THF at −78° for 5 hr gives an 88% yield of **4c** with 97.5% stereospecificity. Compound **5** is in turn obtained *via* the known stereoselective addition of a sulfonyl iodide to an acetylene,[14] in 56% isolated yield.

It is interesting to note that, while monoalkylcopper(I) reagents add cleanly to α,β-acetylenic sulfoxides, lithium dialkylcuprates may also give a product resulting from the cleavage of the acetylenic sulfoxide. While lithium dimethylcuprate adds normally to **1a** (83%) and **1b** (97.5%, >96% cis addition), the more reactive lithium di-*n*-butylcuprate reacts to give appreciable quantities of *n*-butyl ethyl sulfoxide (**6**) as well, apparently arising from attack by the organocopper(I) reagent at sulfur rather than on the triple bond.

$$1 + (n\text{-}C_4H_9)_2CuLi \xrightarrow[-78°]{THF} \underset{\mathbf{6}}{n\text{-}C_4H_9S(O)C_2H_5} + 3 \qquad (5)$$

Like results have been observed for additions of organocopper(I) reagents to α,β-acetylenic sulfones,[8] ethyl 1-propynyl sulfone giving an 81% yield of adduct with lithium di-*n*-butylcuprate and a 90% yield with *n*-butylcopper. However, here a difference between the two types of organocopper(I) reagents is manifest in the stereochemistry of the product, *n*-butylcopper giving 92% cis addition while di-*n*-butylcuprate gives, on work-up, 81% of the product, which would correspond to overall trans addition.[15]

References and Notes

(1) Presented at the 167th National Meeting of the American Chemical Society, Los Angeles, Calif., March 31–April 5, 1974, Abstract ORGN-70.
(2) Financial support for this work was provided in part by the National Institutes of Health, Grant CA-04536, for which the authors are grateful.
(3) For a recent review, see G. H. Posner, *Org. React.*, **19**, 1 (1972).
(4) G. H. Posner and D. J. Brunelle, *J. Org. Chem.*, **38**, 2747 (1973).
(5) (a) E. J. Corey and J. A. Katzenellenbogen, *J. Amer. Chem. Soc.*, **91**, 1851 (1969); (b) J. B. Siddall, M. Biskup, and J. H. Fried, *ibid.*, **91**, 1853 (1969); (c) J. Klein and R. M. Turkel, *ibid.*, **91**, 6186 (1969).
(6) (a) Very recently, the addition of organocopper(I) reagents, generated from Grignard reagents, to α,β-acetylenic sulfides has been reported: P. Vermeer, C. de Graff, and J. Meijer, *Recl. Trav. Chim. Pays-Bas*, **93**, 24 (1974). (b) A study of the reaction of organocopper(I) reagents with α,β-acetylenic sulfoxides has also been undertaken: J. Meijer, private communication.
(7) W. E. Truce and G. J. W. Tichenor, *J. Org. Chem.*, **37**, 2391 (1972).
(8) Prepared from the corresponding α,β-acetylenic sulfides[9] by oxidation with 1.0 equiv of *m*-chloroperbenzoic acid in chloroform at 0° for 24 hr, whereas reaction of the sulfide with 2.0 equiv of the peracid under the same conditions produces the corresponding α,β-acetylenic sulfones: W. E. Truce and L. D. Markley, *J. Org. Chem.*, **35**, 3275 (1970).
(9) For the preparation of α,β-acetylenic sulfides, see J. F. Arens, *Advan. Org. Chem.*, **2**, 117 (1960), and references cited therein.
(10) Glpc analysis of the product of **1a** and **2b**, after oxidation to the sulfone, on an Aerograph Autoprep A-700 chromatograph using an 8 ft × 0.25 in. 15% neopentyl glycol isophthalate on 60–80 mesh Chromosorb W column at 190° and 45 ml/min shows 98.8% cis addition. Similarly, **1b** and **2a** give >96% cis addition. The direct glpc analysis of the sulfoxide products from these reactions, however, proves to be difficult owing to thermal decomposition at the temperatures necessary to elute them from even nonpolar (SE-30, SF-96) columns.
(11) The stereochemistry of the sulfoxide products and their corresponding sulfones is also indicated by their ^1H nmr spectra [in $CDCl_3$, parts per million (δ) downfield from tetramethylsilane]. The allylic methyl group in **3c** appears further downfield (1.97; sulfone **4c**, 2.14) than in **3d** (1.92; sulfone **4d**, 1.95) and the allylic methylene group in **3c** appears further upfield (2.20; sulfone **4c** 2.22) than in **3d** (2.42; sulfone **4d**, 2.61).
(12) (a) E. J. Corey and G. H. Posner, *J. Amer. Chem. Soc.*, **89**, 3911 (1967). (b) E. J. Corey and G. H. Posner, *ibid.*, **90**, 5616 (1968). (c) We have found that a similar reaction of lithium di-*n*-butylcuprate with **5** in THF at −78° is *not* stereospecific, giving an 80:20 mixture of **4c** and **4d**.
(13) E. J. Corey and R. H. K. Chen, *Tetrahedron Lett.*, 1611 (1973).
(14) W. E. Truce and G. C. Wolf, *J. Org. Chem.*, **36**, 1727 (1971).
(15) J. R. Allison, unpublished results, this laboratory.
(16) Texaco Fellow in Organic Chemistry, 1973–1974.

