essential oils by preparative GLC. Confirmation of these structures was achieved by GLC coinjection studies and spectral comparisons to authentic samples. Santolina triene, α-pinene, camphene, and sabinene were identified as the remaining components of the fraction containing rothrockene. The presence of sabinene was not expected since the corresponding GLC peak was tentatively identified as β-pinene during the GCMS survey. The mass spectra of these compounds are similar, therefore a small impurity could lead to erroneous results.

A second fraction yielded optically pure (+)-artemiseole (**15**), (+)-(2*R*,3*S*)-oxidosantolina triene **16** (90% pure by GLC), and optically pure (−)-camphor. The absolute configuration of the epoxide was proven by acid-catalyzed rearrangement to optically pure **15**, since the 2*R*,3*S* stereoisomer is the exclusive source of (+)-artemiseole via rearrangements of this type.[28] The presence of these (3*S*)-santolinyl derivatives in the oils implies that (1*R*,3*R*)-*trans*-chrysanthemyl pyrophosphate is the biogenetic precursor of the irregular monoterpenes in *A. tridentata rothrockii* according to the unified pathway.

The isolation and identification of these monoterpenes, which comprise more than 85% of the volatile oils, support the GCMS survey results except in the case of sabinene.

A previously undetected compound was isolated from a less volatile essential oil fraction by silica gel chromatography and preparative GLC. Subsequent purification by Silica Gel MPLC removed an aldehyde impurity[29] (IR bands at 2715 and 1720 cm^{-1}). The resulting single component oil, $[\alpha]_D$ +78.7°, proved to have a $C_{10}H_{16}O$ molecular formula by high-resolution mass spectroscopy.

IR bands at 3300 and 1055 cm^{-1} are typical of primary alcohols, while absorptions at 3065, 1640, and 1630 cm^{-1} are indicative of unsaturated carbon–carbon bond systems. Furthermore, the presence of vinyl (1410, 995, and 913 cm^{-1}) and trisubstituted (838 cm^{-1}) double bonds are suggested by the IR spectral data.

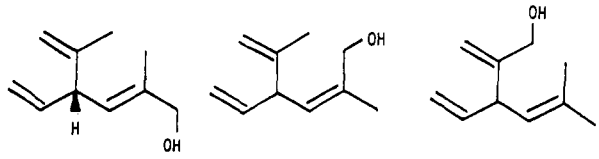
Three singlets corresponding to seven protons are seen in the shielded region of the ^1H NMR spectrum. The 3-H signals at 1.63 and 1.73 ppm can be assigned to a pair of vinyl methyl groups, and the absorption at 1.65 ppm to the hydroxyl proton of the alcohol moiety. A 1-H resonance at 3.65 ppm appears as an overlapping doublet of doublets similar to the triply allylic C_3 proton of santolina triene and lyratol[30,31] **17**, while the 2-H singlet at δ 4.05 can be attributed to α-hydroxy protons (CCH_2OH). The olefinic region of the spectrum integrates to six protons: a 2-H singlet at 4.92, a 3-H multiplet at 5.07, and a complex vinyl hydrogen absorption at 5.78 ppm. Irradiation of the vinyl proton multiplet collapses the signal at 3.65 ppm to a doublet, as does irradiation of the absorption at 5.07 ppm.

The carbon NMR spectrum contains six olefinic absorptions at δ 109.7 (t), 114.4 (t), 124.5 (d), 133.3 (s), 139.7 (d), and 151.0 (s) and implies the presence of vinyl ($CH{=}CH_2$), gem-disubstituted ($C{=}CH_2$), and tribsubstituted ($CH{=}C$) double bonds in view of the IR and ^1H NMR spectral data. Since three degrees of unsaturation are required by the molecular formula, and are fulfilled by double bonds, the molecule must be acyclic.

Three santolinyl systems, lyratol isomers **18** and **19**, and lyratol itself, are consistent with the spectral data as well as biogenetic considerations. A comparison of the ^1H NMR spectra and GLC retention times of this compound with authentic lyratol is sufficient to insure that the unknown was not lyratol.

In theory, **18** and **19** can be differentiated by saturating the terminal double bond systems of the alcohol, and observing the respective changes in the ^1H NMR spectrum. Compound **18** would be expected to yield a product con-

(23) Poulter, C. D.; Muscio, O. J.; Goodfellow, R. J. *J. Org. Chem.* **1975**, *40*, 139.
(24) Uijttewaal, A. P.; Jonkers, F. L.; van de Gen, A. *J. Org. Chem.* **1978**, *43*, 3306.
(25) Uijttewaal, A. P.; Jonkers, F. L.; van de Gen, A. *J. Org. Chem.* **1979**, *44*, 3157.
(26) The ylide had been previously prepared under "salt free" conditions from sodium amide and methyltriphenylphosphonium bromide in refluxing tetrahydrofuran.[30]
(27) Johnson, C. R.; Barbachyn, M. R.; Glick, M. D. *J. Org. Chem.*, preceding paper in this issue.
(28) Shaw, J.; Noble, T.; Epstein, W. W. *Chem. Commun.* **1975**, 590.
(29) The aldehyde most likely arises via a rearrangement process occurring on the GLC column during isolation.
(30) Köster, R.; Sinic, D.; Grassberger, M. A. *Liebigs Ann. Chem.* **1970**, *739*, 211.
(31) Bose, A. K.f Trivedi, G. K.; Chakravarti, K. K. *Tetrahedron* **1969**, *25*, 3217.



