

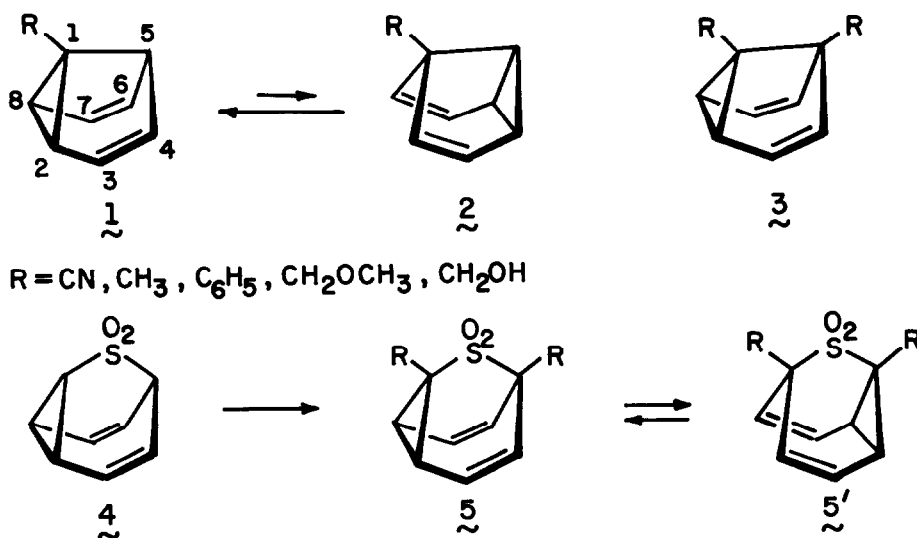
SYNTHESIS AND CRYSTAL STRUCTURE ANALYSIS OF 1,5-DISUBSTITUTED
9-THIABARBARALANE 9,9-DIOXIDES

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(Received in USA 27 January 1977; received in UK for publication 23 February 1977)

As a consequence of the highly fluxional nature of bridged homotropilidenes, such molecules are particularly sensitive to electronic perturbational effects. The large shifts in structural equilibrium resulting from monosubstitution of the semibullvalene nucleus has recently attracted considerable theoretical² and experimental attention.³ Of the known 1(5)-substituted derivatives, equilibration in favor of $\tilde{1}$ is seen, irrespective of the nature of R.³ However, unsymmetric functionalization as in $\tilde{1} \rightleftharpoons \tilde{2}$ is not particularly well suited to the creation of a stabilized transition state and attainment of neutral homoaromatic character. According to theory,² the optimum situation for a delocalized ground state could obtain upon symmetric π -donor substitution at C₁ and C₅, since the C₂-C₈ (and C₄-C₆) bond strengths should thereby be weakened. Because the energy gap separating ground state and activated complex for Cope rearrangement is smallest for semibullvalene ($\Delta H^\ddagger = 4.8$ kcal/mol)⁴ due to the minimal C₁-C₅ internuclear separation, a systematic study of $\tilde{2}$ should in principle afford the most definitive information. However, synthetic access to suitable 1,5-disubstituted semibullvalenes has remained elusive.⁵ On the other hand, the readily available⁶ and highly



\tilde{a} , R = CH₃; \tilde{b} , R = CN; \tilde{c} , R = Cl
 \tilde{d} , R = Br; \tilde{e} , R = I; \tilde{f} , R = F

crystalline 9-thiabarbaralane 9,9-dioxide (4) exhibits good capability for fluxional isomerism ($\Delta H^\ddagger = 9.4$ kcal/mol)⁷ combined with facile carbanion formation at both of its α -sulfonyl positions.⁸ We have therefore chosen to investigate various 1,5 functionalization schemes for 4 and to examine three such sulfones by three-dimensional X-ray crystallography.

