Since the Cope rearrangement of substituted divinylcyclopropanes has been shown by Baldwin\textsuperscript{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.\textsuperscript{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.

Table II

<table>
<thead>
<tr>
<th>R</th>
<th>Yield\textsuperscript{b} of 4a + 5a</th>
<th>Olefin stereochemistry of 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>4a - CO\textsubscript{2}Et</td>
<td>90%</td>
<td>100% trans</td>
</tr>
<tr>
<td>4b - SC\textsubscript{2}H\textsubscript{5}</td>
<td>67%</td>
<td>50:50 trans:cis</td>
</tr>
<tr>
<td>4c - SO\textsubscript{2}C\textsubscript{2}H\textsubscript{5}</td>
<td>81%</td>
<td>100% cis</td>
</tr>
<tr>
<td>4d - SO\textsubscript{2}C\textsubscript{2}H\textsubscript{5}</td>
<td>80%</td>
<td>100% trans</td>
</tr>
</tbody>
</table>

\textsuperscript{a} The carbonyl 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. * These are isolated yields which have not yet been maximized. \textsuperscript{c} Wittig-type reagents which contain an \(\alpha\)-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 phenyl-sulfinylmethyl 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\textsuperscript{2} 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 Wittig-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 cyclopropanes 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.\textsuperscript{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.\textsuperscript{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.

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.


(4) For a recent review in this area, see J. A. Marshall, Synthesis, 517 (1972).


(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\textsubscript{3}, gpm), 1.60 (3, s, 3 H), 2.33 (m, 2 H), 2.78 (m, 2 H), 3.44 (a, 6 H), 4.00 (broad s, 1 H); ir (KBr) 1620, 1515, 1045 cm\textsuperscript{-1}.

(9) The following structural assignments have been made for the crotonaldehyde adducts 3b (see ref 5a).


(11) The olefin stereochemistry was determined by the coupling constants for the vinyl protons in compounds 4a–e; 4a trans (J = 16 Hz), 4b cis (J = 9 Hz), 4b trans (J = 15 Hz), 4c cis (J = 10 Hz).


(13) A NOE experiment was performed at 100 MHz on a ~4% solution of 5a in CD\textsubscript{3}OD. 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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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.\textsuperscript{1,2} Several years ago we initiated
1-Alkyl-1-cyclopentene-cis-3,5-diols 15,17

<table>
<thead>
<tr>
<th>R-X a</th>
<th>% yield b</th>
<th>mp (°C, °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I(CH₃)₂CH₃</td>
<td>50–60</td>
<td>(75, 5 × 10⁻² mm)</td>
</tr>
<tr>
<td>I(CH₂)₂CH</td>
<td>54 (63)</td>
<td>51–52, 5</td>
</tr>
<tr>
<td>I(CH₂)₂CO₂-t-Bu 18</td>
<td>45 (57)</td>
<td>(110, 0.01 mm)</td>
</tr>
<tr>
<td>BrCH₂C≡C(CH₃)₂CO₂-t-Bu 15</td>
<td>33 (48)</td>
<td>(60, 5 × 10⁻² mm)</td>
</tr>
<tr>
<td>BrCH₂C₃H₅</td>
<td>50</td>
<td>95–96, 5</td>
</tr>
<tr>
<td>BrCH₂CH=CHCH₄H₂</td>
<td>(64)</td>
<td>103–105</td>
</tr>
</tbody>
</table>

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.

