Table I. Quantum Yield for the Formation of IIa from Ia as a Function of Intensity[a]

Intensity, photons ml^{-1} sec^{-1}	3.8×10^{14}	1.5×10^{15}	3.1×10^{15}	6.1×10^{15}
Quantum yield of IIa	0.33	0.31	0.29	0.17

[a] Concentration, 0.042 *M;* solvent, CH$_3$OH; wavelength, 313.0 nm; degassed solution.

2.85 (6 H), 6.44 (3 H, singlet), 6.88 (1 H)) when compared to that of the undeuterated compound (τ 2.35 (2 H), 2.80 (6 H), 6.15 (1 H), 6.44 (3 H, singlet), 6.83 (2 H) indicated that the proton at τ 6.15 and one of the two protons at τ 6.83 had been replaced by deuterium atoms. These are the protons that can be located on the 9 and 10 positions in IIa. Evidently, irradiation of Ia in a deuterated solvent has caused the molecule to lose two hydrogen atoms from the rings and acquire two deuterium atoms from the solvent to give IIa.

When 1,2-diphenylfumaronitrile was irradiated in CDCl$_3$ (1.3 *M*), the yield of 9,10-dicyano-9,10-dihydrophenanthrene was less than 15%. Nmr analysis of the recrystallized product showed that the absorption at τ 5.6 which in the undeuterated compound is due to the two protons in the 9 and 10 positions was still present but its intensity corresponded to a deuterium content of 44% in these two positions. A second experiment in CDCl$_3$ (2.2×10^{-2} *M*) resulted in a product with a deuterium content of 40% in these positions. This suggests that the hydrogens in the 9 and 10 positions (when the reaction is run in a normal solvent) come from the solvent almost as often as from the starting material itself. The fact that the reaction goes in poor yield even in dilute solution indicates that side reaction(s) complicate the issue.[9]

As a second test of the free-radical mechanism, we have determined the quantum yield for the formation of IIa from Ia (0.042 *M* in CH$_3$OH) at 313.0 nm as a function of intensity. The results are given in Table I. If the isomerization is a purely intramolecular process which proceeds from an excited state of Ia *via* a derivative of III to give IIa, the quantum yield should be insensitive to changes in intensity.[10] The inverse dependence of the quantum yield on a fractional power of the intensity that these data show definitely rule out an intramolecular reaction path. Instead, a short-chain reaction to give product IIa, that is terminated by radical–radical recombination, would better fit the intensity dependence.

A variation in this mechanism (reactions 3, 4, etc.) can occur if the radical VI tended to lose an H atom instead of abstracting one. This would lead to a phenanthrene derivative from a stilbene precursor on irradiation even in the absence of any oxidizer. We have observed that irradiation of α-phenylcinnamic acid in methanol at 313.0 nm in a degassed solution gave 9-phenanthroic acid as a major C$_{15}$ product (yield <10%).

In addition to the examples cited by Sargent and Timmons, we have found that reaction 1 is a useful synthetic route to other 9-substituted 9,10-dihydrophenanthrenes of biological interest. Further studies on the scope of this reaction are in progress.

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[9] In their initial report, Sargent and Timmons[1a] do not give a yield for this reaction when it is run in degassed ethanol but indicate a yield of 7% in undegassed chloroform. In a later report[1b] they used benzene as the solvent and reported a yield of 85%. In this work, it was found impractical to use an alcohol as solvent because the diphenylfumaronitrile was only sparingly soluble. CDCl$_3$ was chosen over C$_6$D$_6$ as the solvent in order to have a ready source of abstractable D atoms.

[10] For theoretical analyses of intensity dependence in photochemical reactions, see J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., 1966, p 651.

Chiral Nuclear Magnetic Resonance Solvents. XI. A Method for Determining the Absolute Configuration of Chiral *N*,*N*-Dialkylarylamine Oxides

Sir:

Configurational assignments of chiral tertiary amine oxides are rare.[1,2] Accordingly, it is deemed worthwhile to report an nmr method for the determination of the absolute configurations of *N*,*N*-dialkylarylamine oxides. The method is based upon a hypothetical model for specific chiral solvent–solute interactions which cause the enantiomers of amine oxides to have nonidentical nmr spectra.[3]

