

Figure 1. A plot of emission maxima (in kcal/mol) vs. the solvent polarity parameter, $E_T(30)$ (in kcal/mol), derived from fluorescence spectra of 2-*N*-(3-methoxyphenyl)-amino-6-naphthalenesulfonate in a series of dioxane-water mixtures. The linear extrapolations illustrated yield estimated emission maxima for the $S_{1,np}$ state in hydrocarbon ($E_T(30) = 31$), for the $S_{1,np}$ state in glycerol ($E_T(30) = 57.0$), and for the $S_{1,ct}$ state in hydrocarbon.

derivatives in glycerol can be assigned to $S_{1,np}$ emissions. The basis is a good fit between observed emission energies and those predicted from the linear relationship between emission energy and solvent polarity in dioxane-water solutions. The latter correlations also generate estimated emission energies for the $S_{1,np}$ and $S_{1,ct}$ states in hydrocarbon solvent, leading to Hammett ρ values of -2.8 (np emissions) and -10.2 (ct emissions).

The observed and predicted maxima are listed in Table I, along with the quantum yields of fluorescence

Table I. Fluorescence Data for ANS Derivatives in Glycerol^a

Compound 1, X =	Obsd $\lambda_{max},^b$ nm	Predicted $\lambda_{max},^c$ nm	Quantum yield, ϕ_F^d
Br	436	433.2	0.43
Cl	430	432.5	0.47
F	437	438.4	0.43
H	437.5	436.2	0.49
CH ₃	458	459.6	0.40
OCH ₃	480	^e	0.14
OCH ₃ ^f	439	441	0.49

^a All derivatives (as Na⁺ salts) were carefully purified by multiple chromatographies. Structures were confirmed by nmr, ir, and uv spectra. ^b Spectra corrected using corrected spectra accessory of the Perkin-Elmer-Hitachi spectrofluorophotometer MPF-3. Excellent agreement with corrected spectra in the literature was obtained with known substances like anthracene. Positions ± 1 nm or less. ^c From the intersection of the linear correlation of emission energies classified as np and the vertical line for $E_T(30) = 57.0$ measured value for glycerol. ^d By digital integration of the corrected spectrum and comparison to quinine sulfate in 0.1 N H₂SO₄ ($\phi_F = 0.55$). Corrected for the refractive index of glycerol, ± 0.04 or less. ^e The slope of the correlation line reported in ref 1 for the emission maxima in dioxane-water indicates that only charge-transfer emissions can be observed in solvents of low viscosity. ^f Substituent on 3-position of *N*-aryl group.

in glycerol. Except for the methoxy derivative (1, X = OCH₃), the quantum yields are very similar ($0.44 \pm$

0.05) and, in particular, fail to reveal an internal heavy atom effect on intersystem crossing. That heavy atom effects are to be expected is demonstrated by the pattern of quantum yields as a function of solvent polarity observed for halogenated ANS derivatives. The yields are diminished for $S_{1,np}$ emission, in the order $\phi_F(1, X = F) > \phi_F(1, X = Cl) > \phi_F(1, X = Br)$, whereas the quantum yields of fluorescence for the $S_{1,ct}$ emission are unaffected by heavy-atom effects, decreasing with solvent polarity only as expected for most ANS derivatives. Thus, high quantum yields of fluorescence can arise from the $S_{1,np}$ state in solvents as polar as glycerol.

We may conclude that enhanced emission from ANS derivatives in viscous polar solvents occurs because the pathway to the charge-transfer state (and quenching reactions), electron-transfer, and CQ ("chemically quenched") formation² is blocked. It is also obvious that restricted rotation in polar binding sites of biological systems can strongly enhance fluorescence, and conclusions about the hydrophobicity of such sites must now be regarded with proper skepticism.

Figure 1 illustrates the extrapolations utilized to obtain (a) the predicted emission energy in glycerol, (b) the emission energy from the np state in hydrocarbon, and (c) the emission energy for the ct state in hydrocarbon.

(9) Also Department of Chemistry, State University of New York, Stony Brook, N. Y. 11790.

