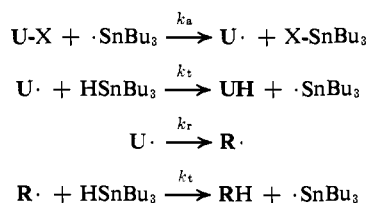


studies of rearrangement during such reductions using both chlorides and bromides are rare at best. In one, however, 5-chloro- and 5-bromonorbornenes gave an essentially identical mixture of norbornene and nortricyclene upon reduction with $n\text{-Bu}_3\text{SnH}$.¹⁵

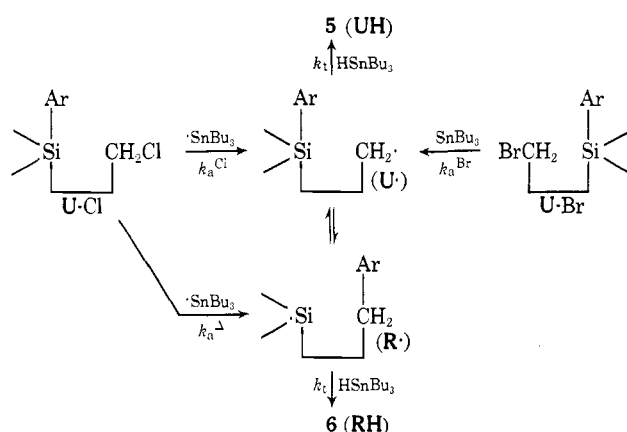
Mechanistically, the reactions of U-Cl and U-Br obviously differ in some regard. The accepted¹ chain process for such reactions is given in Scheme I, from

Scheme I



which it may be seen that the formation of rearranged product RH depends upon k_r , k_t , and the tin hydride concentration only. The extent of rearrangement of radical U· should be independent of its origin. Just how this sequence may be modified in the present case is not totally understood. Nonetheless, the fact that this halogen effect leveled off as the concentration of the reactants decreased, even as the extent of rearrangement expectedly³ increased, indicates that Scheme I may apply under very dilute conditions. That is, X plays no role and the extent of rearrangement is indeed governed by the ratio $k_r/k_t[\text{HSnBu}_3]$. There may be, in fact, an equilibrium¹⁶ established between U· and R· such that the extent of rearrangement under dilute conditions measures this equilibrium, assuming that the k_t values do not vary. At higher reactant concentrations some mechanistic feature must intrude, a feature that accommodates both an *increased extent of rearrangement* and an *increased reactivity* for U-Cl relative to U-Br. We suggest that a competitive process from U-Cl directly to R· can occur (k_a^Δ), utilizing anchimeric assistance by the propitiously positioned aryl group *via* an Ar₁-5 migration pathway, as shown in Scheme II. At any

Scheme II



concentration of reactants above that which would allow

(15) C. R. Warner, R. J. Strunk, and H. G. Kuivila, *J. Org. Chem.*, **31**, 3381 (1966). In this paper, a citation is made that the relative reactivity of *endo*-5-chloronorbornene (their *endo*-4c) is 0.37 times that of cyclopentyl bromide. In another place, this reactivity ratio was assigned to *endo*-5-bromonorbornene (their *endo*-4b) *vs.* cyclopentyl bromide. Because bromides are usually so much more reactive than chlorides in such reductions, we believe that the first citation contains a misprint (4c should be 4b).

(16) For discussions on such reversible processes in group IV radicals, see H. Sakurai, ref 2, Vol. 2, pp 795-799; ref 2, pp 374-377.

equilibration of U· and R·, this scheme would correctly predict more RH from U-Cl than from U-Br. Moreover, the additional pathway available to U-Cl could allow its overall rate of reduction to approach that of U-Br.¹⁷

The effect of the para substituents thus far examined reflects a combination of processes: k_a^Δ , the U· and R· equilibrium, and the k_t 's. The fact that the rearrangement seems to be mildly increased by electron donors must be further tested with a wider variety of substituents. The present data allow no quantitative conclusions as to the various rates involved, but further studies are contemplated toward this end.