1,5-Dimethyl derivative 5a (mp 237° dec)⁹ was previously obtained by alkylation of the dianion of 4 with methyl iodide.⁸ The dicyano (5b, mp 200-201° dec),⁹ dichloro (5c, mp 210-212° dec),⁹ dibromo (5d, mp 198-199° dec),⁹ and diiodo 9-thiabarbaralane 9,9-dioxides (5e, mp 202-206° dec)⁹ were synthesized by analogous procedures using cyanogen, cyanogen chloride, cyanogen bromide,¹⁰ and iodine,¹⁰ respectively, as coreagents. All attempts to prepare 5f from 4 and perchloryl fluoride¹¹ were uniformly unsuccessful.

Table I. ¹H NMR Chemical Shifts (90 MHz, CDCl₃, FT, 30° C) for the 9-Thiabaralane 9,9-Dioxides (8 units).

Compd	H ₃ ,H ₇	H ₂ ,H ₄ ,H ₆ ,H ₈	Other
<u>4</u>	5.96 (m)	4.45 (m)	
<u>5a</u>	5.85 (m)	4.14 (m)	1.58 (s)
<u>5b</u>	6.12 (m)	4.75 (br d)	
<u>5c</u>	5.86 (m)	4.59 (m)	
<u>5d</u>	5.80 (m)	4.70 (m)	
<u>5e</u>	5.57 (m)	4.72 (m)	

Sulfones 5a-e are characterized as being highly crystalline and sparingly soluble in organic solvents such as CDCl₃. Their ¹H NMR spectra (Table I) were accordingly recorded employing Fourier Transform techniques.¹²

Crystallographic data for 4 and 5b were obtained at 20 ± 1° C, while dichloro derivative 5c was studied at -57 ± 1° C to avoid the greater anticipated thermal motion of this derivative. Graphite monochromatized MoK α radiation ($\lambda = 0.71069$ Å) was used throughout. With the small crystals used, absorption effects were negligible. Cell constant and space group information for each of the compounds is summarized in Table II. All structures were solved using the heavy-atom Patterson technique and refined by standard least squares and difference Fourier methods using the CRYM system programs.¹³ Hydrogen atoms were located on difference Fourier maps and included in the calculations, but not necessarily refined. The crystal structure of 4 contains two independent molecules per asymmetric unit, one of which is disordered. Fortunately, the parameters of the ordered molecule were fairly insensitive to how the disorder was treated, and the bond values given in Table III are the average of two types of treatment for which R-factors are also given. The structure of 5c was completely disordered, with about half of the molecules oriented 180° to the remainder by a pseudo-twofold axis passing through the sulfur atom and bisecting the O-S-O angle. Although the indices of the refinement for 5c appear reasonable, the apparent thermal vibration amplitudes were unusually large as reflected for example in the apparent shortness of C₁-C₂ (1.470Å) and C₄-C₅ (1.474Å) and the nonequivalence of the sulfur-carbon distances (1.776Å vs. 1.792Å).¹⁴ Table

Table II. Crystal and Refinement Data for 4, 5b, and 5c.

	<u>4</u> ^a	<u>5b</u>	<u>5c</u>
Space group	P2 ₁ /c	P2 ₁ /c	Cmc2 ₁
z	8	4	4
a	9.805(1) Å	10.985(2) Å	9.154(5) Å
b	10.234(1)	6.577(1)	11.471(3)
c	14.968(2)	13.148(4)	8.720(3)
β	83.41(1) ^o	104.08(1) ^o	90.000 ^o
Data ^b	[4625] (4131)	2266	1030
R(F) ^c	[0.074] (0.109)	0.053	0.062
R _w ^c	[0.088] (0.156)	0.074	0.080
GOF ^d	[1.58] (2.76)	1.49	1.49
parameters	[262] (137)	149	78

^a Square brackets indicate values arrived at for unconstrained refinement using only anisotropic thermal parameters to account for disorder. Values in parentheses are for the constrained refinement of two half-weighted molecules for the disordered molecule. ^b $R(F) = \sum |F_o - F_c| / \sum F_o$. ^c $R_w = \{ \sum w |F_o^2 - F_c^2|^2 / \sum w F_o^4 \}^{1/2}$. ^d GOF = $\{ \sum w |F_o^2 - F_c^2|^2 / (n_o - n_p) \}^{1/2}$. Function minimized in L.S. = $\sum w |F_o^2 - F_c^2|^2$.