Department of Chemistry
Purdue University
West Lafayette, Indiana 47907

William E. Truce*
Michael J. Lusch[16]

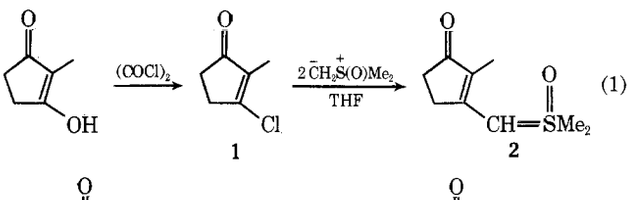
Received July 17, 1974

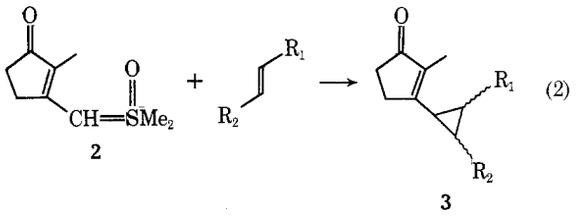
A New and Efficient Approach to Functionalized Hydroazulenes *via* 2-Methylcyclopentenone 3-Dimethylsulfoxonium Methylide[1]

Summary: A three-step sequence for the construction of functionalized hydroazulenes **5** is described starting from the novel cyclopentenone ylide **2.** The preparation of **2,** its reactions with Michael acceptors to produce vinyl cyclopropanes such as **3,** and the use of the divinylcyclopropane rearrangement to generate the bicyclo[5.3.0]decadienone system are described.

Sir: Recently, many sesquiterpenes possessing a hydroazulene skeleton have been isolated,[2] some of which have exhibited significant medicinal properties.[3] Despite the many efforts in the area of hydroazulene synthesis,[4] there are a very limited number of approaches which could accommodate a multitude of sensitive oxygen functionality. Our interest in sesquiterpene lactones possessing the guaiane and pseudoguaiane skeletons has resulted in the development of the synthetic scheme described in this communication. We have recently reported on the reactions and synthetic applications of carbonyl stabilized allyl sulfoxonium ylides.[5] In this communication we wish to report on the preparation of 2-methylcyclopentenone 3-dimethylsulfoxonium methylide (**2**), its reactions with several Michael acceptors, and its utility in the synthesis of functionalized hydroazulenes.

