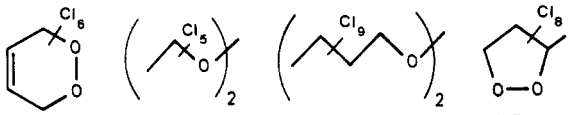
oxidation reaction;[17] these appear, rather, to arise from peroxides such as 11 and 12, which we have not detected. The existence of a peroxidic component in the chlorine-sensitized oxidation of 5 is indicated only by the detection of a short-lived, nonpolar component giving the peroxide test with Ph_2NH. The hazards of assigning a structure from the nature of the products are evident from the preceding example.



9 10 11 12

We are presently investigating further the product resulting when bromine, rather than chlorine, is used to sensitize the oxidation of 1. This is a bromine-containing peroxide which may be an analogue of 6.

Although no explosions or spontaneous decompositions were observed with these peroxides, care should be exercised in handling them. In view of their high chlorine content, they should also be assumed to be toxic.

Registry No. 1, 77-47-4; 2, 2227-17-0; 3, 87-68-3; 4, 127-18-4; 5, 1888-71-7; 6, 79991-54-1; 7, 79991-55-2; 8, 79991-56-3; 9, 79991-57-4; 10, 79991-58-5; hexachloro-3-cyclopentenone, 15743-12-1; hexachloro-2-cyclopentenone, 2514-52-5; perchloro-3a,4,7,7a-tetrahydro-4,7-methanoinden-1-one, 5263-60-5.

Supplementary Material Available: Table of atomic positional and thermal parameters for 6 and a structure showing the complete numbering scheme (2 pages). Ordering information is given on any current masthead page.

(17) These are perchloropropene and pentachloroacetone, believed to arise from 11 and 12, respectively.

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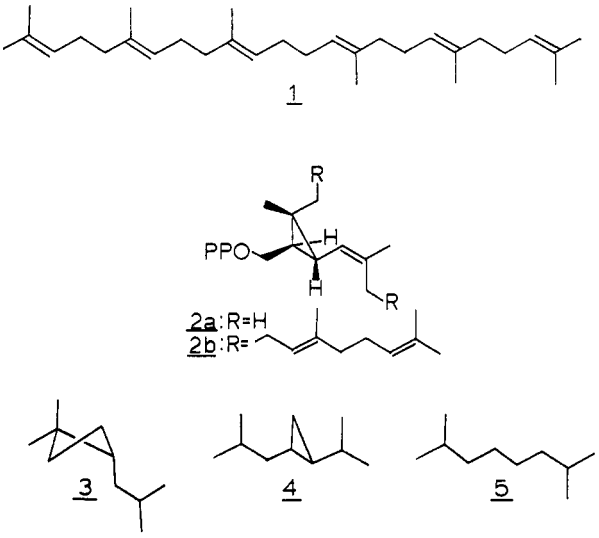
trans-2-(2-Propenyl)-1-(2-methyl-1-propenyl)cyclopropane (Rothrockene). A Non-Head-to-Tail Monoterpenoid with a New Skeletal System from *Artemisia tridentata rothrockii*[1]

Summary: The structure of *trans*-2-(2-propenyl)-1-(2-methyl-1-propenyl)cyclopropane (6), a monoterpene possessing a new non-head-to-tail carbon skeleton, has been determined by spectral and chemical means. The isolation of 6 supports the hypothetical analogy drawn between non-head-to-tail monoterpene biosynthesis and squalene biogenesis.

Sir: It has been proposed that non-head-to-tail monoterpene biosynthesis might serve as a model for the study of the biogenesis of the important triterpene squalene 1.[2] The formation of these non-head-to-tail terpenes presumably involves ionization and rearrangement of the structurally analogous cyclopropyl intermediates, chrysanthemyl pyrophosphate 2a[2] and presqualene pyrophosphate 2b.[3] This hypothetical analogy predicts the occurrence of three irregular monoterpenoid skeletal systems 3, 4, and 5, in addition to those already known.