II gives the bonding parameters of interest for 4 and 5b.

All three molecules have point symmetry C_s. Except for the variations due to the anticipated substituent effects, all of the bond distances are reasonable, and are indicative of the stable ground state structures 5 or 5'. The difference in hybridization between C₁ and C₅ is apparent in the differences in the bond lengths to these carbons. In particular, the S-C distances are decidedly unequal, with the C-R bond lengths also reflecting the nonequivalence of the two ends of the molecules. Within each structure the six-membered thiacyclohexene rings are both in boat conformations with C₃ and C₇ bent outwards away from each other.

On the basis of extended Hückel calculations, Hoffman and Stohrer predicted an increase

Table III. Structural Data for 4 and 5b.^a

Parameter	<u>4</u>	<u>5b</u>
S-C(1)	1.729(6)	1.770(2)
S-C(5)	1.783(6)	1.835(2)
C(1)-C(2)	1.501(6)	1.524(3)
C(2)-C(8)	1.561(6)	1.537(3)
C(2)-C(3)	1.457(6)	1.466(3)
C(3)-C(4)	1.312(6)	1.321(3)
C(4)-C(5)	1.497(6)	1.513(3)
C(4)···C(6)	2.428(6)	2.480(3)
C(1)-X(1)	0.89(2)	1.438(3)
C(5)-X(2)	0.91(2)	1.466(3)
<C2-C1-C8	62.7(2) ^o	60.5(2) ^o
<C2-C5-C8	108.5(2) ^o	110.0(2) ^o

^aChemically equivalent distances have been averaged assuming C_s molecular symmetry.

of 0.02 in the bond order for C₂-C₈ with 1,5-dicyano substitution of semibullvalene.^{2a} If we assume that this change in bond order depends only on the change in π -acceptor-donor properties of the R group, then clearly we should expect a change in bond order for C₂-C₈ of similar magnitude in comparing the sulfones 4 and 5b. The observed difference in C₂-C₈ distance in going from 4 to 5b is +0.024(7) Å, which compares favorably with the predicted change of 0.031 Å (0.02 x 1.54 Å). Although structural data for 1,5-dicyanosemibullvalene are unavailable, comparison of the C₂-C₈ distance of 1-cyanosemibullvalene³ with that of semibullvalene¹⁵ gives an observed change of 0.028 Å,¹⁶ in good agreement with a predicted 0.031 Å. Both sets of results apparently support the predictions of Hoffman and Stohrer.^{2a} We should therefore expect the prediction of a change in bond order of -0.02 on 1,5-disubstitution with the strongly π -donating group fluorine to be equally valid, leading to a lengthening of ca +0.03 Å on going from the parent semibullvalene to its 1,5-difluoro derivative, or in our case, from 4 to 5f. Certainly, the lengthening for 5c should be no more than this. That a mixture of valence tautomers is observed regardless of whether the disorder is static or dynamic indicates that the delocalized form has still not become adequately stabilized by this substitution plan. We conclude that even in the case of 5f, it is very unlikely that a Cope transition state with a negative activation barrier will be reached. Clearly, a formal decrease in C₂-C₈ bond order to 0.5 (corresponding to ca 1.8 Å) is required. In this regard, the semibullvalene nucleus still holds some promise, inasmuch as its C₂-C₈ bond (1.600 Å) is longer than that of 4 (1.56 Å) and therefore already weaker. Experiments designed to gain access to 3 (R=F) are planned.¹⁷

FOOTNOTES AND REFERENCES

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- (16) The estimated error in this quantity is probably at least as large as 0.01 Å; no estimates of error were made in ref. 15, however, C₂ and C₈ have large thermal motion and the range of values contributing to each bond distance in ref. 15 is roughly 0.05 Å.
- (17) We are grateful to the National Science Foundation for their support of this work.