Sulfoxonium ylide **2** was prepared in at least 50% overall yield from the commercially available 2-methyl-1,3-cyclopentanedione. The 1,3-dione was treated with excess oxalyl chloride to produce the 3-chloro-2-methyl-2-cyclopentenone (**1**).[6] Treatment of the vinyl chloride **1** with 2 equiv of dimethylsulfoxonium methylide in tetrahydrofuran resulted in the formation of the crystalline ylide **2** (mp 170–173°).[7,8]





This new allyl ylide reacted cleanly with Michael acceptors such as acrolein, crotonaldehyde, and methyl vinyl ketone to produce vinyl cyclopropanes **3a–c** (see Table I).[5a]

Table I

	R_1	R_2	React temp, °C	React time, hr	Yield, %
3a	CHO	H	R.T.	3	70
3b	CHO	CH_3	56	8	50
3c	$COCH_3$	H	56	4	75

Usually the reaction was carried out using 1.5 to 2.0 equiv of the Michael acceptor in acetonitrile. Cyclopropanes **3a–c** were isolated in a very pure state by evaporation of the acetonitrile and washing the ethyl acetate solution of the residue with water. Cyclopropane **3a** consisted of a 7:1 mixture

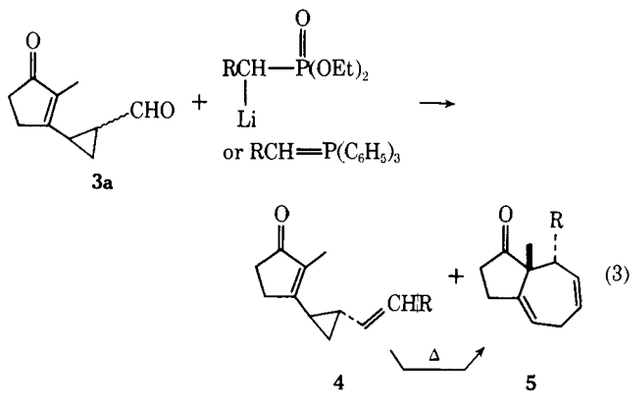
Table II

	R[a]	Yield[b] of 4 + 5, %	Olefin stereochemistry of 4
4a	$-CO_2Et$	90	100% trans
4b	$-SC_6H_5$	67	50:50 trans:cis
4c	$-SOC_6H_5$	81	100% cis
4d	$-SO_2C_6H_5$	80	100% trans

[a] The carbethoxy group was introduced as the phosphonium Wittig reagent, while the sulfur groups were introduced *via* the lithio phosphonates. All reactions were performed in tetrahydrofuran under standard conditions. [b] These are isolated yields which have not yet been maximized. [c] Wittig-type reagents which contain an α-carbanion-stabilizing group usually give predominately trans stereoisomers. The exclusive cis stereochemistry for the phenyl sulfinyl case (**4c**) is quite dramatic and surprising. We are currently investigating the generality of cis stereochemistry from phenylsulfinylmethyl phosphonate carbanions.

of trans:cis isomers while the methyl vinyl ketone adduct **3c** was exclusively the trans cyclopropane. Nmr analysis of the crotonaldehyde adduct **3b** indicated a mixture of three cyclopropanes[9] in a ratio of 3:3:1.

The cyclopropane **3a** derived from acrolein can serve as an important relay compound in the synthesis of hydroazulenes containing an angular methyl group. To this end, selective Wittig reactions were carried out at the aldehyde carbonyl in order to construct divinylcyclopropane systems (eq 3). Treatment of **3a** with various monosubstituted Wit-



tig-type reagents at room temperature or below resulted in the production of a trans divinylcyclopropane **4** and a rearranged product **5** (see Table II). The hydroazulene system **5** is formed directly from the cis cyclopropane aldehyde **3**, while the more stable trans divinylcyclopropanes **4** survive the reaction conditions. When the trans cyclopropanes, which also contain a trans olefin (**4a,b,d**), are heated at 100–140° in a sealed tube (chloroform), they smoothly rearrange to the corresponding hydroazulene isomers **5**, in quantitative yield.

The stereochemical prerequisites for the divinylcyclopropane rearrangement were clearly manifested in the thermal behavior of the various sulfur-substituted divinylcyclopropanes **4b–d**. When an approximately 1:1 mixture of trans:cis alkenes of **4b** was heated at 100°, the trans alkene rearranged to **5b** in 50 hr, while the cis alkene remained unchanged.[11] The cis vinyl sulfoxide **4c** did not cleanly rearrange to the hydroazulene but instead gave a complex mixture when heated at 135° for 30 hr. The difficulties in the rearrangements of the cis alkenes **4b** and **4c** are presumably due to steric hindrance in the transition states.[12] The pure trans alkenes **4a** and **4d** quantitatively rearranged to the corresponding hydroazulenes below 140°, thus affording the latter systems in overall yields of 60% or better starting from ylide **2**.

