J. Am. Chem. Soc. 1984, 106, 7260-7261

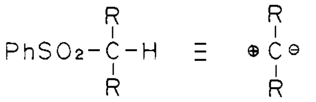
Sulfones as Chemical Chameleons. Cyclization via 1,1-Dipole Synthons

Barry M. Trost* and M. Reza Ghadiri

McElvain Laboratories of Organic Chemistry
Department of Chemistry, University of Wisconsin
Madison, Wisconsin 53706

Received July 11, 1984

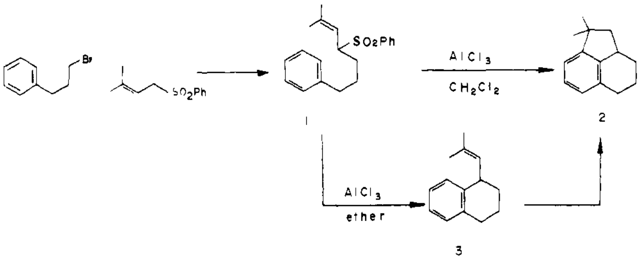
While the ability of the sulfone to stabilize an adjacent carbanion has been well recognized and utilized in synthesis, the displacement of the sulfone by a carbon nucleophile is relatively rare.[1] In spite of a long history of sulfone chemistry,[2] the susceptibility of these very weak Lewis bases to Lewis acids is absent from the literature. We wish to report that some sulfones show a remarkable sensitivity toward such acids.[3,4] The combination of the above reactivities converts an organosulfone into a 1,1-dipole, A.



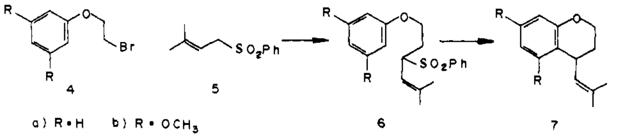
$$PhSO_2-\overset{\displaystyle R}{\underset{\displaystyle R}{C}}-H \equiv \oplus\overset{\displaystyle R}{\underset{\displaystyle R}{C}}\ominus$$

A

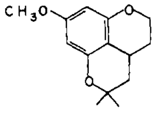
Exposure of the allyl sulfone **1**, simply available by alkylation of prenyl sulfone, to 2 equiv of aluminum chloride in methylene chloride at -78 °C led to *total disappearance of starting material within 0.5 h*! The only identifiable product was the tricyclic compound **2**.[5] Attenuating the Lewis acidity of $AlCl_3$ by using ether as solvent at reflux produces a 61% yield of the simple cyclic product **3**.[5] That **3** is an intermediate in the formation of the tricycle **2** is established by its near quantitative conversion to **2** upon reacting **3** with 2 equiv of $AlCl_3$ and 1 equiv of benzenesulfinic acid in methylene chloride at -78°. Alternatively, dissolving **3** in trifluoroacetic acid also converts **3** to **2** quantitatively.



Considering the carbon skeletons of robustadials[6] and euglobals,[7] we were interested in the effect of an oxygen in the intervening chain. Simple alkylation of the sulfone-stabilized anion from **5** with β-bromophenetole **4a** (THF, -78 °C to room temperature, 80%) produces the requisite substrate **6a**.[5] While slower than the cyclization of **1**, **6a** smoothly forms the chromane **7a**,[5] in 82% yield



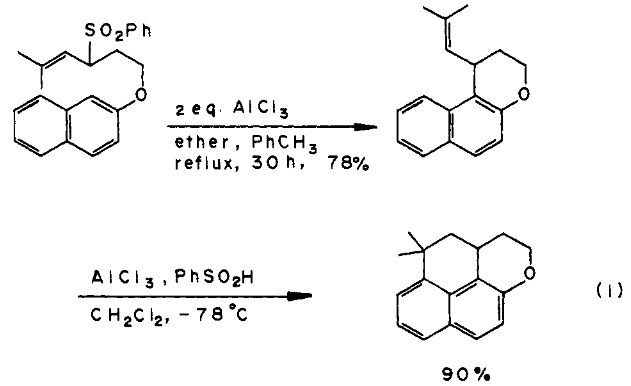
(3 equiv of $AlCl_3$, ether, reflux, 20 h). Interestingly, molybdenum hexacarbonyl also catalyzes this reaction although less efficiently[8] [2 equiv of $Mo(CO)_6$, $PhCH_3$, reflux, 43%]. Use of similar conditions for **6b**[5] led to a 1:1 mixture of **7b** and **8** in 62% yield.