Edward M. Kosower,*⁹ Hanna Dodiuk
Department of Chemistry, Tel-Aviv University
Ramat-Aviv, Tel-Aviv, Israel
Received March 6, 1974

Radical Anions of Bicyclo[2.2.1]hept-5-ene-2,3-diones

Sir:

In 1965 Russell and coworkers reported long-range coupling in several bicyclic systems containing semidiones.¹ Similar observations have since been reported for bicyclic semiquinones,^{2,3} semifuraquinones,⁴ nitroxides,⁵ hydrazine cations,⁶ and semidiones.⁷ In the bicyclo[2.2.1]heptene skeleton, the semiquinone **1**^{2a} and semifuraquinone **2**^{4a} have been observed and discussed.²⁻⁴ An attempt to prepare bicyclo[2.2.1]hept-5-ene-2,3-semidione (**3**^{·-}) resulted in the observation of **4**.⁸ More recently, however, **3**^{·-} has been observed by reaction of esters or silyl ethers of *endo*-3-hydroxy-2-norbornenone with base and DMSO.⁹ We wish to report our preparation of **3**^{·-}, **5**^{·-}, and **6**^{·-} and long-range coupling which occurs in these radical anions.

Electrolytic reduction of **3**¹⁰ in DMSO with *n*-Bu₄-

(1) G. A. Russell and K.-Y. Chang, *J. Amer. Chem. Soc.*, **87**, 4381 (1965); G. A. Russell, K.-Y. Chang, and C. W. Jefford, *ibid.*, **87**, 4383 (1965).

(2) (a) D. Kosman and L. M. Stock, *J. Amer. Chem. Soc.*, **88**, 843 (1966); (b) **91**, 2011 (1969), and references therein.

(3) S. F. Nelsen and B. Trost, *Tetrahedron Lett.*, 5737 (1966).

(4) (a) S. F. Nelsen and E. D. Seppanen, *J. Amer. Chem. Soc.*, **89**, 5740 (1967); (b) *ibid.*, **92**, 6212 (1970); (c) S. F. Nelsen, E. F. Travaccedo, and E. D. Seppanen, *ibid.*, **93**, 2913 (1971).

(5) A. Rassat and J. Ronzaud, *J. Amer. Chem. Soc.*, **93**, 5041 (1971).

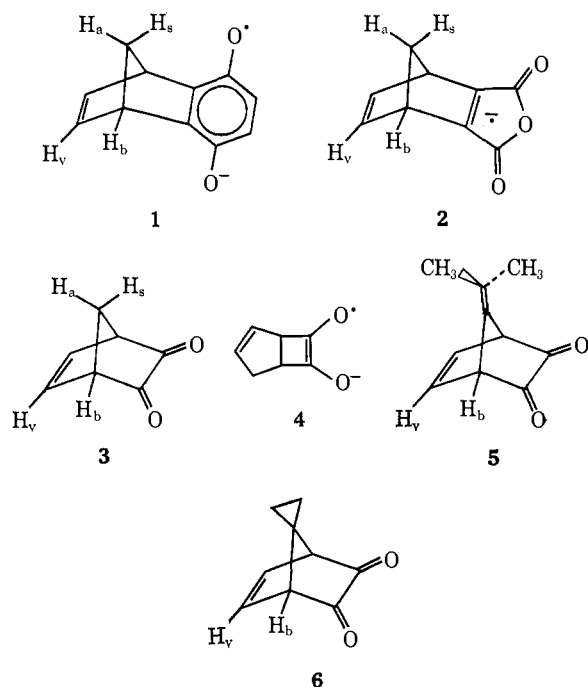
(6) S. F. Nelsen and P. J. Hintz, *J. Amer. Chem. Soc.*, **92**, 6215 (1970).

(7) G. A. Russell, P. R. Whittle, and R. G. Keske, *J. Amer. Chem. Soc.*, **93**, 1467 (1971), and references therein.

(8) G. A. Russell and K. Schmitt, *J. Amer. Chem. Soc.*, **94**, 8918 (1972).

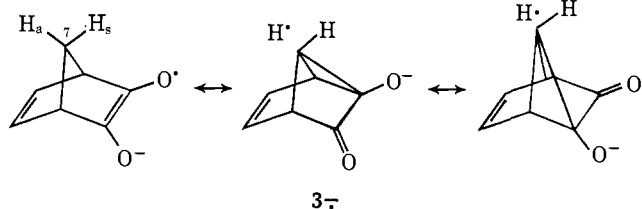
(9) K. Schmitt, Ph.D. Dissertation, Iowa State University, 1973.

(10) H.-D. Scharf, W. Droste, and R. Liebig, *Angew. Chem., Int. Ed., Engl.*, **7**, 215 (1968).