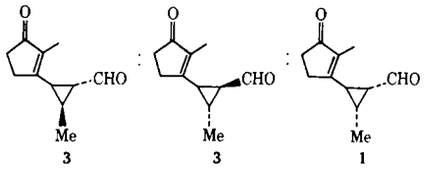
Since the Cope rearrangement of substituted divinylcyclopropanes has been shown by Baldwin[12] and others to be stereospecific and since only one stereoisomeric hydroazulene is produced in our systems, we have assigned the relative stereochemistry of the angular methyl and the R group as being trans.[13]

In summary, our approach to functionalized hydroazulenes not only utilizes mild reaction conditions and provides for flexibility in substitution patterns, but its final step furnishes a crowning touch of stereospecificity. We believe that the above synthetic scheme, because of its efficiency and high overall yields, will be invaluable for the total synthesis of guaianolides and pseudoguaianolides.

Acknowledgement is made to the Donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this research.

References and Notes

(1) Presented in part at the 6th Central Regional Meeting of the American Chemical Society, Detroit, Mich., April 22, 1974, Paper No. 207.
(2) J. S. Roberts, "Terpenoids and Steroids," Vol. 3, Specialist Periodical Reports, The Chemical Society, London, 1973, Chapter 2.
(3) S. M. Kupchan, M. A. Eakin, and A. M. Thomas, *J. Med. Chem.*, **14**, 1147 (1971).
(4) For a recent review in this area, see J. A. Marshall, *Synthesis*, 517 (1972).
(5) (a) J. P. Marino and T. Kaneko, *Tetrahedron Lett.*, 3971 (1973); (b) *ibid.*, 3975 (1973).
(6) A recent report describes this compound and other vinyl halides: R. D. Clark and C. H. Heathcock, *Synthesis*, 47 (1974).
(7) All new compounds gave satisfactory elemental analyses (±0.3%). Nmr, ir and mass spectral data were all in agreement with the designated structures.
(8) Nmr ($CDCl_3$, ppm), 1.60 (s, 3 H), 2.33 (m, 2 H), 2.78 (m, 2 H), 3.44 (s, 6 H), 4.00 (broad s, 1 H); ir (KBr) 1620, 1515, 1045 cm^{-1}.
(9) The following structural assignments have been made for the crotonaldehyde adducts **3b** (see ref 5a).



(10) E. J. Corey and J. I. Shulman, *J. Org. Chem.*, **35**, 777 (1970); I. Shahak and J. Almog, *Synthesis*, 144 (1970); M. Mikolajczyk and A. Zatorski, *ibid.*, 669 (1973).
(11) The olefin stereochemistry was determined by the coupling constants for the vinyl protons in compounds **4a–c**, **4a** trans (J = 16 Hz), **4b** cis (J = 9 Hz), **4b** trans (J = 15 Hz), **4c** cis (J = 10 Hz).
(12) J. E. Baldwin and G. Ullenius, *J. Amer. Chem. Soc.*, **96**, 1542 (1974).
(13) A NOE experiment was performed at 100 MHz on a ~4% solution of **5a** in CCl_4. Saturation of the angular methyl protons enhanced the methine proton signal by 9%, indicating the angular methyl group and the methine proton were in close proximity.

Department of Chemistry
University of Michigan
Ann Arbor, Michigan 48104

Joseph P. Marino*
Takushi Kaneko

Received June 18, 1974

A General Synthesis of 1-Alkyl-1-cyclopentene-*cis*-3,5-diols. Useful Intermediates in Prostaglandin Synthesis

Summary: A simple one-step conversion of sulfoxides **2a** or **2b** to cis diols of general structure **1** is reported.

Sir: Advances in prostaglandin synthesis have resulted in the development of some highly ingenious approaches to this class of hormones.[1,2] Several years ago we initiated