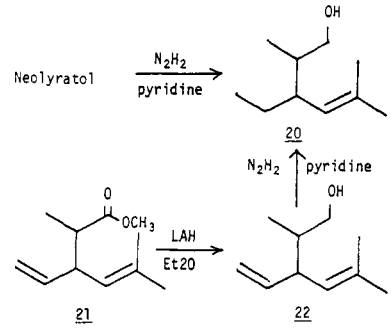
17 18 19

taining three methyl groups attached to saturated carbon atoms and one vinyl methyl group, while **19** would contain two shielded CH_3 groups and retain the isobutenyl [$CH{=}C(CH_3)_2$] moiety. This transformation was achieved by reacting neolyratol, the trivial name given to this compound, with diimide generated from potassium azodicarboxylate (Scheme V). The crude product was shown to be a two component mixture by GLC (80:20), which could be separated by preparative GLC. The IR and ^1H NMR spectra of the major component are completely consistent with structure **20** for the reduction product. Thus alcohol **19** represents neolyratol, since two shielded methyl groups are now evident in the ^1H NMR as a 6-H multiplet at 0.85 ppm, and the two 3-H singlets at 1.62 and 1.72 ppm remain essentially unchanged. The α-hydroxy protons at δ 3.45 also show the expected additional splittings. The second component was identified as the dihydro reduction product (saturated vinyl system) from the corresponding IR and ^1H NMR spectra. $LiAlH_4$ reduction of known methyl santolinate (**21**), followed by diimide reduction of the resulting dienol **22**, afforded an alcohol with identical spectral characteristics to **20** obtained from the previously unknown oil component, further confirming the gross structure assigned to neolyratol.

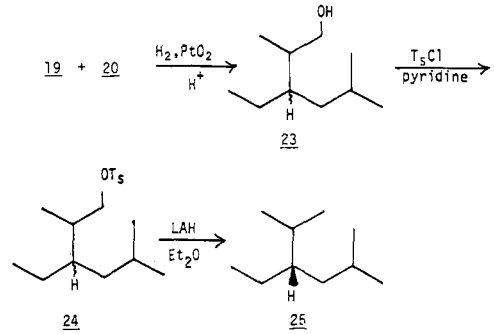
The absolute configuration of **19** was determined by conversion to a known compound as illustrated in Scheme VI. Catalytic hydrogenation of combined (+)-neolyratol and neolyratol-derived **20** afforded a saturated product **23** with spectral and GLC properties characteristic of the alcohol derived from methyl santolinate. This alcohol was reacted with tosyl chloride in pyridine to yield sulfonate ester **24**, as evidenced by the corresponding spectral data. The IR spectrum shows the expected loss of absorptions due to the hydroxyl group (3300 and 1030 cm^{-1}), and new bands indicating the presence of the tosyl system appear (3040, 1600, 840, 1190, and 1185 cm^{-1}). The ^1H NMR spectrum is also consistent with the formation of the tosylate containing 2-H doublets at 7.77 and 7.31 ppm corresponding to the aromatic ring protons, and a 3-H singlet at 2.40 ppm attributable to the phenyl methyl group. Reduction of the tosylate with excess $LiAlH_4$ in ether generated the desired saturated santolinyl hydrocarbon **25**, $[\alpha]_D$ -11.3°. The spectral data obtained from this material are identical to that found by Poulter[32] for the 3*S* hydrocarbon, $[\alpha]_D$ -9.8°, derived from (1*R*,3*R*)-*trans*-chrysanthemol (91.7% optically pure). Thus it follows that the hydrocarbon obtained from **19** is optically pure and possesses the 3*S* absolute stereochemistry. Neolyratol must also exist as the optically pure 3*S* enantiomer since the configuration at C-3 of this system should remain unaltered during the preceding chemical transformations.

The co-occurrence of (1*R*,3*S*,6*S*)-artemiseole, (2*R*,3*S*)-oxidosantolina triene, and (3*S*)-neolyratol provides support for the biosynthetic pathway illustrated in Scheme VII. In vitro experiments have demonstrated that the epoxide readily rearranges to the ether under acid catalysis, presumably via a reactive intermediate such as **26**. This ionic species might also lose a proton from the adjacent methyl group to yield neolyratol in what would have to be an enzyme-mediated step, since no trienol was formed during the in vitro studies. In addition, this sequence is stereochemically consistent with the known absolute configurations of artemiseole, oxidosantolina triene, and neolyratol isolated from *A. tridentata rothrockii*.