(17) This is a qualitative view. Further work must be done to establish more conclusively the existence and the extent of this participation pathway.

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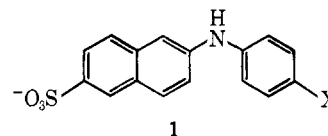
Fluorescence of

2-N-Arylamino-6-naphthalenesulfonates in Glycerol

Sir:

Fluorescence from 2-N-arylamino-6-naphthalenesulfonate (ANS) derivatives (1) occurs from either a naphthalene-centered ($S_{1,np} = (D - {}^1A)_{1,np}$) or a charge-transfer ($S_{1,ct} = (D^+ - A^-)_{1,ct}$) state.^{1,2} Conversion of the $S_{1,np}$ state to the $S_{1,ct}$ is effected by an intramolecular electron-transfer reaction which can occur only in a solvent of the appropriate polarity and fluidity. The latter requirement is related to the necessity for partial rotation of the 2-N-aryl group to a position in which overlap of the aryl π -orbitals with those of the naphthalene ring is sufficient to permit electron transfer.

The solvent glycerol is polar enough to stabilize the $S_{1,ct}$ state (Z value, 86.5; $E_T(30)$ value, 57.0³) and too viscous to allow rotation on the time scale of fluorescence. It was already known that viscous solvents (glycerol, 20% Ficoll, 60% sucrose) markedly enhanced the fluorescence of ANS derivatives over that expected in highly polar solvents⁵⁻⁷ and that anhydrous TNS (1,



X = CH₃) was strongly fluorescent, without any clear explanation for the phenomenon.⁸ We now report that the fluorescence maxima observed for ANS de-

(1) E. M. Kosower and K. Tanizawa, *Chem. Phys. Lett.*, **16**, 419 (1972).

(2) E. M. Kosower, H. Dodiuk, M. Ottolenghi, and N. Orbach, to be submitted for publication.

(3) Solvent polarity was measured with betaine-30 kindly supplied by Professor K. Dimroth (see ref 4) and the Z -value derived from the linear relationship between Z -value and $E_T(30)$ value shown in E. M. Kosower, "An Introduction to Physical Organic Chemistry," Wiley, New York, N. Y., 1968, p. 303.

(4) C. Reichardt and K. Dimroth, *Fortschr. Chem. Forsch.*, **11**, 1 (1968).

(5) W. O. McClure and G. M. Edelman, *Biochemistry*, **5**, 1908 (1966).

(6) C. J. Seliskar and L. Brand, *J. Amer. Chem. Soc.*, **93**, 5414 (1971).

(7) D. C. Turner and L. Brand, *Biochemistry*, **7**, 3381 (1968).

(8) A. Camerman and L. H. Jensen, *J. Amer. Chem. Soc.*, **92**, 4200 (1970).

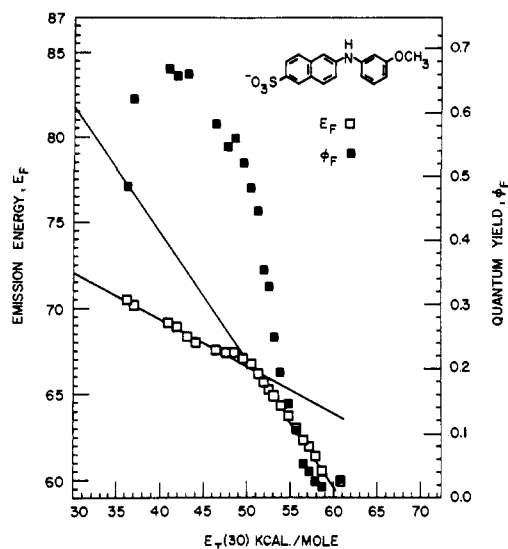


Figure 1. A plot of emission maxima (in kcal/mol) vs. the solvent polarity parameter, $E_T(30)$ (in kcal/mol), derived from fluorescence spectra of 2-*N*-(3-methoxyphenyl)-amino-6-naphthalenesulfonate in a series of dioxane-water mixtures. The linear extrapolations illustrated yield estimated emission 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.

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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. Travecedo, 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).