Reversible 1,3 transposition of sulfoxide and alcohol functions. Potential synthetic utility

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straction, leading to the well-stabilized ion d, based on

$$CH_3(CH_2)_8\overset{+}{C}H{=}\overset{+}{O}H$$
d, $(M - H)^+$

two factors: (1) strong attraction of the attacking reagent ions to the site of the polar group due to dipole interactions, (2) the absence of $(M - H)^+$ in the spectra of tertiary alcohols which bear no α-hydrogens.[1,2] To test this hypothesis we examined the chemical ionization spectra of **1a**-*1,1-d*$_2$ and **2a**-*1,1,10,10-d*$_4$, and found that only 10 (**1a**) and 3% (**2a**) of the hydrogen lost originates from the α positions (neglecting isotope effects). The values expected from statistically random abstraction are 9.5 and 4%, respectively. Although these results seem to oppose the concept of localized attack at the site of the polar group, a reasonable explanation may lie in the proposal, convincingly developed by Meyerson,[1a] that the functional group is internally solvated by the polymethylene chain, and hence is surrounded by a number of other eligible alkyl hydrogens at the time of attack by the reagent ion. In addition, the ratio of abundances $(M - H)^+/(M + H)^+$ on a % Σ_{60} basis increases with chain length (**2a**, 0.16; **3a**, 0.81; **3b**, 1.7; **3c**, 2.2), which also reflects decreased influence of the polar hydroxyl group in favor of the alkyl chain.

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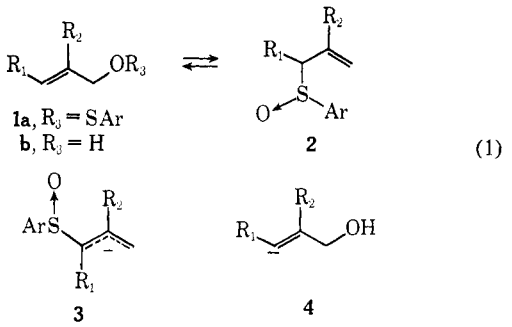
Reversible 1,3 Transposition of Sulfoxide and Alcohol Functions. Potential Synthetic Utility

Sir:

Synthetic operations which serve to "reverse" the normal reactivity of a functionalized carbon moiety have received scant attention.[1] However, as has been pointed out, this class of transformations holds forth great promise as a general manipulative operation which may create added flexibility in synthesis.[2] Herein we wish to illustrate the synthetic utility and scope of the *completely reversible* 1,3 transposition of sulfoxide and alcohol functions, the overall transformation being represented by eq 1. A representative demonstration of the flexibility that such a functional group interconversion creates is illustrated by the synthetic equivalence of the sulfoxide-stabilized anion **3** and the hypothetical vinyl anion **4**.[3]

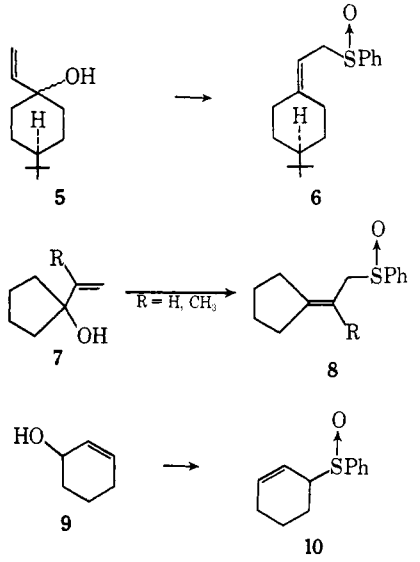
Recently, Mislow and coworkers have demonstrated that simple allylic alcohols such as **1b** (R_1, R_2 = H; R_1 = CH_3; R_2 = H), on conversion to the corresponding lithium alkoxides followed by treatment with aryl-



(1)

sulfenyl chlorides, may be smoothly transformed *via* the sulfenate esters **1a** into the rearranged allylic sulfoxides **2**,[4,5] this isomerization being a typical example of the generalized class of [2,3]-sigmatropic rearrangements.[6] As part of our general plan to utilize this rearrangement in synthesis we have demonstrated, indeed, that this reaction appears to be general and proceeds in excellent yields for the structurally diverse alcohols shown below (Scheme I). In the cases illustrated, the conversion of alcohol into rearranged sulfoxide may be executed in isolated yields in excess of 80% using conditions similar to those reported.[7]