![Diagram of Scheme I](image)

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 treatment of a 0.25 M solution of 3 in dry tetrahydrofuran (THF) with 1 equiv of n-butyllithium (hexane) at −60° followed by titration with phenylsulfinyl chloride (~1.25 equiv) until the persistence of a yellow color. The resulting sulfinate 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 (99°, 0.05 mm) afforded 2a, mp 102–112°, in 55–70% yield.7 The relatively slow rate of rearrangement of 4 as compared to the analogous rearrangement of noncyclic sulfinate esters 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 thiope-
The following general procedure is representative for the transformation of 2a or 2b to the substituted cis diols I. To a cooled (−40°C) 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 hexamethylylphosphoramide 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°C and 2 ml of a 50% aqueous solution of diethylammonium chloride (from butyllithium and diethylamine) in 10 ml of dry THF is added to give the deep red solution of the anion. The reaction mixture is allowed to warm to room temperature and stirred. The red solution of the active intermediates is readily observed by comparison of the 1H nmr chemical shifts and splitting patterns of the C=4-methylene protons.14

This approach to substituted, dioxygenated cyclopentanediols differs from the alternate synthesis of such derivatives obtained via singlet oxygenation of alkylcyclopentadienes15 in one significant aspect. The inherent design of the reaction sequence affords the possibility of obtaining cyclopentanediols 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 prostanooids 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.

References and Notes


(5) Detailed experimental procedures will be provided upon request for all reactions reported herein.


(7) Satisfactory elemental analyses and spectral data were obtained on all compounds reported.

(8) Both 2a and 2b were prepared as a mixture of sulfide diastrereoisomers. Stereochemical assignments are based upon synthesis of (9) V. Rautenstrauch, Chem. Commun., 526 (1970).


(11) The filtered benzene solution of crude epoxycyclopentadiene 5 obtained in this procedure may be treated with triphenyl-methylamine to give the stilbene directly in 54% yield.


(15) F. G. Cucu, G. Wollucnowicz, L. Boris, and Th. Posternak, Helv. Chim. Acta, 52, 736 (1969). In 1 (R = CH3C6H5), the 1H nmr chemical shifts of the C4 protons (CDCl3) are at 5 2.60 (five-line multiplet) and 5 1.58 (doublet of triplets). The corresponding protons in 3 appear at 5 2.66 and 1.51.


(17) Prepared from methyl 7-dromooephanate17 by reduction with disoultiamylum hydride, ketallzation, and halide exchange (65% overall yield).


(19) Prepared by the alkylation of the lithium enolate of tert-butyl acelate with 1,5-dihoropentanone followed by halide exchange (50% overall yield).

(20) For a general approach, see J. Martel and E. Toromanoff, Chem. Abstr., 78, 24712d (1972).


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Singlet Oxygen Oxidation of Phosphites to Phosphates

Summary: Singlet oxygen is shown (by means of Stern-Volmer analysis using 3-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 in acetone solution in the presence of Rose Bengal (RB) 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

<table>
<thead>
<tr>
<th>Compound</th>
<th>Yield</th>
<th>( k_{rel} )</th>
<th>( k_{obs} )</th>
<th>1,1 Mat-1 s-1</th>
<th>107</th>
</tr>
</thead>
<tbody>
<tr>
<td>(MeO)3P</td>
<td>85.4</td>
<td>0.65</td>
<td>1.52 \times 10^7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(EtO)3P</td>
<td>87.9</td>
<td>1.00</td>
<td>2.45 \times 10^7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(n-PrO)3P</td>
<td>66.2</td>
<td>0.60</td>
<td>0.28</td>
<td>7.4</td>
<td></td>
</tr>
<tr>
<td>(n-BuO)3P</td>
<td>82.4</td>
<td>0.78</td>
<td>0.10</td>
<td>3.9</td>
<td></td>
</tr>
<tr>
<td>(c-C6H5)3O</td>
<td>83.0</td>
<td>0.60</td>
<td>0.09</td>
<td>1.5</td>
<td></td>
</tr>
</tbody>
</table>

* Products isolated by distillation or chromatography and crystallization, and identified by boiling point or melting point and ir comparison to authentic samples. * Determined by parallel irradiations using RB in acetone. * Determined by means of Stern-Volmer plot, employing MB, 3-carotene, and benzene-methanol, 4:1 (v:v).

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