Table I. Cleavage of Allylic Sulfoxides[a]

Sulfoxide[b]	Alcohol	Conditions[c]	Yield, %[d]
2 (R₁, R₂ = H)	1 (R₁, R₂ = H)	65°, 6 hr	(77)
2 (R₁ = CH₃; R₂ = H)	1 (R₁ = CH₃; R₂ = H)	60°, 4 hr	(89)
6	5[e]	37° 15 hr	95
8 (R = H)	7 (R = H)	60°, 2 days	87
8 (R = CH₃)	7 (R = CH₃)	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.
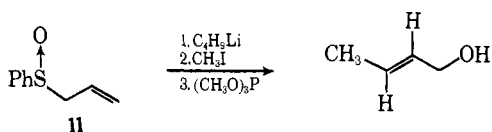
A demonstration of the synthetic utility of this 1,3-functional group transposition operation to a potentially new and useful allylic alcohol synthesis is illustrated above. Treatment of phenyl allyl sulfoxide (11) with butyllithium at −50° affords the allylic anion 3 (R₁, R₂ = H). On further reaction 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.

(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 C₁₀H₁₀ Hydrocarbon

Sir:

Although there now exist several examples of molecules capable of undergoing facile degenerate Cope rearrangements, bullvalene[1] affords the first and only

(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).

example of a hydrocarbon in which, through a sequence of such rearrangements, all atoms become equivalent on a time-averaged scale. Another C₁₀H₁₀ 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.
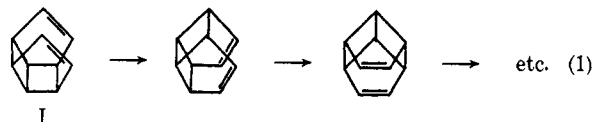
The synthesis of hypostrophene was accomplished through the sequence of steps outlined below. Cyclobutadiene was liberated by oxidative degradation with ceric ion from its iron tricarbonyl complex II in the presence of benzoquinone to yield the Diels–Alder adduct III (56%) as a pale yellow crystalline solid: mp 77–77.5°; nmr (CDCl₃) τ 3.25 (s, 2 H), 3.8 (m, 2 H), and 6–6.5 (bm, 4 H).[3]
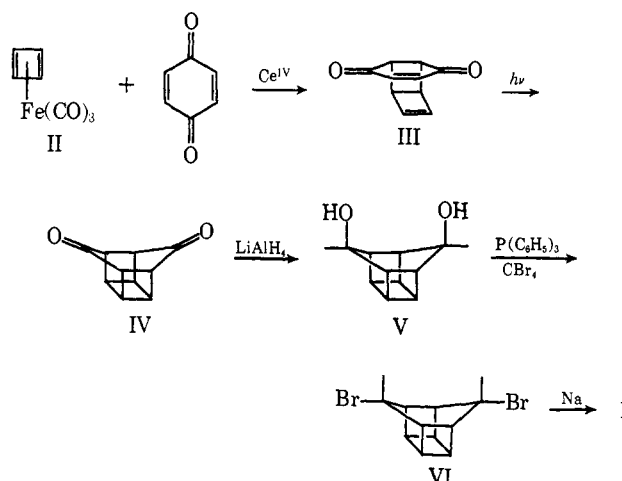
Irradiation of the adduct III in benzene with a 100-W immersion lamp afforded the caged ketone IV (45%), which formed white prisms from acetone [mp 218–221°; nmr (CDCl₃) τ 6.25 (m, 4 H) and 6.65 (m, 4 H)]. Reduction of the diketone IV with LiAlH₄ gave the corresponding diol V[4] [65%; mp 190–192°; nmr (CDCl₃) τ 4.5 (bs, 2 OH), 6.15 (bs, 2 H), and 7.0 (bs, 8 H)] which, upon treatment with P(C₆H₅)₃ and CBr₄,[5] yielded the corresponding dibromide VI [35%; mp 155–156°; nmr (CDCl₃) 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%).

(2) This name is derived from the Greek word hypostrophe meaning "a turning about, a recurrence." The systematic name for the molecule is tetracyclo[5.3.0.0²·⁶.0³·¹⁰]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).

Hypostrophene sublimes readily under reduced pressure at room temperature as colorless plates; the nmr spectrum ($CDCl_3$) of the material at room temperature consists of two singlet absorptions at τ 3.9 (4 H) and 6.8 (6 H).

The nmr spectrum of hypostrophene indicates that the degenerate rearrangements shown in eq 1, if they are occurring at all, must be slow with respect to the nmr time scale. Unfortunately, attempts to demonstrate the degenerate isomerization by having the nmr absorptions coalesce upon raising the temperature were thwarted due to the inception of a nondegenerate irreversible rearrangement of I leading to an isomeric compound having the proposed structure VII [nmr ($CDCl_3$) τ 3.7 (bs, 2 H), 4.3 (bs, 2 H), 7.0 (bs, 2 H), 7.4 (bs, 2 H), and 8.0 (bs, 2 H)]. The appearance of VII sets in at about 80°, at which point the nmr absorptions of hypostrophene remain as two relatively sharp singlets, and, although these absorptions show signs of broadening at temperatures near 100°, the results are inconclusive due to the rapid rearrangement to the isomer VII. It is of interest to note that the conversion of I to VII is "forbidden" by any concerted mechanism[6] and presumably proceeds (eq 2) via the intermediate diradical VIII.