Scheme I



The reverse transformation, *i.e.*, that of sulfoxide **2** into rearranged allylic alcohol **1b**, is highly desirable if the former function is to be employed as a temporary activating group in synthesis. We have shown that this transfer of functionality may be readily accomplished by simply heating the allylic sulfoxide in the presence of a suitable thiophile.[8] The allylic sulfenate esters (*e.g.*, **1a**), although usually present in low equilibrium concentration with the isomeric sulfoxides,[4,5] may be efficiently trapped by thiophenoxide to afford the rearranged allylic alcohols in good yields. Although the interception of an allylic sulfenate ester generated as a result of a [2,3]-sigmatropic process has

(1) D. Seebach, *Synthesis*, 17 (1969); E. J. Corey, B. W. Erickson, and R. Noyori, *J. Amer. Chem. Soc.*, **93**, 1724 (1971).
(2) E. J. Corey, *Pure Appl. Chem.*, **14**, 19 (1967).
(3) This equivalence is only possible if **3** reacts at the α rather than the γ position relative to the sulfoxide function.
(4) P. Bickart, F. W. Carson, J. Jacobus, E. G. Miller, and K. Mislow, *J. Amer. Chem. Soc.*, **90**, 4869 (1968), and references cited therein.
(5) R. Tang and K. Mislow, *ibid.*, **92**, 2100 (1970).
(6) J. E. Baldwin, R. E. Hackler, and D. P. Kelly, *Chem. Commun.*, 538 (1968).
(7) As a minor modification we use THF as a solvent and add the sulfenyl chloride to the alkoxide at −50°.
(8) A. J. Parker and N. Kharasch, *Chem. Rev.*, **59**, 583 (1959).

Table I. Cleavage of Allylic Sulfoxides[a]

Sulfoxide[b]	Alcohol	Conditions[c]	Yield, %[d]
2 (R_1, R_2 = H)	1 (R_1, R_2 = H)	65°, 6 hr	(77)
2 (R_1 = CH_3; R_2 = H)	1 (R_1 = CH_3; R_2 = H)	60°, 4 hr	(89)
6	5[e]	37° 15 hr	95
8 (R = H)	7 (R = H)	60°, 2 days	87
8 (R = CH_3)	7 (R = CH_3)	60°, 3 days	65 (>95)
10	9	60°, 3 days	74 (>95)

[a] Consistent spectral data and combustion analyses were obtained on all compounds reported. [b] Prepared by the method of Mislow, ref 4. [c] Standard conditions for cleavage consisted of heating a methanolic solution of 1 equiv of sulfoxide, 2–3 equiv of thiophenol, and 0.1 equiv of thiophenoxide. Reaction conditions were not optimized. [d] Figures in parentheses refer to glc yields relative to internal standard; other figures refer to isolated yields. [e] Mixture containing 85% equatorial O–H, 15% axial O–H.

been reported,[9] the general value of this transformation has gone unrecognized. The conditions and yields of these trapping experiments are reported in Table I.

11

A demonstration of the synthetic utility of this 1,3-functional group transposition operation to a potentially new and useful allylic alcohol synthesis is illustrated above. Treatment of phenyl allyl sulfoxide (**11**) with butyllithium at −50° affords the allylic anion **3** (R_1, R_2 = H). On further reaction of this species with excess methyl iodide followed by subsequent cleavage with either thiophenoxide in methanol or with other suitable thiophiles such as trimethyl phosphite[10] in methanol, *trans*-crotyl alcohol may be cleanly produced in 70–75% yields. This particular olefin synthesis offers the advantage of exercising some control on the types of olefin geometry generated as a result of the concerted nature of the sulfoxide rearrangement.[4] The application of these concepts to the synthesis of natural products is currently being pursued.

Acknowledgment. We wish to thank the U.S. Public Health Service, the Petroleum Research Fund, administered by the American Chemical Society, and Eli Lilly and Company for their support of this research.

(9) D. J. Abbott and C. J. M. Stirling, *J. Chem. Soc. C*, 818 (1969).
(10) Sulfenic acids have been intercepted with this reagent; *cf.* R. D. G. Cooper and F. L. José, *J. Amer. Chem. Soc.*, **92**, 2575 (1970).