1 2a: R=H 2b: R= 3 4 5

As part of this study we have been screening plants of the Anthemideae tribe of the Compositae family for irregular monoterpenoid components, and a number of new compounds have been identified.[4-8] We now report the isolation of a structurally novel compound obtained from the volatile oils of the sagebrush *Artemisia tridentata rothrockii* for which we propose the trivial name rothrockene and structure 6.

Essential oils of *A. tridentata rothrockii*[9] were obtained by techniques developed previously[5] and shown to contain a previously unidentified component. Isolation by silica gel chromatography, with final purification by preparative gas chromatography, afforded a fragrant oil which analyzed for $C_{10}H_{16}$ (13.8% of oil): $[\alpha]_D$ -64.8° (*c*, 1.33, $CHCl_3$); IR (neat) 3060, 2950, 2900, 1635, 1450, 1440, 1410, 1375, 970, 885 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.61 (1 H, m), 0.95 (1 H, m), 1.32 (1 H, m), 1.52 (1 H, m), 1.67 (6 H, s), 1.72 (3 H, s), 4.62 (1 H, m), 4.67 (2 H, m); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 13.8 (t), 18.3 (q), 19.2 (q), 20.8 (q), 25.6 (d), 27.1 (d), 108.0 (t), 127.5 (d), 131.2 (s), 145.7 (s); EI mass spectrum, *m/z* (relative intensity, %) 93 (100), 91 (40), 79 (33), 80 (32), 77 (27), 121 (22), 105 (18), 92 (18), 67 (13), 136 (8).

A consideration of the above data suggested the presence of isopropenyl [$-C(CH_3)=CH_2$] and isobutenyl [$-CH=C(CH_3)_2$] double bond moieties. A 1,2-disubstituted cyclopropyl ring system was indicated by the ^1H NMR chemical shifts and line patters exhibited by the four protons at 0.61, 0.95, 1.32, and 1.52 ppm and by the fact that a ring is required to complete the three degrees of unsaturation dictated by the molecular formula. These units can be assembled to yield either a *cis*- or *trans*-dialkenylcyclopropane; however, the known thermal insta-

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(9) A voucher specimen, collected near Ephraim, UT, is available at the University of Utah Herbarium.

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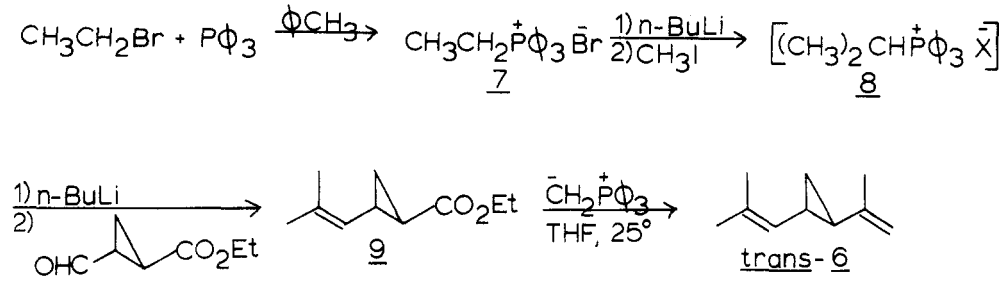
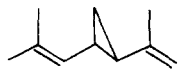
Scheme I



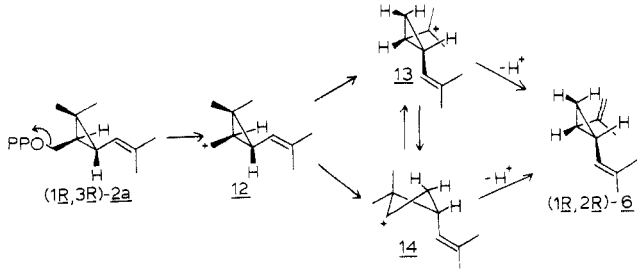
bility of *cis*-dialkenylcyclopropanes[10] argues against this possibility, leaving structure **6** for rothrockene.