The enantiomers of both *N*-methyl-*N*-ethyl-α-naphthylamine oxide (**1**) and *N*-methyl-*N*-ethylaniline oxide (**2**) show nmr spectral nonequivalence in (*S*)-(+)-2,2,2-trifluorophenylethanol (**3**) (see Figure 1). We have resolved[4] oxides **1** and **2** and determined their senses[5] and magnitudes[6] of nonequivalence in chiral **3** and several related chiral alcohols. In optically pure (*S*)-(+)-**3**, the *C*-methyl and *N*-methylene groups of (−)-enriched **1** show high-field senses of nonequivalence (0.019 and 0.017 ppm, respectively) whereas the *N*-methyl group shows low-field nonequivalence of 0.029 ppm. For (−)-enriched **2**, the senses of nonequivalence are the same, but the respective amounts of nonequivalence are 0.028, 0.005, and 0.019 ppm.

This spectral nonequivalence is explained in the following way. Rapid reversible hydrogen bonding between the chiral alcohol and the amine oxide enantiomers affords conformationally mobile 1:1 diastereomeric solvates. Secondary attractive interactions between the acidic carbinyl hydrogen of **3** and the basic π-electron clouds of the oxides' aryl groups leads to the conformations presently believed responsible for spec-

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(1) S. I. Goldberg and F. Lam, *J. Amer. Chem. Soc.*, **91**, 5113 (1969).

(2) M. Moriwaki, S. Sawada, and Y. Inouye, *Chem. Commun.*, 419 (1970).

(3) W. H. Pirkle, S. D. Beare, and R. L. Muntz, *J. Amer. Chem. Soc.*, **91**, 4575 (1969).

(4) J. Meisenheimer, *Ber.*, **41**, 3966 (1908).

(5) Sense of nonequivalence refers to the field positions, in the chiral solvent, of the resonances of the major solute enantiomer relative to the corresponding resonances of the minor enantiomer.

(6) Unless otherwise noted, spectra were obtained at 100 MHz and 29° employing samples composed of 2:1:*ca.* 5 mmol of chiral solvent–solute–deuteriochloroform.

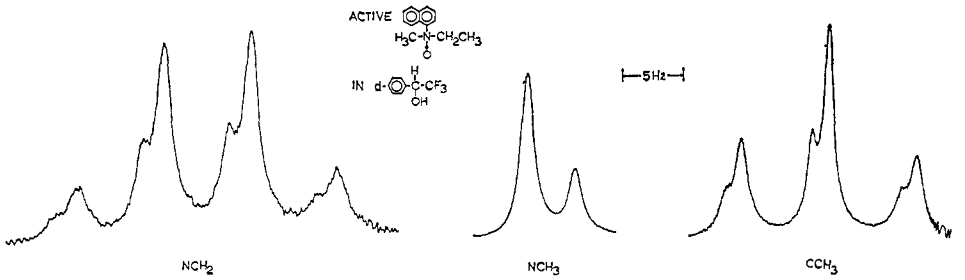

Figure 1. Enantiomeric nonequivalence exhibited by (−)-enriched oxide **1** in optically pure carbinol **3** at 100 MHz and 29°.

tral nonequivalence.[7] In this type of conformation, the (*S*)-(*S*) diastereomer formed from **1** and **3** (shown in Figure 2) has the ethyl group cis to the phenyl causing it to experience shielding relative to the trans methyl group. In the related conformation of the (*R*)-(*S*) diastereomer, the positions of the methyl and ethyl groups are reversed. Accordingly, the ethyl resonances should appear at higher field in the (*S*)-(*S*) solvate than in the (*R*)-(*S*) solvate while the opposite should be true for the methyl resonances.[10] Similar arguments apply for **2** and it is on this basis that (−)-**1** and (−)-**2** were originally assigned the *S* configuration.

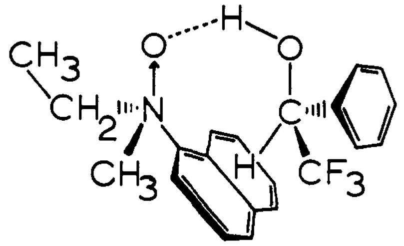

Figure 2. Conformation of the solvate between (*S*)-**1** and (*S*)-**3** resulting from the postulated secondary interaction. This model is employed to relate senses of nonequivalences to absolute configurations.