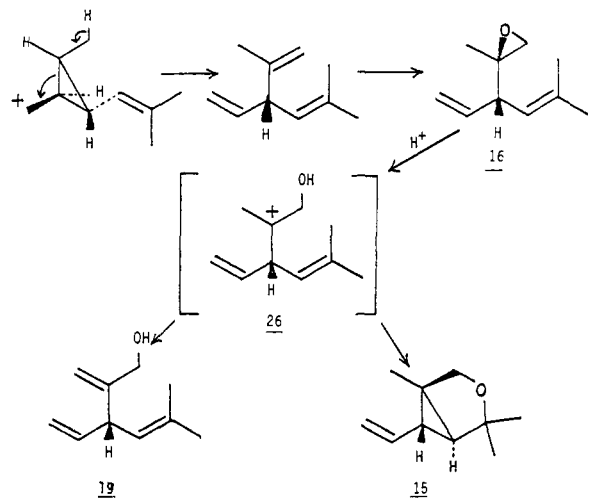
Scheme V



Scheme VI



Scheme VII



The isolation of (1*R*,2*S*)-rothrockene, possessing the previously unknown but predicted "rothrockyl" carbon skeleton, clearly provides support for the proposed unified approach to irregular monoterpene biosynthesis. Furthermore, the absolute configuration of this molecule is stereochemically consistent with the proposed pathway. These results also give credence to the suggestion that plant enzyme systems might function as models for the study of the biosynthesis of squalene in mammals.

The identification of irregular monoterpenes in *A. tridentata rothrockii* may additionally provide useful taxonomic information. We are currently compiling a base of chemotaxonomic data with respect to the genus *Artemisia*, and the evidence suggests that the presence and absolute stereochemistry of irregular monoterpenes may be taxonomically significant.

(32) Poulter, C.D. University of Utah, unpublished results.

Experimental Section

General Methods. The methods employed here are the same as those reported earlier,[33] except that low-resolution GCMS was also obtained from a Shimadzu 9000-S model fitted with a 6 ft × 14 in. glass OV-17 (1%) column. High-resolution mass spectral data (HRMS) were obtained from the laboratory of James McCloskey, University of Utah.

Isolation. The leaves and flower heads of *Artemisia tridentata rothrockii* collected outside of Ephraim, UT, on October 6, 1978,[34] were ground and extracted with pentane for five days in a large soxhlet. The combined extracts were concentrated in vacuo, and vacuum bulb-to-bulb distilled to yield two fractions of a clear oil [60 °C and 65 °C (0.002 mmHg)]. The oil (0.71% dry weight) was eluted through a silica gel column with ethyl acetate:hexanes (v/v, 5:95), and the fractions containing an R_f 0.65 spot were combined and carefully concentrated in vacuo over a cold water bath. GLC analysis of the colorless oil indicated the presence of five major components, with the desired material predominating.

Rothrockene (8) was isolated by preparative GLC on the 15-ft Tween-80 column as a clear oil[4]. Anal. Calcd for $C_{10}H_{16}$: C, 88.16; H, 11.84. Found: C, 88.00; H, 11.76.

The remaining oils were further purified by silica gel column chromatography and MPLC with ethyl acetate:hexanes (v/v, 20:80) to yield an oil with R_f 0.32. GLC analysis showed this material to contain five major components.

Neolyratol (19) was isolated as a colorless oil by preparative GLC on the 15-ft Tween-80 column: $[\alpha]^{26}_D$ +78.7° (*c* 1.60, $CHCl_3$); IR (neat) 3300, 3065, 2970, 2910, 1640, 1630, 1440, 1410, 1400, 1373, 1055, 1025, 995, 913, and 838 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 1.63 (3 H, s), 1.65 (1 H, s), 1.73 (3 H, s), 3.65 (1 H, dd, *J* = 6.0 and 8.0 H), 4.05 (2 H, s), 4.92 (2 H, s), 5.07 (3 H, m), and 5.78 (1 H, m); ^{13}C NMR ($CDCl_3$) δ 17.9 (q), 25.8 (q), 45.6 (d), 65.0 (t), 109.7 (t), 114.4 (t), 124.5 (d), 133.3 (s), 139.7 (d), and 151.0 (s); MS (EI), *m/e* 119 (100%), 41 (98), 91 (79), 79 (66), 67 (64), 39 (50), 55 (48), 77 (45), 93 (39), 95 (37), and 134 (12); calcd for $C_{10}H_{16}O$ 152.1201, found 152.1200.