$$I \rightarrow \text{VIII} \rightarrow \text{VII} \quad (2)$$
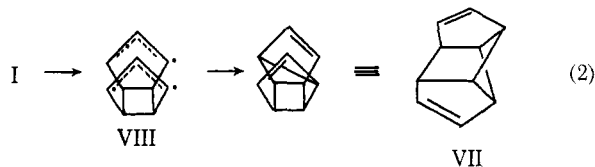
Despite the inability to obtain a definitive answer to the question of possible degenerate rearrangements occurring in hypostrophene by the simple technique of coalescence of nmr absorption bands, recourse to specific deuterium labeling experiments was successful.

Reduction of the caged diketone IV with $LiAlD_4$ afforded the dideuteriodiol IX (R = OH; R' = D), which was converted to the corresponding dideuterio dibromide derivative (IX, R = D; R' = Br) in the manner indicated earlier. The nmr spectra of the dideuteriodiol and dibromide were similar to the corresponding perhydro compounds except for the lack of absorptions of relative area two at τ 6.15 and 5.4,

$$\text{IX} \rightarrow \text{X} \quad (3)$$
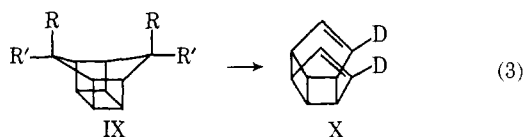
respectively, indicating that the deuterium atoms are at the positions shown in IX, as would be expected from their method of synthesis. However, dehalogenation of the dideuterio dibromide with sodium at 50° produced dideuteriohypostrophene in which the ratio of olefinic to saturated protons was found to be 1:1.5 rather than the 1:3 ratio to be expected from the synthetic conversion given in eq 3. The observed ratio of 1:1.5 is most readily explained by a mechanism involving initial formation of the specific dideuteriohypostrophene X followed by the extensive Cope type rearrangements as shown in eq 1.

(6) R. B. Woodward and R. Hoffmann, *Angew. Chem.*, 81, 797 (1969); *Angew. Chem., Int. Ed. Engl.*, 8, 781 (1969).

Dehalogenation of the dideuterio dibromide at −40° with sodium naphthylide in dimethyl ether[7] and maintenance of the temperature at −40° during subsequent separation steps afforded dideuteriohypostrophene in high yield. The nmr spectrum of this product at −50° possessed an olefinic to saturated proton ratio of 1:3, the expected ratio were no rearrangement occurring. Upon warming to 0°, the intensity of the olefinic peak began to increase while that associated with the saturated protons decreased. At 35°, the ratio was observed to be 1:1.5 and showed no further change with time. This ratio is that to be expected on a time-averaged basis were rearrangement occurring.

This latter result demonstrates that the hypostrophene molecule continually undergoes the sequence of degenerate Cope rearrangements outlined in eq 1. Further chemistry pertaining to the hypostrophene molecule is being studied and will be reported at a later date.

(7) *Vicinal* dihalides have been dehalogenated with sodium naphthylide [C. G. Scouten, *et al.*, *Chem. Commun.*, 78 (1969)]. The reaction of the dibromide with sodium naphthylide in dimethyl ether at −40° (formally a 1,4 elimination) was extremely rapid and appeared to be complete in approximately 15 sec.

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γ- vs. δ-Hydrogen Abstraction in the Photochemistry of β-Alkoxy Ketones. An Overlooked Reaction of Hydroxy Biradicals

Sir:

Two recent reports[1,2] on the photochemistry of β-alkoxy ketones of structure 1 confirm an earlier report[3] that very little Norrish type II photoelimination or cyclobutanol formation occurs. Instead 1 undergoes tetrahydrofuranol formation and elimination of alcohol. These reports all imply that rates of δ-hydrogen abstraction greatly surpass rates of γ-hydrogen abstraction in the excited states of 1. We report here results which indicate that such a conclusion is incorrect and that γ-hydrogen abstraction in ketones of structure 1 must lead to elimination of alcohol instead of to the normal type II products.[4]

We have studied the photochemistry of β-ethoxypropiophenone (2) and δ-methoxyvalerophenone (3), both of which possess a methylene bonded to oxygen at the δ position relative to the carbonyl. In benzene or *tert*-butyl alcohol, 3130-Å irradiation of 3 yields acetophenone, two cyclobutanols, and two cyclopentanols, the quantum yields for which are listed in Table I. Each cyclic product was collected and identified by its

(1) P. Yates and J. M. Pal, *Chem. Commun.*, 553 (1970).
(2) L. M. Stephenson and J. L. Parlett, *J. Org. Chem.*, 36, 1093 (1971).
(3) D. J. Coyle, R. V. Peterson, and J. Heicklen, *J. Amer. Chem. Soc.*, 86, 3850 (1964).
(4) For an earlier such suggestion which even the present authors temporarily forgot about, see P. J. Wagner and G. S. Hammond, *Advan. Photochem.*, 5, 108 (1968).