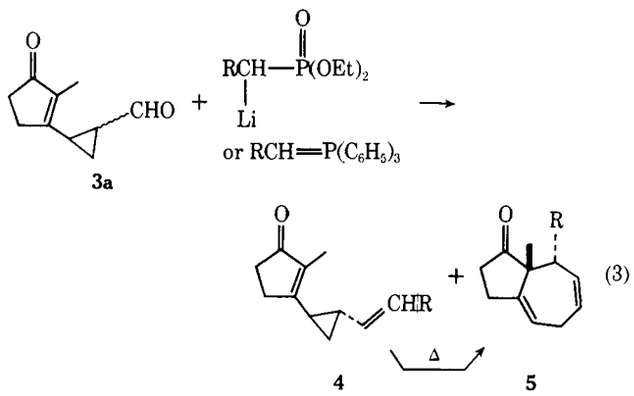
Table II

	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.

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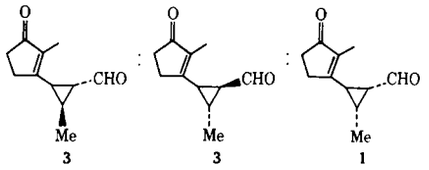
(6) A recent report describes this compound and other vinyl halides: R. D. Clark and C. H. Heathcock, *Synthesis*, 47 (1974).
(7) All new compounds gave satisfactory elemental analyses (±0.3%). Nmr, ir and mass spectral data were all in agreement with the designated structures.
(8) Nmr ($CDCl_3$, ppm), 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).



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(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.

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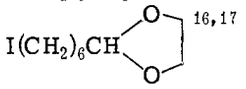
Received June 18, 1974

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.

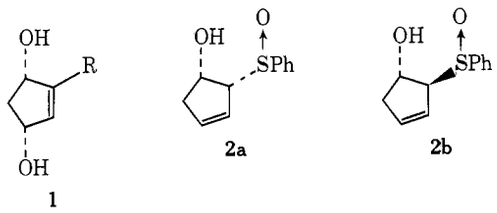
Sir: Advances in prostaglandin synthesis have resulted in the development of some highly ingenious approaches to this class of hormones.[1,2] Several years ago we initiated

Table I
1-Alkyl-1-cyclopentene-*cis*-3,5-diols [15,7]

R–X[a]	% yield 2[b]	Mp (bp), °C[c]
$I(CH_2)_5CH_3$	50–60 (70–77)	(75, 5 × 10^{-3} mm)
 [16,17]	54 (63)	51–52.5
$I(CH_2)_6CO_2$-*t*-Bu[18]	45 (57)	(110, 0.01 mm)
$BrCH_2C{\equiv}C(CH_2)_3CO_2$-*t*-Bu[19]	33 (48)	(60, 5 × 10^{-3} mm)
$BrCH_2C_6H_5$	50	95–96.5
$BrCH_2CH{=}CHC_6H_5$	(64)	103–105

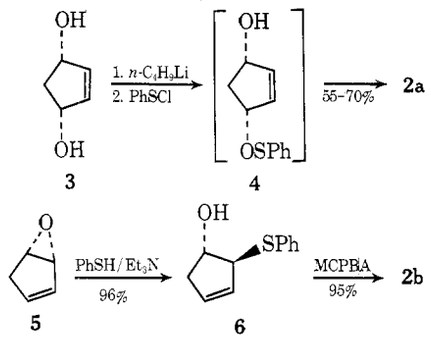
[a] See reference for mode of synthesis. [b] Yields in parentheses determined by nmr; all others are of purified product. [c] Values in parentheses are conditions employed for molecular distillation.

work on a general approach to the synthesis of allylic alcohols which would be amenable to the stereoselective synthesis of 1-alkyl-1-cyclopentene-*cis*-3,5-diols **1**.[3] Various derivatives of **1** may be readily perceived to be useful precursors to prostaglandins of both the E and F type.[4] This communication outlines a general approach to the stereoselective synthesis of *cis*-cyclopentenediols **1** which employs the hydroxy sulfoxides **2a** or **2b** as complementary precursors.



Synthesis of both the *cis*- and *trans*-hydroxy sulfoxides **2a** and **2b** was readily accomplished by the two routes outlined in Scheme I.[5] The cis isomer **2a** was prepared by