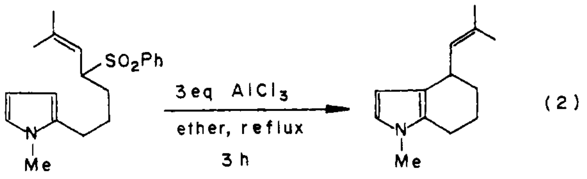


8

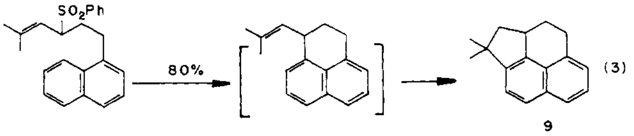
To probe whether the demethylation-cyclization product arose due to the presence of protonic acids in the reaction medium, the cyclization of **6b** was also performed with aluminum chloride (3 equiv) in the presence of ethylaluminum dichloride (1 equiv) in 4:1 ether/methylene chloride. Indeed, in this case, **7b**[5] was formed in 66% yield.

Variation of the aromatic ring was briefly examined. As shown in eq 1 and 2 both a naphthalene system as an example of a polycondensed aromatic and a pyrrole system as an example of an acid-sensitive heteroaromatic successfully underwent cyclization. The double cyclization was further demonstrated in the former case to determine if six- as well as five-membered rings can be formed in the second cyclization.





Five- vs. six-membered ring formation in the first cyclization was examined (eq 3). Tetracyclic product **9** is formed in 80% yield (2.5 equiv of $AlCl_3$, 1 equiv of $EtAlCl_2$, CH_2Cl_2, -78 °C, 0.5 h). Geometric constraints disfavoring a 5-endo-trig reaction rationalize this result.



The effect of the allyl substituents on the cyclization was also examined in the context of a model toward cannabinoid metabolites.[9] The requisite substrate **11** was readily available by the

---

[1] For reviews, see: Magnus, P. D. *Tetrahedron* **1977**, *33*, 2019. Durst, T. *Compr. Org. Chem.* **1979**, *3*, 171. While eliminations of sulfones to olefins is well documented, base-catalyzed alkylations are restricted to a few examples of cyclopropane formation in which substrate structure is critical (Parker, W. L.; Woodward, R. B. *J. Org. Chem.* **1969**, *34*, 3085. Campbell, R. V. M.; Crombie, L.; Findley, D. A. R.; King, R. W.; Pattenden, G.; Whiting, D. A. *J. Chem. Soc., Perkin Trans. 1* **1975**, 897).

[2] Cf.: Jensen, F.; Goldman, G. In "Friedel-Crafts and Related Reactions"; Olah, G.; Ed.; Wiley-Interscience: New York, 1964; Vol. III p 1319. For a recent reference, see: Hyatt, J. H.; White, A. W. *Synthesis* **1984**, 214.

[3] Cf.: Trost, B. M.; Adams, B. R. *J. Am. Chem. Soc.* **1983**, *105*, 4849.

[4] A thienylalkyl phenyl sulfone has been reported to survive electrophilic aromatic substitution but to be reductively cleaved with dibal-H. See: Janssen, C. G. M.; van Lier, P. M.; Schipper, P.; Simons, L. H. J.; Godefroi, E. F. *J. Org. Chem.* **1980**, *45*, 3159.

[5] All compounds have been fully characterized by spectral means. Elemental composition of new compounds have been determined by high-resolution mass spectroscopy and/or combustion analysis.

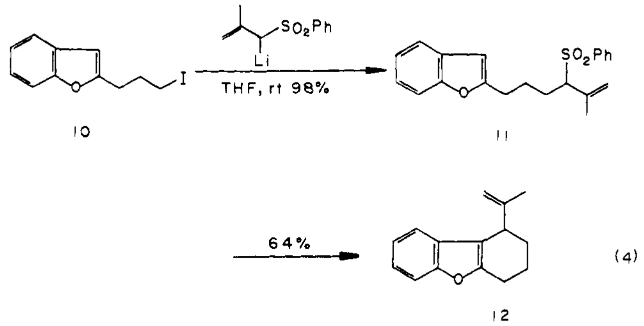
[6] Xe, R.; Snyder, J. K.; Nakanishi, K. *J. Am. Chem. Soc.* **1984**, *106*, 734.

[7] Kozuka, M. *Chem. Pharm. Bull.* **1982**, *30*, 1952, 1964.

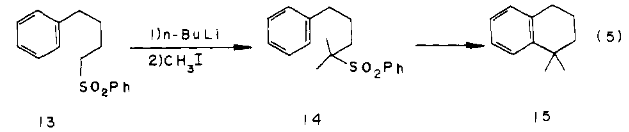
[8] For $Mo(CO)_6$ in Friedel-Crafts reactions, see: Forona, M. F.; White, J. F. *J. Organomet. Chem.* **1973**, *63*, 329; *J. Am. Chem. Soc.* **1971**, *93*, 2826.