A conclusive demonstration that (−)-**2** has the *S* configuration was achieved by the X-ray analysis of the salt[5] of (−)-**2** and (+)-3-bromocamphor-9-sulfonic acid, of known absolute configuration.[11] Crystal data observed are: colorless needles; $C_{19}H_{28}BrNO_5S$; mol wt 462.42; monoclinic, a = 14.620 (4), b = 7.062 (5), c = 11.534 (5) Å, β = 114° 42′ (1′); $V = 1081.9 \times 10^{-24}$ cm^3; ρ_{obsd} = 1.42 g cm^{-3}; Z = 2; ρ_{calcd} = 1.43 g cm^{-3}; space group $P2_1$. The structure has been refined to an R factor of 0.045 on 1669 independent nonzero reflections collected on a Picker FACS-1 diffractometer (Cu Kα radiation). The structure and conformation of the salt in the crystal are shown in Figure 3.[12]

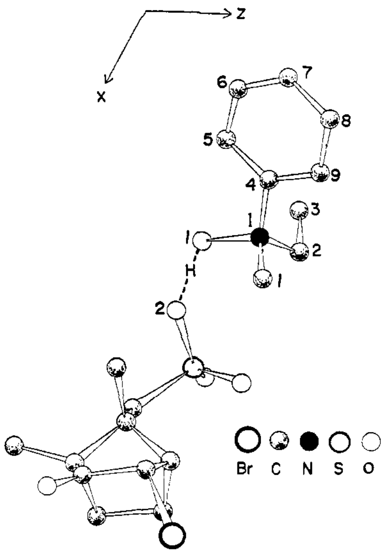

Figure 3. View of the salt looking along the *b* axis.

Further support for the conformational model comes from spectral changes observed when the structure of solvent or solute is altered. When (*S*)-2,2,2-trifluoro-(1-naphthyl)ethanol (**4**) is used as solvent, the magnitudes of nonequivalence of (−)-enriched **1** and (−)-enriched **2** are approximately doubled owing to the greater diamagnetic anisotropy associated with 1-naphthyl than with phenyl; however, the senses of nonequivalence are unchanged. No nonequivalence is observed in the spectrum of oxide **2** in chiral 2,2,2-trifluorocyclohexylethanol, presumably a result of the cyclohexyl's reduced diamagnetic anisotropy. Moreover, the finding that *N*-methyl-*N*-ethylcyclohexylamine oxide does not show perceptible nonequivalence in chiral **3** reinforces the view that the secondary interaction is essential to the population of the proposed conformations since, in this instance, the absence of the electron-rich aromatic group precludes the secondary interaction.

It should be noted that replacement of nitrogen with phosphorus should not alter the model's stereochemical predictions. Indeed, the model correctly accounts for the senses of nonequivalence observed in chiral **2** for

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[7] Inductive and resonance effects cause the carbinyl hydrogen to be sufficiently acidic so that the carbinol, like chloroform, may form "collision complexes" with aromatic rings.[8] Burlingame[9] has shown that interactions of this type occur between the methyl ether of **3** and α-methylnaphthalene.

[8] A. L. Alfred, *J. Phys. Chem.*, **64**, 1469 (1962).

[9] T. G. Burlingame, Ph.D. Thesis, University of Illinois, 1970.

[10] The observation that the methyls of *N*,*N*-dimethylaniline oxide are perceptibly diastereotopic (0.038 ppm) in chiral **2** demonstrates that neither differential extents of solvation nor differential steric factors need be invoked to account for the nonequivalence observed. The conformational argument presented implies that other conformations make insignificant contributions toward the sense or magnitude of nonequivalence.

[11] J. A. Wunderlich, *Acta Crystallogr.*, **23**, 846 (1967); S. M. Johnson, I. C. Paul, K. L. Rinehart, Jr., and R. Srinivasan, *J. Amer. Chem. Soc.*, **90**, 136 (1968); F. H. Allen and D. Rogers, *Chem. Commun.*, 837 (1966).

[12] While the absolute configuration of (−)-**2** is based principally on the configuration of **2** in the salt, relative to that of the bromocamphorsulfonate, refinement incorporating the anomalous dispersion effect also supports this absolute configuration The distinction between the oxygen atom and the methyl group on the nitrogen is clearly evident from consideration of bond lengths, hydrogen bonding assignments, location of hydrogen atoms around the methyl carbon atom, and the results of refinement of both atoms with carbon scattering curves.

configurationally known[13] P-alkyl-P-methylphenylphosphine oxides (alkyl = cyclohexyl, benzyl, or n-propyl).

Acknowledgment. This work has been supported by U. S. Public Health Service Grant No. GM 14518. Funds for the 220-MHz nmr spectrometer were provided in part by the National Science Foundation.