NCIO₄ as supporting electrolyte in the cavity of an esr spectrometer (Varian 4502) produced the spectrum of 3^{•-} shown in Figure 1. The spectrum gives no evidence for the presence of 4 even when the signal level is increased tenfold. Spectra of 5^{•-} and 6^{•-} were similarly obtained from 5 and 6¹¹ also with no other radicals present in detectable amounts. These results suggest that rearrangement of these semidiones to the [3.2.0]-bicyclic system (*e.g.*, 3^{•-} → 4) does not occur to any appreciable extent under these conditions. The stability of these radical anions differs significantly. When the electrolysis was terminated, 3^{•-} and 5^{•-} were undetectable after several minutes whereas 6^{•-} decayed with a half-life of ~15 min.

Rather large W-plan couplings have been observed in bicyclic semidiones.^{1,7,13} This strong coupling also occurs in 3^{•-} where a splitting of 8.08 G (Table I) is



obtained for H_a primarily through a homohyperconjugation interaction.^{13a} In contrast to 3^{•-}, the H_a-C₇-H_s group in 1 and 2 lies in a nodal plane of the highest occupied MO of the semiquinone and semifuraquinone π -systems so that contributions to the H_a coupling from homohyperconjugation cancel,¹⁴ resulting in hyper-

(11) Compounds 5 and 6 were prepared by heating a sixfold mole excess of dichlorovinylene carbonate with dimethylfulvene or spiro[4.2]-hepta-2,4-diene¹² in a sealed tube at 115° for 1 hr. With each diene a mixture of *exo* and *endo* Diels-Alder adducts was formed. Hydrolysis of these adducts in 50% aqueous dioxane at 90° for 1 hr or by the addition of 4 equiv of a 0.25 M KOH solution in ethanol gave 5 as red crystals (mp 99–100°) and 6 as yellow needles (mp 67–68°).

(12) K. Alder, H.-J. Ache, and F. H. Flock, *Chem. Ber.*, **93**, 1888 (1960).

(13) (a) G. A. Russell, G. Holland, K.-Y. Chang, and L. H. Zalkow, *Tetrahedron Lett.*, 1955 (1967); (b) G. A. Russell, G. W. Holland, and K.-Y. Chang, *J. Amer. Chem. Soc.*, **89**, 6629 (1967); (c) G. A. Russell, J. J. McDonnell, P. R. Whittle, R. S. Givens, and R. G. Keske, *ibid.*, **93**, 1452 (1971).

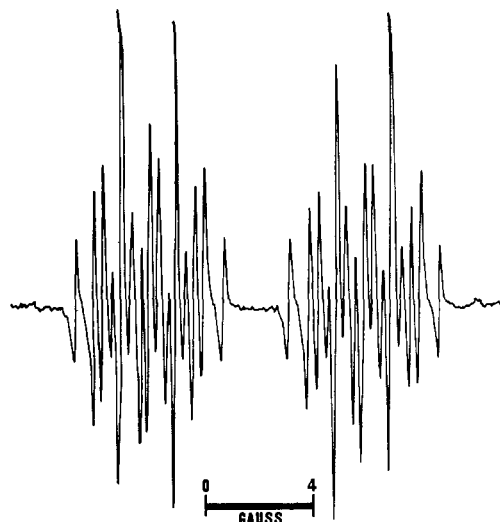


Figure 1. First derivative esr spectrum of semidione 3^{•-} in DMSO at 25°.

Table I. Hyperfine Splitting Constants for Some Bicyclic Radical Anions

Radical anion	Splitting (no. H)	Assignment
1 ^{2a}	2.36 (2)	H _{aromatic}
	0.81 (1)	H _a
	0.50 (2)	H _v
	0.36 (1)	H _s
2 ^{4a}	1.41 (1)	H _a
	0.79 (3)	H _v , H _s
	0.40 (2)	H _b
3 ^{•-}	8.08 (1)	H _a ^a
	2.14 (1)	H _s ^a
	1.04 (2)	H _b ^a
	0.70 (2)	H _v ^a
5 ^{•-}	1.63 (6)	H _{Me}
	0.89 (2)	H _b
	0.56 (2)	H _v
	1.07 (2)	H _a '
7 ^{4c}	0.81 (2)	H _v
	0.52 (2)	H _s ' or H _b
	0.46 (2)	H _b or H _s '
	2.40 (2)	H _{aromatic}
	0.47 (2)	H _v or H _a '
8 ^{2b}	0.38 (2)	H _s ' or H _b
	0.18 (2)	H _b or H _s '
	0.10 (2)	H _a ' or H _v
	0.95 (2)	H _b
	0.68 (2)	H _v
6 ^{•-}	0.20 (2)	H _{cyclopropane}
	0.98 (2) ^b	H _v
	0.34 (2) ^b	H _b
9 ^{4c}	0.15 (6) ^b	H _{Me}