0002-7863/84/1506-7260$01.50/0

straightforward alkylation of the iodide, itself prepared from 2-lithiated benzofuran (eq 4). Exposure of **11**^{5} to aluminum chloride (3 equiv, CH$_2$Cl$_2$, −78 °C, 1.5 h) gave **12**^{5} in 64% yield. Thus, relatively simple allyl groups provide sufficient activation to facilitate cyclization.

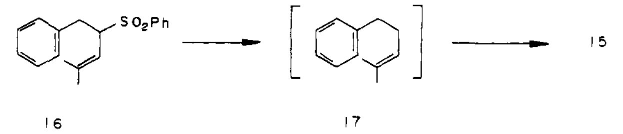


Since a tertiary carbonium ion is about as stable as a simple allyl cation, tertiary sulfones are also candidates as substrates. Treating **14** with 2 equiv of aluminum chloride (CH$_2$Cl$_2$; −78 to 0 °C, 1 h) gave the cyclic product **15**^{5} in 70–80% yield (eq 5).



This example also illustrates the umpolung provided by the sulfone since carbanion chemistry introduces the two methyl groups.

The question of an endo vs. exo type of cyclization was briefly examined. Aluminum chloride induced reaction of **16** led to a complex mixture of products. On the other hand, 2 equiv of ethylaluminum dichloride (CH$_2$Cl$_2$, −78 °C, 15 min) led to **15** in 44–51% yields—a net reductive cyclization. The failure of the allyl cation derived from **16** to cyclize may derive from geometrical constraints of the cisoid isomer or from preferential formation of the transoid cation which is geometrically precluded from cyclizing. However, if it is reduced by hydride delivery from the ethyl group of the Lewis acid to the less substituted carbon to form **17**, then acid-type cyclization would be expected to produce **15** as observed.



The surprising facility of these Lewis acid catalyzed cyclization reactions extends the prospects for application of sulfones in synthesis. Clearly, aromatic nucleophiles are only one type of many that can be envisioned. Sulfones appear to be chemical chameleons; they become either nucleophiles or electrophiles depending upon their environment.^{10}

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

Registry No. 1, 92643-23-7; **2**, 92643-24-8; **3**, 92643-25-9; **4a**, 589-10-6; **4b**, 85262-44-8; **5**, 15874-80-3; **6a**, 92643-26-0; **6b**, 92643-27-1; **7a**, 92643-28-2; **7b**, 92643-29-3; **8**, 92643-30-6; **9**, 92643-31-7; **10**, 92643-32-8; **11**, 92643-33-9; **12**, 92643-34-0; **13**, 92643-35-1; **14**, 92643-36-2; **15**, 1985-59-7; **16**, 92643-37-3; Ph(CH$_2$)$_3$Br, 637-59-2; AlCl$_3$, 7446-70-0; Mo(CO)$_6$, 13939-06-5; 2-[[5-methyl-3-(phenylsulfonyl)hex-4-en-1-yl]oxy]naphthalene, 92643-38-4; 1-(2-methyl-1-propenyl)-2,3-dihydro-1*H*-naphtho[2,1-*b*]pyran, 92643-39-5; 9,9-dimethyl-1,9,10,10a-tetrahydro-2*H*-phenaleno[9,1-*bc*]pyran, 92643-40-8; 2-[6-methyl-4-(phenylsulfonyl)hept-5-en-1-yl]-1-methylpyrrole, 92643-41-9; 1-methyl-4-(2-methyl-1-propenyl)-4,5,6,7-tetrahydro-1*H*-indole, 92643-42-0; 1-[5-methyl-3-(phenylsulfonyl)hex-4-en-1-yl]naphthalene, 92643-43-1.

Supplementary Material Available: Spectral data for **1-3**, **6a,b**, **7a,b**, **11**, **12**, **14**, **15**, and the starting material and products of eq 2 (3 pages). Ordering information is given on any current masthead page.

---

(9) Friedrich-Fiechtyl, J.; Spiteller, G. *Tetrahedron* **1975**, *31*, 479.

(10) Transition metals facilitate coupling with allyl sulfones. See: Trost, B. M.; Schmuff, N. R.; Miller, M. J. *J. Am. Chem. Soc.* **1980**, *102*, 5979. Cuvigny, T.; Julia, M. *J. Organomet. Chem.* **1983**, *250*, C21. Julia, M.; Righini, A.; Verpeaux, J. N. *Tetrahedron* **1983**, *39*, 3283.