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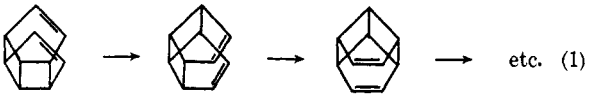
The Degenerate Cope Rearrangements in Hypostrophene, a Novel $C_{10}H_{10}$ Hydrocarbon

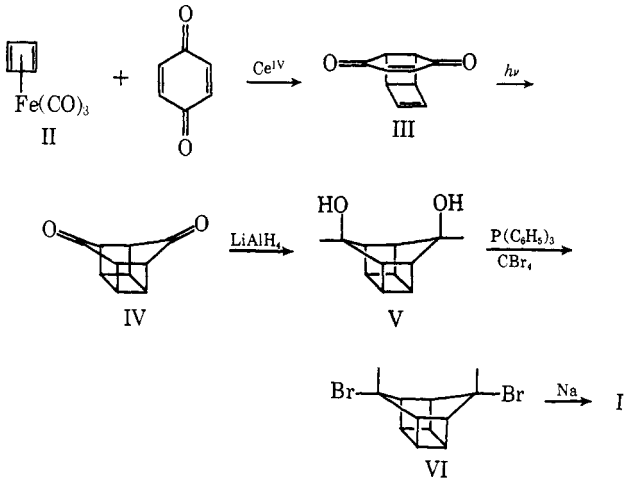
Sir:

Although there now exist several examples of molecules capable of undergoing facile degenerate Cope rearrangements, bullvalene[1] affords the first and only example of a hydrocarbon in which, through a sequence of such rearrangements, all atoms become equivalent on a time-averaged scale. Another $C_{10}H_{10}$ hydrocarbon isomeric with bullvalene which would also seem to have the potential capability of undergoing an endless sequence of degenerate Cope rearrangements resulting in complete time-averaged equivalence of the atoms is the compound I, for which we offer the trivial name hypostrophene.[2] We report here the synthesis of hypostrophene and offer evidence indicating that the sequence of degenerate Cope rearrangements indicated in eq 1 is occurring at room temperature.



I

The synthesis of hypostrophene was accomplished through the sequence of steps outlined below. Cyclobutadiene was liberated by oxidative degradation with ceric ion from its iron tricarbonyl complex II in the presence of benzoquinone to yield the Diels–Alder adduct III (56%) as a pale yellow crystalline solid: mp 77–77.5°; nmr ($CDCl_3$) τ 3.25 (s, 2 H), 3.8 (m, 2 H), and 6–6.5 (bm, 4 H).[3]



Irradiation of the adduct III in benzene with a 100-W immersion lamp afforded the caged ketone IV (45%), which formed white prisms from acetone [mp 218–221°; nmr ($CDCl_3$) τ 6.25 (m, 4 H) and 6.65 (m, 4 H)]. Reduction of the diketone IV with $LiAlH_4$ gave the corresponding diol V[4] [65%; mp 190–192°; nmr ($CDCl_3$) τ 4.5 (bs, 2 OH), 6.15 (bs, 2 H), and 7.0 (bs, 8 H)] which, upon treatment with $P(C_6H_5)_3$ and CBr_4,[5] yielded the corresponding dibromide VI [35%; mp 155–156°; nmr ($CDCl_3$) τ 5.4 (s, 2 H) and 6.7 (s, 8 H)]. The dibromide upon treatment with sodium sand for 3 hr at 50° in dioxane underwent dehalogenation and concomitant ring opening to yield hypostrophene (60%).

(1) W. v. E. Doering and W. R. Roth, *Tetrahedron*, **19**, 720 (1963); G. Schröder, *Angew. Chem.*, **75**, 722 (1963); *Angew. Chem., Int. Ed. Engl.*, **2**, 481 (1963); M. Saunders, *Tetrahedron Lett.*, 1699 (1963).

(2) This name is derived from the Greek word *hypostrophe* meaning "a turning about, a recurrence." The systematic name for the molecule is tetracyclo[5.3.0.$0^{2,6}$.$0^{3,10}$]deca-4,8-diene.

(3) J. C. Barborak, L. Watts, and R. Pettit, *J. Amer. Chem. Soc.*, **88**, 1328 (1966). This compound as well as all new compounds gave satisfactory analyses.

(4) An X-ray structure of the diol confirms the stereochemistry of the hydroxy groups depicted in structure V. We thank Drs. M. Wood and S. H. Simonsen for this structural analysis.

(5) R. Rabinowitz and R. Marcus, *J. Amer. Chem. Soc.*, **84**, 1312 (1962); F. Ramirez, N. B. Desai, and N. McKelvie, *ibid.*, **84**, 1745 (1962); J. Hooz and S. S. H. Gilani, *Can. J. Chem.*, **46**, 86 (1968).