^a Assignment based on methyl labeling⁹ and on an INDO calculation with an optimized geometry of 3^{•-}.¹⁵ ^b Hfsc recently obtained from a well-resolved spectrum of 9.¹⁶

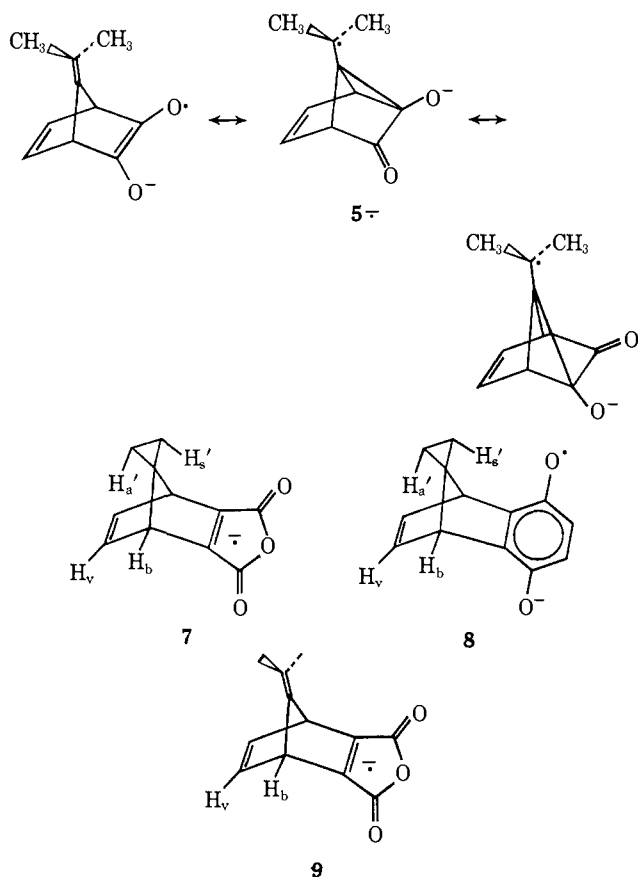
fine splittings of only 0.8^{2a} and 1.46^{4a}, respectively. This effect is also nicely illustrated in a comparison between 5^{•-} and 9 where methyl splittings of 1.63 and 0.15 G are obtained. The homohyperconjugation interaction which occurs in 5^{•-} cancels in 9 giving a considerably smaller coupling.

It is somewhat surprising that a coupling of only 0.20

(14) G. A. Russell and P. R. Whittle, *J. Amer. Chem. Soc.*, **89**, 6781 (1967).

(15) Unpublished results of R. L. Blankespoor and C. S. C. Chung.

(16) J. R. Mattox, Ph.D. Dissertation, Iowa State University, 1973.



G for two cyclopropane hydrogens in 6^- is observed. In **7** and **8** couplings for both H_a' and H_b' are obtained and are quite large in **7**, 1.07 and ~ 0.5 G, respectively. Possibly the semidione π -system is interacting differently with the cyclopropane Walsh orbitals.¹⁷ The decrease in hyperfine splitting of H_v and H_b in the sequence 3^- , 6^- , and 5^- is likely the result of changes in geometry rather than an electronic effect of the cyclopropyl and isopropylidene groups. Both spin polarization^{2b, 4c} and spin delocalization^{13b} mechanisms appear to be involved in these couplings.

Acknowledgment. Partial financial support from the Research Corporation is gratefully acknowledged.

(17) W. D. Walsh, *Nature (London)*, **159**, 167 (1947).

Ronald L. Blankespoor

Department of Chemistry, Wake Forest University
Winston-Salem, North Carolina 27109

Received July 18, 1974

Stereochemistry of a Silylene Addition Reaction

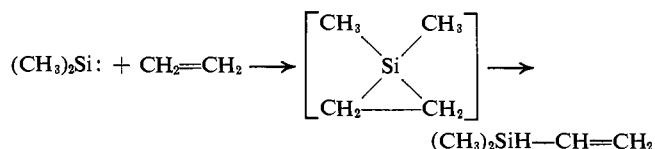
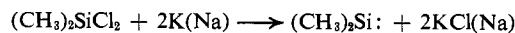
Sir:

While the stereochemistry of carbene addition reactions has provided data useful for the construction of mechanistic models¹ and for the diagnosis of the electronic states of reacting carbenes,² this communication is the first report of the stereochemistry of a silylene addition reaction.