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(14) Alfred P. Sloan Research Fellow, 1970–1972.
(15) National Institutes of Health Predoctoral Fellow, 1970–present.
(16) Alfred P. Sloan Research Fellow, 1968–1970.

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On the Structure of the Activated Complex in Atom-Transfer Reactions

Sir:

When aromatic compounds are reduced with alkali metals to form radical ions, their electron spin resonance (esr) spectra often exhibit splittings which are attributable to interactions of the unpaired electron with the metal nucleus.[1] The "ion-pair"splittings depend on the nature of the metal ions, temperature, and solvents. Several models have been proposed to explain the variation of these splittings with temperature,[1-3] and more recently, some detailed calculations have been reported which study the spin density at the alkali metal nucleus as a function of the metal–hydrocarbon distance.[4-7] To date, however, there has been a notable lack of experimental data on the actual metal–hydrocarbon distances. We present here preliminary results on the sodium naphthalenide system in which we have obtained a measure of the sodium–naphthalene distance in the transition state.

In order to perform this measurement, we have exploited the variation of the rate constant of the atom-transfer reaction with changing dielectric constant

$$\mathrm{Na^+C_{10}H_8^-} + \mathrm{C_{10}H_8} \rightleftarrows \mathrm{C_{10}H_8} + \mathrm{Na^+C_{10}H_8^-} \qquad (1)$$

of the reaction medium. $C_{10}H_8$ and $C_{10}H_8^-$ represent the neutral molecule and the anion radical of naphthalene. We believe that this is the first report of such a measurement involving hydrocarbons, and it supports the suggestion that variations of the rate constant with concentration reported previously are due to changes in the dielectric constant of the solvent.[8]

In 1957 Marcus derived an expression which relates the rate constant of an electron-transfer reaction to the optical and static dielectric constants of the reacting medium.[9] Recently, this equation has been applied with some success to atom-transfer reactions.[10] For our system his equation assumes the form

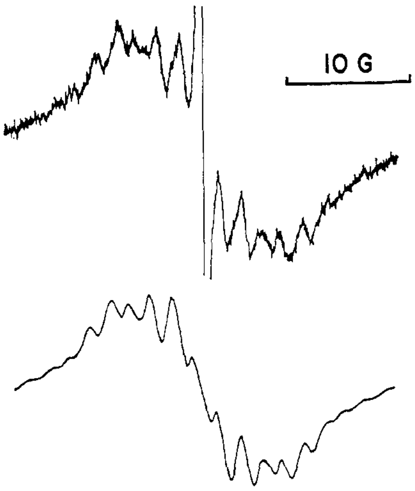

Figure 1. Upper trace: experimental esr spectrum of sodium naphthalenide in tetrahydrofuran at 25°. The concentration of the neutral naphthalene is 0.98 M. The center peak is due to the potassium naphthalenide ion pair or the free ion (see ref 12 and 13). Lower trace: computer-simulated spectrum assuming a second-order rate constant of $2.1 \times 10^7\ M^{-1}\ \mathrm{sec}^{-1}$.

$$\ln k = -\frac{R}{8aRT}\left[\frac{1}{D_{\mathrm{op}}} - \frac{1}{D_{\mathrm{s}}}\right] + \ln Z \qquad (2)$$

where k is the second-order rate constant, R is the gas constant, T is the temperature, Z is the collision frequency, and D_{op} and D_{s} are the optical and static dielectric constants. In (2) a is the distance of closest approach of the reacting species in the transition state, *i.e.*, the radius of the activated complex. Clearly, it would be desirable to have a knowledge of a both in the discussion of the structure of the ion pairs and in elucidating the mechanism of atom transfer.

Rates were measured in the intermediate-exchange region.[11] This region was chosen because it allowed us to monitor the ion-pair species involved in the reaction by simulating the exchange-broadened but uncollapsed spectrum. We wanted to be sure that indeed we were measuring the rate of exchange of a sodium naphthalenide ion pair with a given splitting[12,13] and that we were not changing the structure of the ion pair by varying the dielectric constant of the solution. Since the exchange spectra of ion pairs with different splittings differ markedly, such an effect would be easily observable. Figure 1 is a graphic illustration of the point, the top trace being the experimental spectrum and the lower trace the computer simulation. Altering the sodium splitting by as little as 0.1 G produces a perceptibly different spectrum than that shown in Figure 1.

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