(±)-Ethyl *trans*-2-(2-Methyl-1-propenyl)cyclopropanecarboxylate (12). A nitrogen purged, 250-mL four-neck round-bottom flask equipped with a mechanical stirrer, a glass stopper, a rubber septum, and a thermometer was charged with 13.07 g (35.2 mmol) of freshly prepared ethyltriphenylphosphonium bromide[35] in 80 mL of dry tetrahydrofuran. The solution was cooled to 0 °C and 16.15 mL (35.2 mmol) of a 2.18 M solution of *n*-butyllithium was added via syringe. The mixture was warmed to room temperature and 2.24 mL (5.1 g, 35.9 mmol) of methyl iodide was slowly added via a syringe. The initially colored reaction mixture faded, was cooled to 0 °C, and an additional 16.15 mL (35.2 mmol) of the *n*-butyllithium solution was added. The mixture was warmed to room temperature, then cooled to −78 °C in a dry ice/acetone bath. Ethyl 2-formyl-1-cyclopropanecarboxylate (Aldrich, 5.0 g, 35.2 mmol) was slowly added via syringe, and the reaction mixture was allowed to stand for 2 h. Anhydrous ether (70 mL) was added, the solution warmed to −25 °C for 1 h, and 36 mL of anhydrous ethanol added. This homogeneous solution was allowed to stand overnight, and poured into a 1-L separatory funnel containing 250 mL of ether. The organic layer was washed with water until the aqueous phase was no longer basic to pH test paper, washed with saturated sodium chloride solution (1 × 100 mL), and dried over anhydrous magnesium sulfate. Concentration in vacuo yielded a crude material which was eluted through a plug of silica gel with ethyl acetate:hexanes (v/v, 20:80) to remove triphenylphosphine oxide. Shortpath distillation under reduced pressure [54–56 °C (1.35 mmHg)] yielded 4.56 g of a colorless oil. GLC analysis (38-ft Tween-80, 131 °C) shows the presence of five components with retention times of 12.6, 13.9, 16.8 (82.5%), 21.9, and 23.0 min. The major component was purified (>95%) by silica gel MPLC with dichloromethane as eluent and distilled under reduced pressure to yield an oil: IR (neat) 2960, 2890, 1715, 1380, 1200, and 1180 cm^{-1}; ^1H NMR ($CDCl_3$, 60 MHz) δ 0.60–2.40 (4 H, m), 1.26 (3 H, t, *J* = 7.2 Hz), 1.72 (6 H, s), 4.15 (2 H, q, *J* = 7.2 Hz) and 4.65 (1 H, d, *J* = 9.8 Hz).

Epimerization of Ethyl Ester 12. Excess sodium metal was dissolved in 3 mL of anhydrous ethanol, and 1 mL of this stock solution was diluted with 4 mL of anhydrous ethanol and placed in a 10-mL round-bottom flask equipped with a magnetic stirring bar and condenser. Ester **12** (25 μL) was added and the solution refluxed under an inert atmosphere for 48 h. The contents were diluted with 10 mL of water and extracted with pentane (3 × 5 mL). The combined pentane layers were washed with saturated sodium chloride solution (1 × 5 mL), dried over anhydrous magnesium sulfate, and concentrated in vacuo to yield a yellowish oil. GLC analysis (38-ft Tween-80, 131 °C) shows only starting material to be present.

(±)-*trans*-1-(1-Methylethenyl)-2-(2-methyl-1-propenyl)cyclopropane (8). A dry, nitrogen purged, 100-mL round-bottom flask equipped with a magnetic stirring bar and rubber septum was charged with 6.25 g (23.8 mmol) methylenetriphenylphosphorane in 60 mL of anhydrous tetrahydrofuran. Ethyl ester **12** (1.00 g, 5.9 mmol) was added to the stirred solution via syringe, and the resulting mixture was allowed to stir for 72 h. The contents of the flask were poured into a 500-mL round-bottom flask containing equal volumes of ice and pentane and stirred overnight. The mixture was filtered, the pentane layer separated, and the water layer was extracted with pentane (4 × 20 mL). The combined pentane layers were washed with water (1 × 40 mL) and saturated sodium chloride solution (2 × 40 mL), dried over anhydrous magnesium sulfate, and concentrated to approximately 10 mL by fractional distillation at ambient pressure. These oils were eluted through a silica gel column with pentane at 0 °C, and the fractions with R_f 0.65 (ethyl acetate:hexanes, v/v, 5:95) were combined and concentrated to a volume of approximately 3 mL by fractional distillation. GLC analysis (15-ft Tween-80, 80 °C) indicated the presence of five components with retention times of 7.7, 11.4, 12.3, 17.3, and 22.0 (79.2%) min. The major component was isolated as a colorless oil by preparative GLC on the 15-ft Tween-80 column: IR (neat) 3060, 2950, 2900, 1635, 1450, 1440, 1375, and 880 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.61 (1 H, m), 0.94 (1 H, m), 1.32 (1 H, m), 1.52 (1 H, m), 1.67 (6 H, s), 1.72 (3 H, d, *J* = 1.3 Hz), and 4.67 (3 H, m); MS (EI), *m/z* 93 (100), 79 (45), 80 (44), 91 (36), 77 (35), 53 (23), 67 (20), 92 (18), 121 (17), 55 (16), 136 (7).

