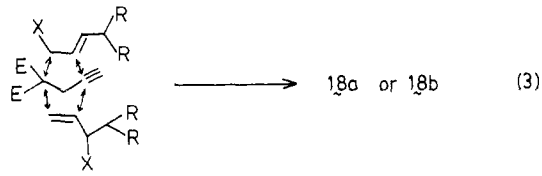
diverted to other products. These possibilities in addition to mechanistic studies form the basis of current studies. Overall, the current reaction allows a novel cyclopentannulation of an allylic derivative (eq 3).



(3)

Acknowledgment. We thank the NSF for support of our programs. Mark Lautens thanks NSERC (Canada) for a predoctoral fellowship.

Registry No. 1, 95123-89-0; **2**, 95123-90-3; **3**, 95123-91-4; **4**, 95123-92-5; **5**, 95123-93-6; *cis*-**6**, 95123-94-7; *trans*-**6**, 95123-95-8; **7**, 95123-96-9; $\Delta^{6,7}$-**8**, 95123-97-0; $\Delta^{7,8}$-**8**, 95123-98-1; **9**, 95123-99-2; **10**, 95124-00-8; **11**, 95124-01-9; **12**, 95124-02-0; **13**, 95124-03-1; **14**, 95124-04-2; **15**, 95124-05-3; $(MeO)_2CH(CH_2)_9CH(OAc)CH{=}CH_2$, 88399-89-7; (E)-$CH_3CH{=}CHCH(OAc)CH_3$, 31001-80-6; $CH{\equiv}CCH_2CH(CO_2C-H_3)_2$, 95124-07-5; $[(o\text{-}CH_3C_6H_4)_3P]_2Pd(OAc)_2$, 69073-98-9; $(CH_3C-N)_2PdCl_2$, 14592-56-4; $(Ph_3P)_2Pd(OAc)_2$, 14588-08-0; methyl *cis*-5-acetoxycyclohex-3-enecarboxylate, 60729-55-7; 1-acetoxy-2-methylenecyclohexane, 53723-50-5; (1-acetoxyprop-2-en-1-yl)cyclohexane, 95124-06-4; 4-(1-acetoxyprop-2-en-1-yl)-2,2-dimethyl-1,3-dioxolane, 18524-20-4; 22(*S*)-(acetyloxy)chola-4,23-dien-3-one, 85994-21-4; maleic anhydride, 108-31-6.

2-Thiabicyclo[2.2.1]hept-5-ene *endo*-2-Oxide Derivatives: Stereospecific Formation, Rearrangement to Bicyclic Sultenes, and Conversion to (*E*)-5-Alkylidene-2-cyclopentenones[1]

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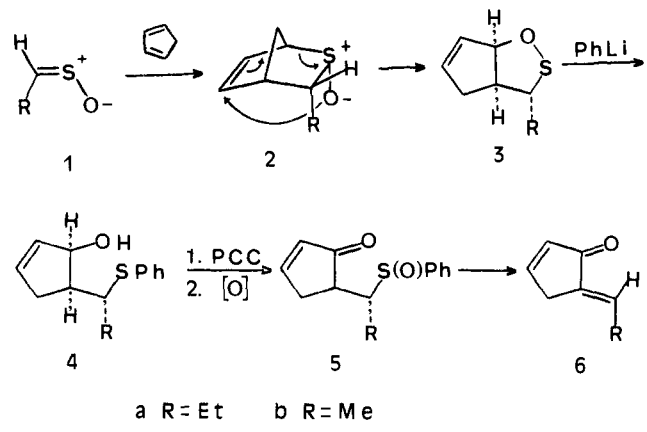
Received September 10, 1984

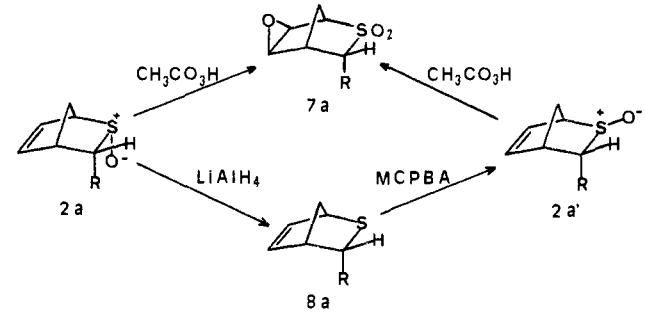
Diels–Alder adducts of cyclopentadiene and thiocarbonyl compounds[2] are attractive intermediates for the controlled synthesis of polyfunctional cyclopentanoids through sulfur-mediated transformations followed by desulfurization. We find that *endo*-sulfoxides **2**, prepared stereospecifically from cyclopentadiene and alkanethial *S*-oxides **1**, readily rearrange to bicyclic sultenes **3**, representatives of a rare class of sulfur heterocycles, which in turn may be easily converted to various cyclopentenoids including (*E*)-5-alkylidene-2-cyclopentenones (**6**) (eq 1).

