

relatively shorter bond distances, i.e., $r_{P-O_1} = 1.499 \text{ \AA}$ and $r_{P-O_2} = 1.488 \text{ \AA}$. On the other hand, the most deshielded direction (σ_{11}) lies primarily in the RO-P-OH plane where only a single-bond character is expected⁷ and is again substantiated by the relatively larger distances, i.e., $r_{P-OH} = 1.585 \text{ \AA}$ and $r_{P-OR} = 1.612 \text{ \AA}$.

As shown in Figure 2, the eigenvectors deviate by less than 10° from the corresponding molecular frame axes. Along with similar findings in BDEP and AEP, these results suggest that ^{31}P shielding tensors in phosphate esters are rather well aligned with the axes of the molecular frame and thus seem to support the assumption of congruency of the principal axes and molecule fixed frames made by Nall et al. in their study of oriented DNA fibers.

Acknowledgment. We acknowledge the assistance of Dr. G. Petsko in the X-ray orientation of the 5'dCMP single crystal.

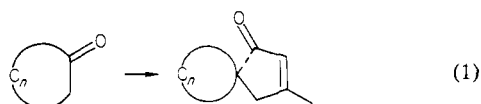
Registry No. 5'-dCMP, 1032-65-1; P, 7723-14-0.

A Cyclocontraction-Spiroannulation: A Stereoselective Approach to Spirocycles

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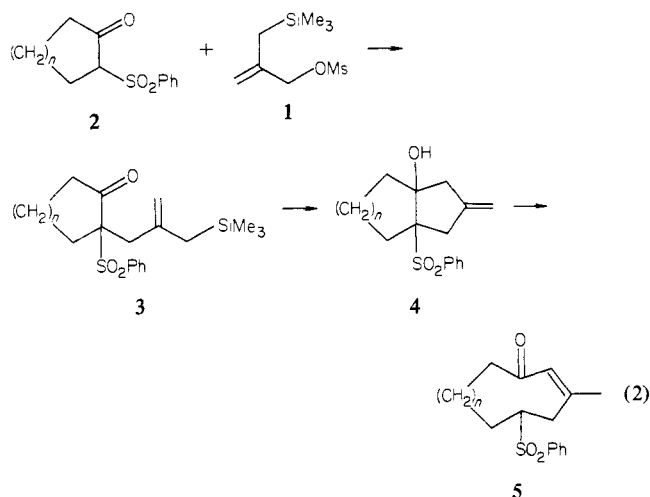
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Spirocycles represent challenging targets in both natural product and theoretical chemistry.¹ We report an annulation reaction that is accompanied by a realignment of the initial rings leading to the unusual overall structural change represented in eq 1. In



addition, this sequence illustrates the ability of a sulfone group to function as a leaving group in the presence of Lewis acids, a previously unobserved phenomenon, and the consequent reorientation of a reaction pathway compared to anionic catalysts.

In conjunction with our study of the intercalation of the bifunctional reagent **1** with β -keto sulfones **2** (eq 2),² we explored



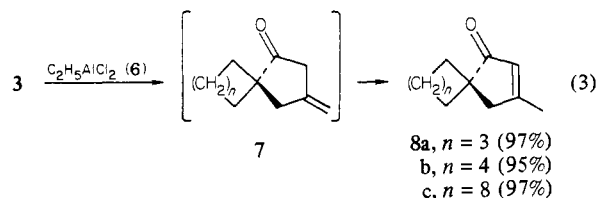
the reaction of **3** with Lewis acids. Performing this reaction with

(1) For reviews see: Magnus, P. D. *Tetrahedron* **1977**, *33*, 2019. Durst, T. *Compr. Org. Chem.* **1979**, *3*, 171.

(2) Trost, B. M.; Vincent, J. E. *J. Am. Chem. Soc.* **1980**, *102*, 5680. Trost, B. M.; Hiemstra, H. *Ibid.* **1982**, *104*, 886.

(3) The preferred procedure for the preparation of **3** involves treating 1 equiv of **2** with 1.1 equiv of **1** in the presence of 1 equiv each of KOH, KI, and $[(\text{C}_4\text{H}_9)_4\text{N}]_2\text{SO}_4$ in CH_2Cl_2 - H_2O at room temperature. After dilution with ether and washing with water, drying and evaporation give the crystalline products **3**. See: Samuelsson, B.; Lamm, B. *Acta Chem. Scand.* **1971**, *25*, 1555.