(±)-*trans*-2-(2-Methyl-1-propenyl)cyclopropanecarboxylic Acid (13). A 150-mL round-bottom flask equipped with a magnetic stirring bar and reflux condenser was charged with 13.42 g (95.73 mmol) of (±)-ethyl *trans*-2-(2-methyl-1-propenyl)cyclopropanecarboxylate (**12**) dissolved in 30 mL of methanol and 10.0 g of KOH in 50 mL of H_2O. This solution was refluxed for 3.5 h, added to 200 mL of H_2O, acidified with concentrated HCl, and extracted with diethyl ether (4 × 200 mL). The combined ether layers were washed with water (2 × 100 mL) and saturated NaCl solution (1 × 150 mL) and dried with anhydrous magnesium sulfate. The mixture was concentrated in vacuo to yield a yellow viscous oil which after reduced pressure distillation gave 10.62 g (75.8 mmol, 95%) of a colorless viscous oil: ^1H NMR (acetone-d_6, 90 MHz) δ 0.7–2.25 (4 H, m), 1.68 (3 H, s), 1.72 (3 H, s), 4.68 (1 H, d, *J* = 9.0 Hz), 9.55 (1 H, br s); IR (neat) 3500–2500, 2985, 2905, 1695, 1260, 1105–1010 cm^{-1}.

(+)-*trans*-2-(2-Methyl-1-propenyl)cyclopropanecarboxylic Acid (13). Quinine (23.42 g, 72.19 mmol, Sigma) was dissolved upon warming in a 1.0-L Erlenmeyer flask containing 420 mL of ethyl acetate. 10.12 g (72.19 mmol) of (±)-*trans*-2-(2-methyl-1-propenyl)cyclopropanecarboxylic acid in 280 mL of anhydrous diethyl ether was added to this solution. The flask was stoppered and the resulting yellow solution allowed to cool to room temperature. At room temperature the solution became slightly turbid but no precipitate formed.

A solid suspension formed when the flask was cooled in a dry ice/2-propanol bath. This solid was collected by drawing off the supernatant liquid with an aspirator while maintaining the flask at −78 °C. The resulting sticky semisolid material was then shaken with 200 mL of pentanes to form a white solid material that could be collected by vacuum filtration. After the second recrystallization it was no longer necessary to isolate the solid quinine salt in this manner. Instead, the quinine salt, dissolved in ethyl

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acetate/diethyl ether (60/40, v/v) was cooled in a dry ice/2-propanol bath and suction filtered directly. Seven recrystallizations yielded 7.66 g (16.49 mmol) of resolved quinine salt. This material was then treated with 10% HCl (70 mL) and extracted (3 × 150 mL) with diethyl ether (3 × 150 mL). The combined ether layers were washed with water (2 × 100 mL) and saturated brine solution (1 × 100 mL) and dried over anhydrous magnesium sulfate. Concentration in vacuo yielded 2.24 g (15.97 mmol) of optically active acid $[\alpha]^{amb}_D$ +155.7° (c 4.45, MeOH).

(+)-Methyl *trans*-2-(2-Methyl-1-propenyl)cyclopropanecarboxylate (14). Diazald was used to generate an ethereal solution of CH_2N_2 which was added to a diethyl ether solution of (2.24 g, 15.97 mmol) of (+)-*trans*-2-(2-methyl-1-propenyl)-cyclopropanecarboxylic acid (13) until the yellow CH_2N_2 color persisted. Glacial acetic acid was added dropwise to quench the excess CH_2N_2 and the solution was concentrated in vacuo. Short path vacuum distillation [72 °C (6 mmHg)] gave 2.26 g (14.66 mmol, 92%) of the colorless, optically active methyl ester: $[\alpha]^{amb}_D$ +185.4° (c 2.68, $CHCl_3$); ^1H NMR ($CDCl_3$, 90 MHz) δ 0.62–2.18 (4 H, m), 1.62 (3 H, s), 1.68 (3 H, s), 3.56 (3 H, s), 4.58 (1 H, d, J = 9.0 Hz); IR (neat) 3010, 2950, 2920, 1725, 1205, 1170 cm^{-1}.

(+)-*trans*-1-(1-Methylethenyl)-2-(2-methyl-1-propenyl)-cyclopropane (8). This compound was prepared from (+)-14 using the same procedure as that employed for the preparation of racemic 8.

Methylenetriphenylphosphorane was prepared following the procedure in ref 26 with the exception that NaH was used in place of sodium amide. The phosphorane was not isolated but used directly as a tetrahydrofuran solution. (+)-Methyl *trans*-2-(2-methyl-1-propenyl)cyclopropanecarboxylate (1.07 g, 4.6 mmol) was added to the phosphorane solution via syringe and the mixture stirred under nitrogen for 72 h. The workup procedure was as previously stated: $[\alpha]^{24.4}_D$ +62.7° (c 1.3, $CHCl_3$); ^1H NMR (benzene-d_6, 300 MHz) δ 0.53 (1 H, ddd, J = 8.49, 5.33, 4.56 Hz), 0.91 (1 H, ddd, J = 8.56, 5.72, 4.49), 1.31 (1 H, multiplet), 1.59 (4 H, multiplet), 1.63 (6 H, s), 4.65 (1 H, d of multiplets, J = 8.80 Hz), 4.74 (1 H, dq, J = 13.24, 1.44 Hz), 4.79 (1 H, dq, J = 13.24, 0.84 Hz).