Addition of cyclopentadiene to a Freon 11 solution of (*Z*)-propanethial *S*-oxide (**1a**),[3] obtained by dehydrochlorination of propanesulfinyl chloride with triethylamine, gave a single product characterized[4] as *endo*-3-ethyl-2-thiabicyclo[2.2.1]hept-5-ene *endo*-2-oxide (**2a**) (eq 1). Thus, on the basis of an X-ray crystal structure of epoxy sulfone **7a** (R = Et),[4] prepared by peracetic acid oxidation of **2a**, we conclude that **2a** has an *endo*-ethyl group. Reduction of **2a** to sulfide **8a** and reoxidation with MCPBA gave a different sulfoxide, **2a′**, also converted to epoxy sulfone **7a** by



(1)

oxidation (eq 2). The presence of an *exo*-sulfoxide oxygen in



(2)

2a′, anticipated on the basis of the stereochemistry of oxidation of 2-thiabicyclo[2.2.1]heptane[5] (**9**; *exo*-sulfoxide favored with MCPBA), was unequivocally established by $Eu(fod)_3$ and aromatic solvent induced shift studies giving results in good agreement with similar studies on the two *S*-oxides of **9**.[6] The endo,endo ethyl group–sulfoxide oxygen relationship in **2a** is consistent with a stereospecific Diels–Alder reaction of (*Z*)-**1a**[7] following the Alder endo rule.

Also consistent with an *endo*-sulfoxide oxygen in **2a** is the striking difference in reactivity of sulfoxides **2a** and **2a′**. While isomer **2a′** was unchanged after refluxing in toluene for 20 h, sulfoxide **2a** rearranges at room temperature, presumably via a [2,3]-sigmatropic shift,[8] to 4-ethyl-2-oxa-3-thiabicyclo[3.3.0]-oct-7-ene (**3a**) (eq 1), a rare example of an isolable sultene.[9] Compound **3a**, obtained in 51% yield (based on propanesulfinyl chloride) after refluxing a methylene chloride solution of **2a** for 1.5 h followed by vacuum distillation (bp 75 °C (0.05 mm)), is a pale yellow oil homogeneous by capillary GC and showing the absence of an S=O group or other functionality other than C=C in the IR.[10] Similarly, 4-methyl-2-oxa-3-thiabicyclo[3.3.0]oct-

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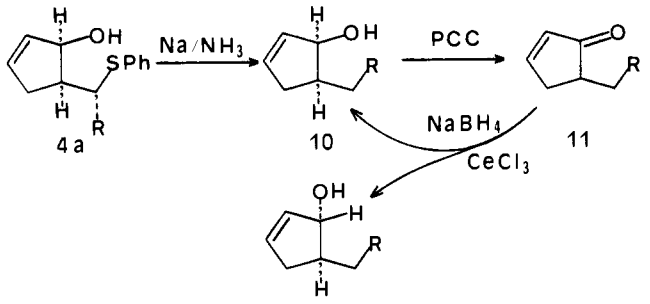
7-ene (**3b**)[4] (bp 55 °C (0.05 mm)), could be prepared by rearrangement of cyclopentadiene–ethanethial *S*-oxide (**1b**) adduct **2b** (67% yield based on **1b** precursor, ethanesulfinyl chloride). Sultene **3a** can be oxidized with MCPBA to a pair of sultines which in turn can be converted to a single sultone.

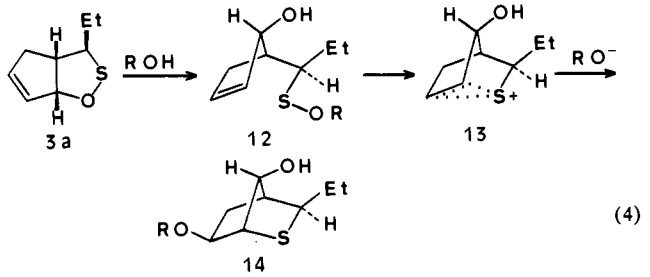
Sultene **3a** readily reacts with phenyllithium giving alcohol **4a** in quantitative yield. In order to establish the structure of alcohol **4a**, it was desulfurized (Na/NH_3) giving unsaturated alcohol **10** (eq 3) which was oxidized (PCC)[11] to 5-propyl-2-cyclopentenone