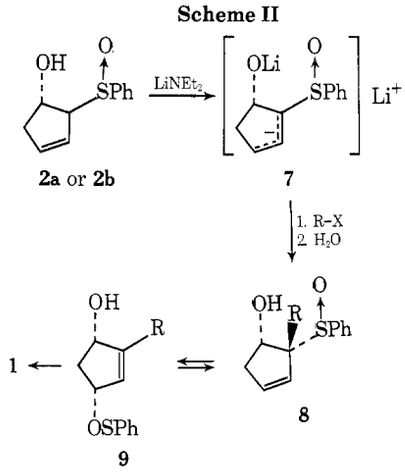
Scheme I



treatment of a 0.25 *M* solution of **3**[6] in dry tetrahydrofuran (THF) with 1 equiv of *n*-butyllithium (hexane) at −60° followed by titration with phenylsulfenyl chloride (~1.25 equiv) until the persistence of a yellow color. The resulting sulfenate ester **4** was allowed to rearrange to the *cis*-hydroxy sulfoxide **2a** at −20 to +5° over a 1.5-hr period. Sublimation of the product (95°, 0.05 mm) afforded **2a**, mp 102–112°, in 55–70% yield.[7,8] The relatively slow rate of rearrangement of **4** as compared to the analogous rearrangement of noncyclic sulfenate esters[3,9] is noteworthy. Synthesis of the *trans*-hydroxy sulfoxide **2b** was accomplished, in two steps in an overall yield of 91% starting from epoxycyclopentene (**5**).[10] Treatment of a 2.5 *M* solution of **5** in dry benzene at 0° with 1 equiv each of thiophenol and triethylamine followed by stirring at 25° for 4 hr afforded *exclusively* the *trans*-hydroxy sulfide as a homogenous liquid (molecular distillation; 90°, 0.05 mm) in 96% yield.[7] The observed regiospecific cleavage of epoxide **5** with a variety of mercaptide nucleophiles appears to be general. This result is in marked contrast to the capricious behavior of **5**, as well as other α,β-unsaturated epoxides, toward other nucleophiles.[10,11] Oxidation of **6** to the *trans*-hydroxy sulfoxide **2b** was carried out with *m*-chloroperbenzoic acid (CH_2Cl_2, 0°) in 95% yield.[5] Sublimation (90°, 10^{-5} mm) afforded a nicely crystalline solid, mp 96–113°.[7,8] Since both **2a** and **2b** are hygroscopic, care must be exercised in handling these compounds in subsequent experiments requiring anhydrous conditions.

The general approach for the conversion of either the *cis*- or *trans*-hydroxy sulfoxides **2a** or **2b** to the substituted cis diols **1** (Scheme II) deserves comment. *A priori* it was not known whether **2a** and **2b** would produce the same carbanion **7** upon metalation since some controversy exists in the literature on the pyramidal stability of α-sulfinyl carbanions.[12] Since the stereochemical course of the alkylation step (*cf.* **7** → **8**) could be influenced not only by substrate steric factors but also by carbanion geometry, it is interesting to note that alkylation appears to proceed only to give **8** and thus the cis diol **1**. These results suggest that the α-sulfinyl carbanion **7** is either planar or is undergoing pyramidal inversion prior to alkylation. On the other hand kinetic protonation of **7** results in the formation of *trans*-hydroxy sulfoxide **2b**. The observed high regioselectivity toward alkylation α to the phenylsulfinyl moiety (*cf.* **7** → **8**) appears to be characteristic of other phenylsulfinyl cycloalkenyl carbanions as well.[3,13]

Scheme II



The following general procedure is representative for the transformation of **2a** or **2b** to the substituted cis diols **1**. To a cooled (−40°) solution of 3.3 mmol of lithium diethylamide (from butyllithium and diethylamine) in 10 ml of dry THF under nitrogen is added 1–1.5 ml of dry hexamethylphosphoramide followed by 1.5 mmol of **2a** or **2b** in 4 ml of THF with stirring. The deep red solution of anion **7** is stirred for 30 min at which time the alkyl halide, R–X (1.6 mmol), is added either as a neat liquid or in a minimum volume of THF. Stirring is continued for an additional 30 min at −40° and 2 ml of a 50% aqueous solution of diethylamine is added to the reaction. The cold bath is removed and the reaction mixture is allowed to warm to room temperature and stirred ~2 hr to effect rearrangement and cleavage of **8** to the cis diol **1**. The cis diols **1** listed in Table I are purified by chromatography on neutral alumina (activity III).[5,7] The cis-diol stereochemistry is readily assigned by examination of the ^{1}H nmr chemical shifts and splitting patterns of the C-4 methylene protons.[14]

This approach to substituted, dioxygenated cyclopentenes differs from the alternate synthesis of such derivatives obtained *via* singlet oxidation of alkylcyclopentadienes[15] in one significant aspect. The inherent design of this reaction sequence affords the possibility of obtaining chiral cyclopentenediols **1** from precursors that may be chemically resolved. We are presently engaged in executing this idea and are developing methods for the elaboration of **1** to optically active prostanoids in the E and F series.

Acknowledgment. We wish to thank the Camille and Henry Dreyfus Foundation and the A. P. Sloan Foundation for unrestricted research support.

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Received July 23, 1974

Singlet Oxygen Oxidation of Phosphites to Phosphates[1]

Summary: Singlet oxygen is shown (by means of Stern–Volmer analysis using β-carotene) to oxidize trialkyl phosphites to trialkyl phosphates in quantitative yield; relative rates of reaction are given for several phosphites.

Sir: We wish to report the dye-sensitized photooxidation of several trialkyl phosphites and the compelling evidence that the active oxidizing agent is singlet molecular oxygen.

Several trialkyl phosphites were irradiated with visible light[2] in acetone solution in the presence of Rose Bengal (RB)[3] while oxygen was bubbled through the solution continuously. In each case, the phosphate was formed in good yield as the only detectable product; the results are summarized in Table I. No reaction occurred in the dark or in the absence of dye.

Table I

Compound	Yield,[a] %	k_{rel}[b]	k_l, l. mol^{-1} sec^{-1}[c]
$(MeO)_3P$	85.4	0.65	1.52×10^7
$(EtO)_3P$	87.9	1.00	2.45×10^7
$(i\text{-}PrO)_3P$	66.2		
$(n\text{-}BuO)_3P$	82.4	0.78	
$(c\text{-}C_6H_{11}O)_3P$	83.0	0.60	
$(CH_2{=}CHCH_2O)_3P$	69.5		

[a] Products isolated by distillation or chromatography and crystallization, and identified by boiling point or melting point and ir comparison to authentic samples. [b] Determined by parallel irradiations using RB in acetone. [c] Determined by means of Stern–Volmer plot, employing MB, β-carotene, and benzene–methanol, 4:1 (v:v).

Although phosphites can be oxidized by ground-state oxygen in a photoinitiated free radical chain process,[4] the dye-sensitized photooxidation was only slightly retarded by