Diimide Reduction of Neolyratol (19). Into a 25-mL three-neck round-bottom flask equipped with a magnetic stirring bar, a rubber septum, a stopper, and a condenser fitted with a drying tube were placed 10 mL of dry pyridine, 0.39 g (2.00 mmol) of freshly prepared potassium azodicarboxylate[36] $(KO_2C)_2N_2$, and 50 mg (0.33 mmol) of alcohol 19. With constant stirring at room temperature, 150 μL of glacial acetic acid were added dropwise through a syringe. After 16 h an additional 150 μL of glacial acetic acid were slowly added, and 142 h later an equal amount of acetic acid was added. An aliquot was removed after 190 h and placed in a 2-mL volumetric tube containing 0.5 mL of ether and 0.5 mL of dilute hydrochloric acid (aqueous). The contents were shaken, the aqueous layer removed, and the ether washed with additional dilute hydrochloric acid (3 × 0.5 mL). GLC analysis of the ether phase revealed the presence of four peaks with retention times 23.5 (11.8%), 26.1 (9.5%), 28.5 (46.0%), and 32.5 (32.7%) min on the 38-ft Tween-80 column at 134 °C. Due to the slow progress of the reaction, 200 μL of glacial acetic acid were added at this time and the reaction mixture was heated to 50 °C in an oil bath for the final 14 days. After 37 days, the contents of the flask were poured into a separatory funnel containing equal portions of ether and dilute hydrochloric acid, shaken, and the phases separated. The aqueous layer was extracted with ether (2 × 20 mL), and the combined ether layers washed with dilute hydrochloric acid (3 × 30 mL) until the pyridine was completely removed. The organic layer was washed with water (1 × 20 mL), dried over anhydrous magnesium sulfate, and concentrated in vacuo. GLC showed two peaks which subsequently proved to be the tetrahydro reduction product (80%) and the dihydro product (20%) with retention times 23.5 and 26.1 min, respectively. The tetrahydro alcohol was isolated as a clear oil by preparative GLC on the 25-ft Carbowax 20 M column: $[\alpha]^{30}_D$ −21.9° (c 2.7, $CHCl_3$); IR (neat) 3290, 2935, 2850, 1445, 1370, and 1025 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 0.85 (6 H, m), 1.30 (4 H, m), 1.62 (3 H, s), 1.72 (3 H, s), 2.20 (1 H, m), 3.45 (2 H, m), and 4.88 (1 H, d, J = 10.5 Hz).

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The dihydro alcohol 20 was also isolated as a colorless oil by preparative GLC on the 25-ft Carbowax 20-M column: IR (neat) 3300, 3060, 2940, 2900, 2850, 1640, 1450, 1380, 1050, 900, and 840 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 0.84 (3 H, t, J = 7.2 Hz), 1.00–1.55 (3 H, m), 1.60 (3 H, s), 1.70 (3 H, s), 2.80 (1 H, m), 4.02 (2 H, s), and 4.90 (3 H, d, J = 9.8 Hz).

$LiAlH_4$ Reduction of Methyl Santolinate (21). Into a 25-mL three-neck round-bottom flask equipped with a magnetic stirring bar, a condenser, a stopper, and a rubber septum were placed 35 mg (0.92 mmol) of $LiAlH_4$ and 10 mL of anhydrous ether. The diastereomeric ester mixture 21 (53 mg, 0.29 mmol) was dissolved in anhydrous ether and added to the stirred suspension in a dropwise manner through a syringe. The reaction mixture was refluxed for 2 h before quenching with 210 μL of saturated sodium chloride solution (aqueous). The ethereal solution was filtered, and the product concentrated in vacuo to yield 43 mg (0.28 mmol), 96%) of a yellowish oil shown to be a single component by analytical GLC: IR (neat) 3300, 3065, 2900, 1635, 1445, 1380, 1035, 915, and 840 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 1.24 (3 H, d, J = 9.5 Hz), 1.63 (3 H, s), 1.75 (4 H, s), 3.00 (1 H, m), 3.53 (3 H, m), 5.03 (3 H, m), and 5.70 (1 H, m).