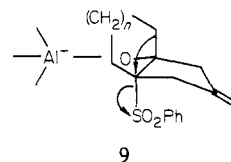
3 ($n = 8$) and ethylaluminum dichloride (**6**) initially at 0°C and then allowing it to warm to room temperature led to a 1:1 mixture of the expected product **4** and a second compound that clearly lost the benzenesulfonyl group (eq 3). The same reaction in



toluene gave only this latter product. Combustion analysis [found: C, 81.89; H, 11.13] combined with mass spectroscopy (m/e 234) established the formula as $\text{C}_{16}\text{H}_{26}\text{O}$. The symmetry was established by the ^{13}C NMR spectrum (δ 208.1, 174.6, 128.0, 51.8, 47.5, 32.5 (2), 27.4 (2), 26.0 (2), 25.2 (2), 21.4 (2), 19.3), which combined with the ^1H NMR (δ 5.74 (sext, $J = 1.3$ Hz, 1 H), 2.3 (quint, $J = 1.3$ Hz, 2 H), 2.05 (q, $J = 1.3$ Hz), 1.2-1.8 (m, 20 H)) and the IR (1687, 1625 cm^{-1}) spectrum establishes **8c**⁴ as the structure.

A typical preparative procedure involves adding 2 equiv of a 2 M solution of **6** in methylene chloride to 1 equiv of a 0.3 M solution of the β -keto sulfone **3** in the same solvent at room temperature and then refluxing for 3 h. After quenching with ethanol and partitioning between ether and aqueous sodium bicarbonate, the product **8**⁴ was isolated pure by simple distillation.

The reaction can be envisioned to involve a pinacol type of rearrangement in which the sulfone group serves as a leaving group in the presence of a Lewis acid as depicted in **9**. That **4** is indeed



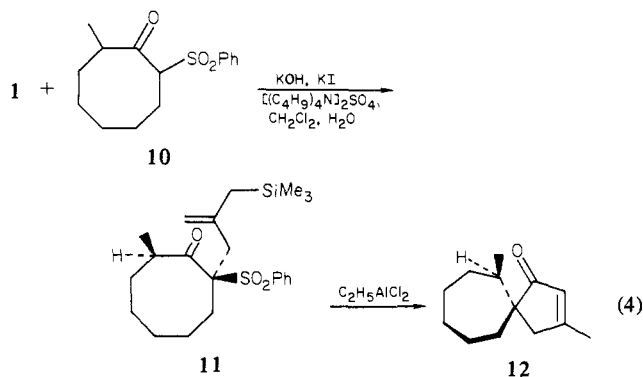
the intermediate can be demonstrated by treating **3** with the Lewis acid **6** at -78°C and quenching at that temperature, in which case only **4** is isolated. On the other hand, allowing the solutions to warm prior to quenching leads to the spirocycle **8**. In addition, subjecting **4c** to the normal preparative conditions for the cyclocontraction-spiroannulation also led to **8c**.

Considering the unprecedented ionization of a sulfone induced by an acid catalyst, this reaction proceeds remarkably readily. In the case of **3b** and **3c**, cyclization and ring contraction occur at -40°C . At these temperatures, the intermediate β,γ isomer **7** is a substantial product as determined by the ^1H NMR absorptions at δ 5.0 and 4.9 (>CH_2) and 2.9 ($\text{COCH}_2\text{C=}$) and 2.3 ($\text{=CCH}_2\text{C}$) for **7c**. The use of refluxing methylene chloride for these cases simply assures complete isomerization of the β,γ isomer **7b,c** to the α,β isomer **8b,c**, which is the slow step in the sequence. The rate of the rearrangement depends on ring size and suggests the optimal alignment depicted in **9** is required. For example, when $n = 3$ the reaction proceeds substantially more slowly—at 0°C only **4a** is isolated after 0.5 h, at room temperature a 1:1 mixture of **4a** and **8a** is isolated, and only after 2 h at reflux is reaction complete. When $n = 1$, a preliminary examination did not lead to isolation of any of the spiro[3.4]octane system—an observation that may reflect the inability of this short bridge to adopt the anti-periplanar arrangement of the migrating ring bond with respect to the departing sulfone group in this case.