Enantiomeric Enrichment of *cis*-Bicyclo[3.2.0]hept-3,6-dien-2-one with Circularly Polarized Light via the Photointerconversion of the Enantiomers

Maurizio Zandomeneghi* and Marino Cavazza*

Istituti di Chimica Fisica e di Chimica Generale
Università di Pisa, 56100 Pisa, Italy

Francesco Pietra*

Istituto di Chimica, Università di Trento
38050 Povo-Trento, Italy

Received May 21, 1984

Photochemical induction of optical activity with circularly polarized light (CPL)[1] is known to occur via either (i) the preferential photodecomposition of one enantiomer of a racemate,[2a–d,g] (ii) asymmetric photosynthesis,[1b,2a,e] or, finally, (iii) the photointerconversion of the enantiomers of a racemate.[2f] However, while the first two modes of inducing optical activity are well established for organic compounds,[1b,2a–e,g] mode iii, despite its fundamental importance, is confined to a few bidentate complexes of transition metals.[2f]

Actually, a variety of optically active organic substrates, such as biaryls,[3a] ketones,[3b] diketones,[3c] thiones,[3d] carboxybenzyl esters,[3e] [2.2]paracyclophanes[3f] and pyramidally blocked oxaziridines[3g] and sulfoxides[3h] have been photoracemized with achiral light. This, however, does not necessarily imply that CPL irradiation would induce optical activity in the corresponding racemates via the

---

(1) (a) Rau, H. *Chem. Rev.* **1983**, *83*, 535–547. (b) Buchardt, O. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 179–185.

(2) (a) Zandomeneghi, M.; Cavazza, M.; Festa, C.; Pietra, F. *J. Am. Chem. Soc.* **1983**, *105*, 1839–1843. (b) Cavazza, M.; Zandomeneghi, M.; Festa, C.; Lupi, E.; Sammuri, M.; Pietra, F. *Tetrahedron Lett.* **1982**, *23*, 1387–1390. (c) Cavazza, M.; Morganti, G.; Zandomeneghi, M. *J. Chem. Soc., Perkin Trans. 2* **1984**, 891–895. (d) Littman, S.; Gedanken, A.; Goldschmidt, Z.; Bakal, Y. *J. Chem. Soc., Chem. Commun.* **1978**, 983–984. Nicoud, J. F.; Moradpour, A.; Kagan, H. B. *J. Am. Chem. Soc.* **1974**, *96*, 5152–5158. (e) Bernstein, W. J.; Calvin, M.; Buchardt, O. *J. Am. Chem. Soc.* **1973**, *95*, 527–532 and references cited therein. (f) Stevenson, K. L.; Verdiek, J. F. *Mol. Photochem.* **1969**, *1*, 271–288. Stevenson, K. L.; Verdiek, J. F. *J. Am. Chem. Soc.* **1968**, *90*, 2974–2975. Stevenson, K. L. *J. Am. Chem. Soc.* **1972**, *94*, 6652–6654. Norden, B. *Acta Chem. Scand.* **1970**, *23*, 349–351. (g) Nelander, B.; Norden, B. *Chem. Phys. Lett.* **1974**, *28*, 384–385.

(3) (a) Tetreau, C.; Lavalette, D.; Cabaret, D.; Geraghty, N.; Welvart, Z. *Nouv. J. Chim.* **1982**, *6*, 461–465. Yorozu, T.; Irie, M.; Hayashi, K. *J. Phys. Chem.* **1978**, *82*, 2301–2304. Irie, M.; Yoshida, K.; Hayashi, K. *J. Phys. Chem.* **1977**, *81*, 969–972. Zimmermann, H. E.; Crumrine, D. S. *J. Am. Chem. Soc.* **1972**, *94*, 498–506. (b) Chae, W. K. *Taehan Hwahakhoe Chi* **1983**, *27*, 302–303; *Chem. Abstr.* **1983**, *99*, 175018. Sadler, D. E.; Hildenbrand, K.; Schaffner, K. *Helv. Chim. Acta* **1982**, *65*, 2071–2076. (c) Wagner, P. J.; Zepp, R. G.; Liu, K. C.; Thomas, M.; Lee, T.; Turro, N. J. *J. Am. Chem. Soc.* **1976**, *98*, 8125–8134. Hamer, N. K.; Samuel, C. J. *J. Chem. Soc., Chem. Commun.* **1972**, 470–471. (d) Couture, A.; Ho, K.; Hoshino, M.; De Mayo, P.; Suau, R.; Ware, W R. *J. Am. Chem. Soc.* **1976**, *98*, 6218–6225. (e) Yoshida, M.; Weiss, R. G. *Tetrahedron* **1975**, 31, 1801–1805. (f) Cram, D. J.; Delton, M. H. *J. Am. Chem. Soc.* **1970**, *92*, 7623–7625. (g) Bjorgo, J.; Boyd, D. R.; Campbell, R. M.; Neill, D. C. *J. Chem. Soc., Chem. Commun.* **1976**, 162–163. (h) Schultz, A. G.; Schlessinger, R. H. *J. Chem. Soc. D* **1970**, 1294–1295. Cooke, R. S.; Hammond, G. S. *J. Am. Chem. Soc.* **1970**, *92*, 2739–2745; **1968**, *90*, 2958–2959.

0002-7863/84/1506-7261$01.50/0