Diimide Reduction of Alcohol 22. Into a 15-mL vial equipped with a rubber septum and a magnetic stirring bar were placed 5 mL of dry pyridine, the alcohol 22 (43 mg, 0.28 mmol), and 140 mg (0.72 mmol) of freshly prepared potassium azodicarboxylate. To the stirred solution were added 42 μL of glacial acetic acid in a dropwise manner, and after 2 h an additional 42 μL were added. After 4 days, the contents of the vial were transferred to a separatory funnel containing equal volumes of ether and dilute hydrochloric acid (aqueous). The mixture was shaken and the ether layer decanted, washed with dilute hydrochloric acid (2 × 10 mL), and dried over anhydrous magnesium sulfate. The solution was filtered and concentrated in vacuo to yield 41 mg (0.26 mmol, 94%) of an orangish oil. The dihydro product was obtained as a colorless oil by preparative GLC on the 25-ft Carbowax 20 M column; IR (neat) 3300, 2900, 1665, 1450, 1375, and 1025 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 0.85 (6 H, m), 1.30 (4 H, m), 1.60 (3 H, s), 1.70 (3 H, s), 2.20 (1 H, m), 3.45 (2 H, m), and 4.90 (1 H, d, J = 9.8 Hz).

Hydrogenation of Combined Alcohols 19 and 20. Neolyratol 19 (41 mg, 0.27 mmol) and neolyratol-derived 20 (33 mg, 0.21 mmol) were combined with 30 mg of PtO_2 and 10 mL of ethanol in a Parr hydrogenation flask. The mixture was shaken for 2 h under 25 psi H_2, filtered, and concentrated to yield 75 mg (0.47 mmol, 98%) of a yellowish oil: IR (neat) 3300, 2920, 2910, 2860, 1460, 1380, 1365, and 1030 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 0.65–2.10 (20 H, m), and 3.54 (2 H, m).

Preparation of Tosylate 24. Into a 10-mL vial equipped with a magnetic stirring bar and rubber septum were placed alcohol 23 (75 mg, 0.48 mmol), tosyl chloride (122 mg, 0.64 mmol), and 2 mL of dry pyridine, and the mixture was stirred at room temperature for 44 h. The contents were diluted with 5mL of ether, the precipitated inorganic salts filtered and washed with ether, and the combined organic layers stirred over 20 mL of 10% sodium hydroxide solution (aqueous) for 24 h. The ether layer was decanted, the aqueous layer extracted with ether (5 × 5 mL), and the combined organic phases washed with water (1 × 5 mL), dried over anhydrous magnesium sulfate, and concentrated in vacuo to yield 127.2 mg (0.41 mmol, 85%) of a yellow oil: IR (neat) 3040, 2940, 2900, 2860, 1600, 1470, 1365, 1190, 1185, 1100, 970, 840, 820, and 670 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 0.65–0.95 (12 H, m), 1.00–2.00 (7 H, m), 2.40 (3 H, s), 3.90 (2 H, m), 7.31 (2 H, d, J = 9 Hz), and 7.77 (2 H, d, J = 9 Hz).

$LiAlH_4$ Reduction of Tosylate 24. Into a 25-mL three-neck round-bottom flask equipped with a magnetic stirring bar, a condenser, a glass stopper, and a rubber septum, were placed 99 mg (2.61 mmol) of $LiAlH_4$ and 10 mL of anhydrous ether. Tosylate 24 (127 mg, 0.41 mmol) was added to the stirred suspension in a dropwise manner, the mixture refluxed for 48 h, and quenched with 595 μL of saturated sodium chloride solution (aqueous). The ethereal solution was decanted from the inorganic salts, transferred to a separatory funnel in a cold room (0 °C), and washed with saturated sodium bicarbonate solution (2 × 20 mL). The aqueous layer was back extracted with ether (1 × 20 mL), and the combined ether layers were dried over anhydrous magnesium sulfate, decanted, and concentrated by fractional distillation to approxi-

mately 1 mL. The product (86% by GLC) was purified by preparative GLC on the 15-ft Tween-80 column: $[\alpha]^{21}_D$ -11.3° (c 1.19, $CHCl_3$); IR (neat) 2930, 2900, 2850, 1460, 1380, and 1360 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 0.76-1.97 (m).

Formic Acid Catalyzed Rearrangement of 16. Into a 10-mL vial fitted with a cap and magnetic stirring bar were placed 1 mL of formic acid (Mallinckrodt, 88%) and epoxide **16**. The mixture was stirred at room temperature for 20 min and transferred to a separatory funnel containing 10 mL of water. The contents were extracted with pentane (4 × 2 mL), washed with water (1 × 2 mL) and saturated sodium bicarbonate solution (1 × 2 mL), dried over anhydrous magnesium sulfate, and concentrated to 0.5 mL in vacuo. GLC (38-ft Tween-80, 100 °C) shows one major component (>95%). This material was isolated by preparative GLC on the 15-ft Tween-80 column and proved to be (+)-artemiseole (**15**): $[\alpha]^{26}_D$ +17.0° (c 0.9, $CHCl_3$); ^1H NMR ($CDCl_3$, 60 MHz) δ 1.15-1.23 (10 H, m), 1.52 (1 H, dd), 3.66 (2 H, dd), 4.88-5.18 (2 H, m), 5.35-5.75 (1 H, m).