The ability to control stereochemistry in this process depends upon controlling the stereochemistry of the alkylation of the β -keto sulfone. Alkylation of **10** under phase-transfer conditions gives a single diastereomer of the product **11**,⁴ whose stereochemistry is assigned by analogy to the alkylation of 2-methylcyclooctanone.⁵ Subjecting **11** to the normal conditions gave an 86% isolated yield

(4) All new compounds have been fully characterized by spectral means and high-resolution mass spectroscopy and/or combustion analysis.

(5) Still, W. C.; Galynker, I. *Tetrahedron* **1981**, *37*, 3981.



of a single product ($^1\text{H NMR } \delta$ 5.74 (q, $J = 1.1$ Hz, 1 H), 2.46 (d, $J = 18$ Hz, 1 H), 2.30 (d, $J = 18$ Hz, 1 H), 2.03 (d, 3 H, $J = 1.1$ Hz), 1.2–2 (m, 11 H, 0.71 (d, $J = 7$ Hz, 3 H)); $^{13}\text{C NMR } \delta$ 208.1, 175.0, 130.2, 54.9, 50.5, 41.7, 38.6, 32.0, 30.4, 30.3, 23.7, 18.9, 18.1). On the basis of the anticipated migration with retention of configuration, the stereochemistry is assigned as depicted in **12**.

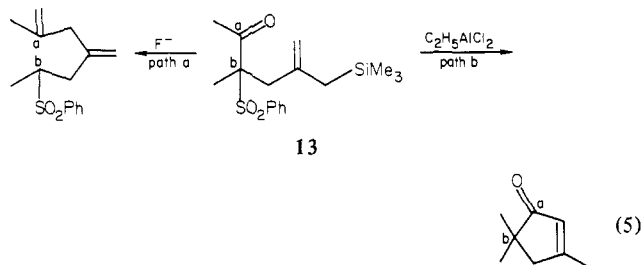
The sensitivity of the sulfone group to Lewis acid induced ionization should open a new dimension to the utility of sulfones in synthesis.⁶ As this example illustrates, a total reorientation

(6) While an arenosulfonyl group serves as a leaving group leading to eliminations, cyclizations, and fragmentations under basic conditions, to our knowledge such reactions have not been recorded in the presence of Lewis acids.

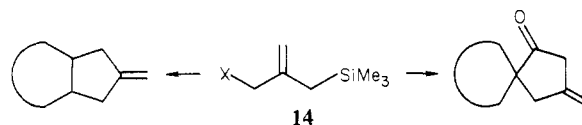
(7) Trost, B. M.; Chan, D. M. T. *J. Am. Chem. Soc.* **1979**, *101*, 6429; **1981**, *103*, 5972; **1982**, *104*, 3733. Trost, B. M.; Curran, D. P. *Ibid.* **1981**, *103*, 7380. Trost, B. M.; Curran, D. P. *Tetrahedron Lett.* **1981**, *22*, 5023. Trost, B. M.; Renaut, P. *J. Am. Chem. Soc.* **1982**, *104*, 6668. Trost, B. M.; Nanninga, T. N.; Chan, D. M. T. *Organometallics* **1982**, *1*, 1543.

(8) Hosomi, A.; Hashimoto, H.; Sakurai, H. *Tetrahedron Lett.* **1980**, *21*, 951. Knapp, S.; O'Connor, V.; Mobilis, D. *Ibid.* **1980**, *21*, 4557; Henning, R.; Hoffmann, H. M. R. *Ibid.* **1982**, *23*, 2305. Hoffmann, H. M. R.; Henning, R.; Lalko, D. R. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 442.

of **13** from an intercalation (eq 5, path a) to a cyclocontraction–



spiroannulation⁹ (eq 5, path b) results upon switching from a catalyst that behaves as a nucleophilic trigger (path a) to an electrophilic acceptor (path b). In addition, the versatility of the bifunctional reagents represented by **14**^{2,7,8} in synthesis in general, and cyclopentane ring synthesis in particular, is enhanced.



Acknowledgment. We thank the National Science Foundation and the National Institutes of Health, General Medical Sciences, for their generous support of our programs.