6

Structure **6** was unambiguously confirmed by the synthetic sequence shown in Scheme I. A "one-pot" conversion of ethyltriphenylphosphonium bromide **7** into cyclopropyl ester **9** was effected by using the procedure of Bertel and Schudel[11] followed by purification by silica gel chromatography (100% CH_2Cl_2).[12,13] Transformation of **9** into **6** was achieved by use of a fourfold excess of "salt-free" methylenetriphenylphosphorane.[14-16] The product was purified by silica gel chromatography (5:95, ethyl acetate–hexanes) and preparative gas chromatography (Tween-80) to yield a colorless oil with IR, MS, and NMR spectral properties identical in every respect except optical activity with those of **6** isolated from *A. tridentata rothrockii*. The possibility that epimerization of **9** had occurred during the Wittig reaction was ruled out when strong base equilibration experiments failed to induce such a transformation, establishing the relative stereochemistry as trans.

Experiments to determine the absolute configuration of **6** are now in progress; however, a consideration of the proposed biosynthetic route suggests the stereochemical outcome. Ionization of **2a** to **12** followed by rearrangement can lead to **6** directly via **13** or indirectly via the cyclobutyl intermediate **14**. In either case, loss of a proton would be expected to yield rothrockene with the 1*R*,2*R* absolute configuration. The assumption that **2a** is the precursor to the non-head-to-tail monoterpenes in *A. tridentata rothrockii* rather than the 1*R*,3*S* cis isomer[7] is in agreement with the chiroptical properties of other non-head-to-tail components isolated from these oils.[17]



Although the "rothrockyl" skeleton represents a new structural class of naturally occurring organic molecules, its biological existence was predicted in 1973.[2] The isolation of **6** provides support for the unified approach to irregular monoterpene biosynthesis and for the proposal that plant enzyme systems might act as simple models for the study of squalene biosynthesis in mammals.

Registry No. (−)-*trans*-**6**, 80082-35-5; (±)-*trans*-**6**, 80082-36-6; **7**, 1530-32-1; (±)-*trans*-**9**, 53166-50-0; ethyl (±)-*trans*-2-formylcyclopropanecarboxylate, 77183-91-6.

(17) Gaudioso, L. A. Ph.D. Dissertation, University of Utah, Salt Lake City, UT, 1980.

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Monobactams. Stereospecific Synthesis of (*S*)-3-Amino-2-oxoazetidine-1-sulfonic Acids

Summary: A facile, stereospecific synthesis of 3-amino-2-oxoazetidine-1-sulfonic acids (monobactams) by the cyclization of acyl sulfamates derived from β-hydroxy amino acids is described.

Sir: In the preceding communication we described initial synthetic work on monobactams in which the characteristic 2-oxoazetidine-1-sulfonic acid functionality **1** was prepared by the sulfonation of penicillin-derived azetidinone **2** (retrosynthetic path a).[2] In this communication we describe a novel, stereospecific synthesis of monobactams (**1**) based on retrosynthetic path b in which an acylic acylsulfamate (**5**) is cyclized to afford **1** directly. Impetus for this investigation was provided by the finding of increased β-lactamase stability and antimicrobial activity for certain 4-methylmonobactams not readily available from penicillin and the inefficiency of the sequence **6** → **4** → **3** → **2** → **1** utilized to convert β-hydroxy amino acids to **1**. This latter sequence incorporates our modifications[3] of the initial Miller methodology.[4] For the conversion of **6** (X = OH) to **1**, the *N*-methoxyl group, used to facilitate cyclization,[5] is replaced by reductive removal followed by sulfonation.

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(1) Present address: FMC Corporation, Agricultural Chemicals Group, Princeton, NJ 08540.
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(4) Miller, M. J.; Mattingly, P. G.; Morrison, M. A.; Kerwin, T. F., Jr. *J. Am. Chem. Soc.* **1980**, *102*, 7026–7032 and references therein.
(5) Miller has discussed the effect of the alkoxyl group on lowering the amide pK_a and the ramifications of this effect.[4] See also Bose, A. K.; Sahu, D. P.; Manhas, M. S *J. Org. Chem.* **1981**, *46*, 1229–1230.

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