Structural Effects in Solvolytic Reactions. 47. Effects of *p*-Alkyl and *p*-Cycloalkyl Groups on the Carbon-13 NMR Shifts of the Cationic Carbon Center in *p*-Alkyl-*tert*-cumyl Cations

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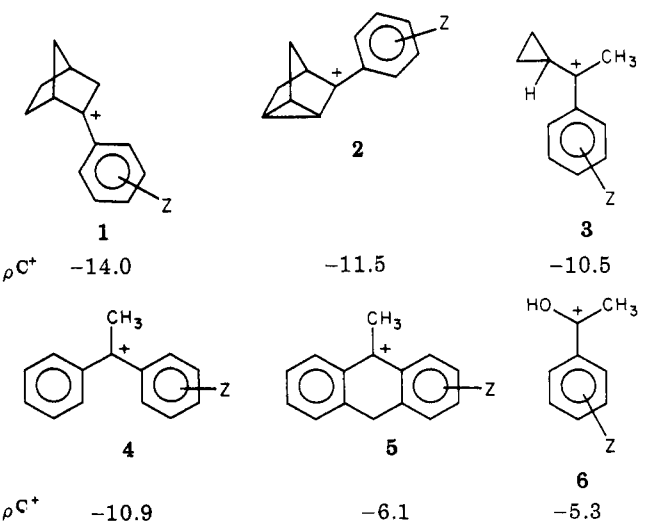
A series of *p*-alkyl- and *p*-cycloalkyl-*tert*-cumyl cations were prepared in $SbF_5/FSO_3H/SO_2ClF$ at -78 °C, and their ^{13}C NMR shifts were measured at -80 °C. The C^+ carbon in the *p*-alkyl derivatives is increasingly deshielded from *p*-methyl through *p*-*tert*-butyl. This observation is in accord with the Baker-Nathan order of stabilization (methyl > ethyl > isopropyl > *tert*-butyl) and in agreement with the rate data for the solvolysis of *p*-alkyl-*tert*-cumyl chlorides but in contrast to the gas-phase stability order for the para-protonated alkylbenzenes ($RC_6H_6^+$). Possible reasons for this difference in the apparent effects of these four alkyl groups are discussed. The stability order achieved by cycloalkyl groups based on the C^+ shifts is *p*-cyclopropyl ≫ *p*-cyclobutyl ≃ *p*-cyclopentyl > *p*-cyclohexyl. In the case of *p*-cyclopropyl-*tert*-cumyl cation, the C^+ signal appears relatively shielded (231.6 ppm) compared to the C^+ shift (244.0 ppm) for the *p*-isopropyl-*tert*-cumyl cation. This observation supports the ability of the cyclopropyl group to supply electrons (through C-C hyperconjugation) to the electron-deficient center without the intervention of σ-bridging through space. For other cycloalkyl derivatives, the C^+ signals of the *p*-cyclobutyl and *p*-cyclopentyl derivatives appear slightly upfield relative to the *p*-cyclohexyl derivatives. This may again be attributed to the greater hyperconjugating (CH and CC) ability of the strained cyclobutyl and cyclopentyl bonds, as compared with the nonstrained cyclohexyl bonds. For the *p*-norbornyl-*tert*-cumyl derivatives examined (*exo*-2- and *endo*-2-norbornyl and *exo*-5,6-trimethylene-*exo*- and -*endo*-2-norbornyl), the C^+ for the exo derivatives is relatively shielded compared to the C^+ of the endo derivatives. Although it may be attractive to interpret this observation in terms of a greater electron supply by the exo derivatives, the small effects may very well arise from the steric factors in the endo derivatives. Accordingly, the apparent stabilizing ability of the norbornyl moiety, as indicated by the relatively less negative ρ^{C^+} value (-14.0) observed in the $\Delta\delta C^+/\sigma^{C^+}$ plot of the 2-aryl-2-norbornyl cations, cannot be confirmed by this direct examination of the comparative electron-releasing characteristics of these two *exo*- and *endo*-norbornyl substituents.

Recently we studied the possibility of achieving linear correlations for the ^{13}C NMR shifts of many aryldialkyl carbocations.[1-6] We have observed that the $\sigma^{C^+}/\Delta\delta C^+$ plots of a number of these cations are linear and give ρ^{C^+} values in the range of -16 to -18, with the exception of the 4-aryl-4-heptyl system, which yielded a ρ^{C^+} value of -14.6.[6] We have also observed that in several other systems (Chart I), the $\sigma^{C^+}/\Delta\delta C^+$ plots are linear only for electron-donating substituents.[7-10] The ρ^{C^+} values observed in these cations are relatively less negative (Chart I). Further, in these systems (**1-6**), the data points for the electron-withdrawing substituents deviate upward from the correlation line

Chart I



defined by the electron-donating substituents.[7-10]

We considered the possibility that the low ρ^{C^+} values and the deviation in the $\rho^{C^+}/\Delta\delta C^+$ plots might arise from the greater conjugating (or hyperconjugating) ability of these

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