Registry No. **1**, 74532-54-0; **2a**, 74532-82-4; **2b**, 74546-10-4; **2c**, 67886-41-3; **3a**, 85923-85-9; **3b**, 74532-64-2; **3c**, 74532-57-3; **4a**, 81302-85-4; **4b**, 85923-86-0; **4c**, 85939-40-8; **6**, 563-43-9; **8a**, 85923-88-2; **8b**, 85923-89-3; **8c**, 85923-87-1; **10**, 85923-90-6; **11**, 85923-91-7; **12**, 85923-92-8; **13**, 85939-41-9.

(9) For reviews of spiroannulations see: Marshall, J. A.; Brady, S. A.; Andersen, N. H. *Fortschr. Chem. Org. Naturst.* **1974**, *31*, 283. Krapcho, A. P. *Synthesis* **1974**, 383; **1976**, 425. Martin, S. F. *Tetrahedron* **1980**, *36*, 419.

Book Reviews *

Environmental and Climatic Impact of Coal Utilization. By J. J. Singh (NASA Research Center) and A. Deepak (Institute for Atmospheric Optics and Remote Sensing). Academic Press, New York, 1980. xvi + 655 pp. \$39.50.

The proceedings of the Symposium on Environmental and Climatic Impact of Coal Utilization held in Williamsburg, Virginia, April 1979 contains 32 papers divided into the following research areas: Aerosol Emissions from Coal Plants (13 papers); Gaseous Emissions from Coal Plants (7 papers); Climatic Impact of Coal Plant Emissions (4 papers); and Environmental Impact of Coal plant Emissions (8 papers). The title of the book is misleading in part because the large majority of papers are concerned with the physics and chemistry of aerosols, sulfur compounds and carbon dioxide in the atmospheric environment, and climatic effects. Topics that are related to the atmospheric environment and climate are well treated, for example aerosol formation and characterization, the COS and CS₂ budget in the atmosphere, and the optical effects of aerosols. However, the book contains little on the effects of coal utilization on the aquatic or terrestrial environment. There is one review of analytical techniques for the determination of trace elements in air particulates but this is somewhat out of place because only one other paper is principally concerned with the trace element contents of aerosols. The environmental fate of trace elements and their species emitted by coal-fired power plants is largely ignored. Other important environmental concerns such as the effects of coal combustion on the carbon dioxide cycle (3 papers) and acid rain effects (1 paper) receive little attention. Only one short general paper addresses the increasingly important contribution of coal gasification and liquefaction processes to coal utilization. Probably the major criticism of the book is that there is no discussion of

some major environmental problems of coal utilization such as thermal effects of discharges to lakes, ash pond discharges to the aquatic environment, and effects of coal combustion on the terrestrial environment. A less general title to the work would have been more appropriate.

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Laser Probes for Combustion Chemistry. ACS Symposium Series. No. 134. Edited by David R. Crosley (SRI International) The American Chemical Society, Washington, D.C. 1980. xii + 495 pp. \$44.50.

This book is based on a symposium sponsored by the Division of Physical Chemistry at the 178th Meeting of the American Chemical Society, Washington, D.C., September 9–14, 1979. It is divided into seven major sections: Overviews; Laser-Induced Fluorescence: Molecules; Laser-Induced Fluorescence: Atoms; Spontaneous Raman Scattering; Coherent Raman Spectroscopy; Modelling and Kinetics; and Other Diagnostic Techniques. The first article in most of the major sections functions as a review and/or overview of the particular technique that the section addresses, although more specific results from the author's own laboratories are usually given in the article as well. These review/overview articles are based on invited lectures at the symposium. Included in this category are the general overviews by David R. Crosley and J. R. McDonald and the articles on Laser-Induced Fluorescence Spectroscopy in Flames by John W. Dailey, on Raman-Scattering Measurements of Combustion Properties by Marshall Lapp, on Spatially Precise Laser Diagnostics for Practical Combustor Probing by Alan C. Eckbreth, and on Detailed Modelling of Combustion: A Noninterfering Diagnostic Tool by E. S. Oran, J. P. Boris, and M. J. Fritts. Following these in each section are shorter articles taken from contributed oral and poster sessions at the Symposium.

The book provides an excellent introduction to the wide variety of

*Unsigned book reviews are by the Book Review Editor.