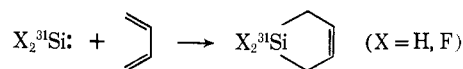
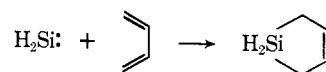
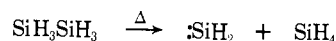
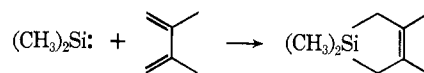
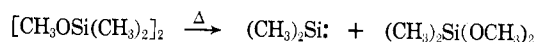
(1) For a review and references see D. Bethell, "Organic Reactive Intermediates," S. P. McManus, Ed., Academic Press, New York N. Y., 1973, Chapter 2.

(2) For a review and references see P. P. Gaspar and G. S. Hammond, "Carbenes," Vol. II, M. Jones, Jr., and R. A. Moss, Ed., Wiley, New York, N. Y., in press.

The scarcity of stereochemical information is due to the reluctance of divalent silicon species to form stable adducts with structures such that they would reveal the stereochemistry of addition.³ The addition of dimethylsilylene to ethylene, for instance, leads to vinyl dimethylsilane as the only product isolated, although the intermediacy of the silacyclopropane was inferred.^{4,5}



There is, however, a reaction which is capable of revealing the stereochemistry of silylene addition. The reaction of dimethylsilylene and 2,3-dimethylbuta-1,3-diene produces 1,1,3,4-tetramethyl-1-silacyclopent-3-ene in 15% yield,⁶ and the addition of silylene to buta-1,3-diene gives the unsubstituted 1-silacyclopent-3-ene in 40% yield.⁷ Nucleogenic $^{31}\text{SiF}_2$ and $^{31}\text{SiH}_2$ also undergo addition to butadiene.⁷⁻⁹



We have studied the gas-phase addition of silylene to *trans*-2-*trans*-4-hexadiene, a substrate capable of yielding stereoisomeric products. Pyrolysis of disilane was the method chosen to generate silylene.^{3,10} Rather than employing a recirculating flow system¹⁰ a single-pass system was utilized in order to minimize the risk of pyrolyzing the silylene addition products. A 1:5 mixture of disilane and the diene was passed once through an 8 mm i.d. Pyrex tube with a 12 cm-long hot zone maintained at 420°. The pressure in the reaction zone was *ca.* 50 Torr and the contact time in the hot zone was *ca.* 1 sec.

Reaction products were trapped at 77°K. Vapor-chromatographic analysis revealed two major products each formed in 10% yield based on the initial amount

(3) For a review and references see P. P. Gaspar and B. Jerosch Herold, "Carbene Chemistry," 2nd ed, W. Kirmse, Ed., Academic Press, New York, N. Y., 1971, Chapter 13.

(4) P. S. Skell and E. J. Goldstein, *J. Amer. Chem. Soc.*, **86**, 1442 (1964) (two papers).

(5) Recently silacyclopropanes have been isolated: R. L. Lambert, Jr., and D. Seyferth, *J. Amer. Chem. Soc.*, **94**, 9246 (1972); D. Seyferth, C. K. Haas, and D. C. Annarelli, *J. Organometal. Chem.*, **56**, C7 (1973).

(6) W. H. Atwell and D. R. Weyenberg, *J. Amer. Chem. Soc.*, **90**, 3438 (1968).

(7) P. P. Gaspar, R.-J. Hwang, and W. C. Eckelman, *J. Chem. Soc., Chem. Commun.*, 242 (1974).

(8) Y.-N. Tang, G. P. Gennaro, and Y.-Y. Su, *J. Amer. Chem. Soc.*, **94**, 4355 (1972).

(9) G. P. Gennaro, Y.-Y. Su, O. F. Zeck, S. H. Daniel, and Y.-N. Tang, *J. Chem. Soc., Chem. Commun.*, 637 (1973).

(10) E. M. Tebben and M. A. Ring, *Inorg. Chem.*, **8**, 1787 (1969); P. Estacio, M. D. Sefcik, E. K. Chan, and M. A. Ring, *ibid.*, **9**, 1068 (1970); M. Bowrey and J. H. Purnell, *Proc. Roy. Soc., Ser. A*, **321**, 341 (1971).