(3)

(**11**).[12] Alcohol **10** formed from **4a** is identical with the major product of reduction of **11** with sodium borohydride–cerium chloride.[13] To demonstrate the synthetic utility of alcohol **4a** we have subjected this compound to sequential oxidation at carbon (PCC) and then at sulfur (MCPBA or sodium metaperiodate) at 0 °C followed by flash distillation at 25 °C giving directly (*E*)-5-propylidene-2-cyclopentenone (**6a**, R = Et)[4] by way of unstable sulfoxide **5a** (eq 1), in 42% overall yield from **3a**. In a similar manner (*E*)-5-ethylidene-2-cyclopentenone (**6b**, R = Me)[14a] could be prepared in 38% overall yield from sultene **3b**. Use of substituted cyclopentadienes together with appropriate sulfines should allow synthesis of more complex 5-alkylidene-2-cyclopentenones, of interest as antibiotics.[14b]

Sultene **3a** also reacts rapidly with thiols giving disulfides analogous to **4a** (R'S instead of Ph) and with alcohols giving *exo*-6-alkoxy-*exo*-3-ethyl-*syn*-7-hydroxy-2-thiabicyclo[2.2.1]-heptanes (**14**; e.g., R = *t*-Bu[4]), all in quantitative yields. Compounds of type **14** are presumably formed by way of sulfenate esters **12** and episulfonium ions **13** (eq 4). Formation of epi-



(4)

sulfonium ions related to **13** from 3-cyclopentenyl derivatives as well as ring opening of these ions to 6,7-disubstituted 2-thiabicyclo[2.2.1]heptanes has been noted previously.[2e,15] On standing sultene **3a** gradually forms a polymer[4] lacking olefinic protons in the NMR; this polymer may involve a repeating 3-ethyl-6,7-oxy-2-thiabicyclo[2.2.1]heptane system similar to **14**.

Acknowledgment. We gratefully acknowledge support for this work by the donors of the Petroleum Research Fund, administered by the American Chemical Society, the National Science Foundation, the Société Nationale Elf Aquitaine, the John Simon Guggenheim Memorial Foundation (E.B.), and the National Institutes of Health (J.Z.). Funding for the SUNYA 300-MHz NMR facility was provided by the National Science Foundation (Grant CHE 8313711). We thank Professors Carl Johnson, Frank Davis, and Amos Smith for helpful discussions and Dr. A. A. Bazzi for initial studies on this project.

Supplementary Material Available: Tables of spectroscopic and crystal data, atomic coordinates and temperature factors, bond lengths and bond angles, anisotropic temperature factors, hydrogen atom positions, and observed and calculated structure factors and a perspective view of **7a**, R = Et (15 pages). Ordering information is given on any current masthead page.

Persulfide-Bridged Iron–Molybdenum–Sulfur Clusters of Biological Relevance: Two Synthetic Routes and the Structures of Intermediate and Product Clusters

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Recent research in this laboratory[2-4] has been directed toward attainment of a synthetic representation of the iron–molybdenum cofactor (FeMo-co) of nitrogenase.[5] Among the relevant species are the double- and single-cubane clusters $[Mo_2Fe_6S_8(\mu_2\text{-}L)_3(SR)_6]^{3-,5-}$ (L = RS^-, RO^-)[3,6] and $[MoFe_3S_4(SR)_3(cat)L']^{2-,3-}$,[4] respectively, which contain the $MoFe_3(\mu_3\text{-}S)_4$ unit. Single cubanes, in particular, display electronic properties[4e] and a Mo coordination site[4bcf] (XAS criteria) similar to those of FeMo-co.[5,7] We report two synthetic routes to a new class of double cubanes, containing persulfide bridges, and the structures of intermediate and product clusters. Reactions were conducted under anaerobic conditions.

A solution of $Li_2[Fe_2S_2(CO)_6]$[8] (5.8 mmol) in 100 mL of THF at −78 °C was treated with equimolar $(Et_4N)_2[Cl_2FeMoS_4]$[9] in

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(10) Compound **3a** shows UV absorption at 310 nm (ε 60), ^{13}C NMR peaks at δ 136.7, 128.1, 95.1, 64.8, 51.0, 39.3, 27.2, and 12.8 ppm, and ^1H NMR peaks at δ 5.85 (m, 1 H), 5.5 (m, 1 H), 5.2 (m, 1 H), 3.25 (d t, 1 H), 2.78 (m, 1 H), 2.4 (m, 2 H), 1.75 (q, 2 H), 0.95 ppm (t, 3 H).
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