was shown to possess an exo formyl group, and the other adduct was found to possess an endo formyl function by nmr spectroscopy.[9] Especially revealing was the chemical shift of the proton α to the formyl group (assignment confirmed by irradiation of the formyl proton) which occurred (in CDCl$_3$, parts per million downfield from internal tetramethylsilane) at 1.66 and 2.36 for the adducts of higher and lower R_f, respectively. The nmr data and the known stereochemistry of the Diels–Alder reaction thus allowed the assignment of structure **9** to the predominating (higher R_f) adduct. Reaction of **9** with the sodio derivative of dimethyl 2-oxoheptylphosphonate[7] produced the cyanoenone **10**.[8] Reduction of **10** with sodium borohydride in methanol at 0° produced a 1:1 mixture of two racemates[8] differing with regard to the newly created stereocenter and separable by tlc (silica gel, 85:15 petroleum ether ether, multiple development). Hydrolysis of the isomeric, racemic carbinols using potassium hydroxide (10 equiv, 0.3 M) in 4:1 ethanol-water at reflux (argon atm) for 48 hr and isolation in the usual way afforded each of the oily isomeric acids **8**.[10]

(8) The infrared, nmr, and mass spectra were in accord with the structure assigned to this oily substance.

(9) See J. C. Davis, Jr., and T. V. Van Auken, *J. Amer. Chem. Soc.*, **87**, 3900 (1965).

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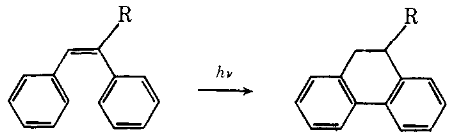
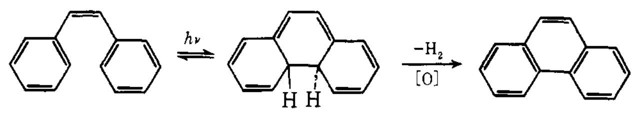
Photoisomerization of Certain Stilbenes to 9,10-Dihydrophenanthrenes

Sir:

Several years ago Sargent and Timmons reported[1] that the irradiation in the absence of oxidizing agents of certain stilbenes with one or more electron-withdrawing substituents on the central double bond, I, led to the formation of the isomeric 9,10-dihydrophenanthrenes (II). In view of the known, well-documented oxidative photocyclization of stilbene to phenanthrene (reaction 2)[2–4] which proceeds through the initial isomerization of the stilbene to the dihydrophenanthrene III it was suggested[1a] that in the case of I, the initial photoproduct was also a derivative of III which under oxidizing conditions gave the corresponding phenanthrene but otherwise rearranged to the 9,10-dihydrophenanthrene (II). However, in a more recent review, Blackburn and Timmons[5] have commented that the "mechanistic implications of this reaction (reaction 1) are not clear."

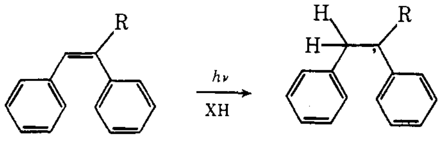


Ia, R = COOCH$_3$ IIa, R = COOCH$_3$ (1)

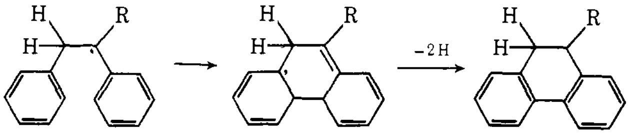


III (2)

We suggest that reaction 1 is most probably a free-radical process consisting of several steps which may be initiated by the abstraction of a hydrogen atom from a donor molecule (XH) by the stilbene I in an electronically excited state (eq 3). The donor molecule can be the solvent and it is noteworthy that this reaction has been observed[1] usually in good hydrogen donating solvents such as chloroform, methanol, and ethanol. The radical IV can cyclize to V which will tend to lose 2 H atoms in order to aromatize again.[6] Hence, it can also serve as a hydrogen donor to another stilbene molecule. The process will end with the abstraction of a hydrogen atom by the radical VI to give the observed product.



IV (3)



IV V VI (4)

We have carried out some tests of this mechanism with methyl α-phenylcinnamate (Ia) which is photoisomerized in methanol (in a nitrogen atmosphere) at 313.0 nm to methyl 9,10-dihydrophenanthrene-9-carboxylate (IIa)[7] in 72% yield, as well as with 1,2-diphenylfumaronitrile which was investigated by Sargent and Timmons.[1]

The first test was to conduct the irradiation in a fully deuterated solvent to determine the extent to which the 9,10 positions in the product were labeled.

A solution of Ia (4.2×10^{-2} M) in CD$_3$OD was irradiated to about 70% conversion. The product IIa that was formed was separated by vapor phase chromatography and characterized by its spectra. The mass spectrum showed a parent peak at m/e 240 which corresponded to the presence of two deuterium atoms in the molecule. The nmr spectrum (τ 2.40 (2 H),

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(1) (a) M. V. Sargent and C. J. Timmons, *J. Amer. Chem. Soc.*, **85**, 2186 (1963); (b) M. V. Sargent and C. J. Timmons, *J. Chem. Soc.*, 5544 (1964).

(2) F. B. Mallory, C. S. Wood, and J. T. Gordon, *J. Amer. Chem. Soc.*, **86**, 3094 (1964), and earlier references therein.

(3) W. M. Moore, D. D. Morgan, and F. R. Stermitz, *ibid.*, **85**, 828 (1963).

(4) K. A. Muszkat and E. Fisher, *J. Chem. Soc. B*, 662 (1967), and earlier references therein.

(5) E. V. Blackburn and C. J. Timmons, *Quart. Rev., Chem. Soc.*, **23**, 482 (1969).

(6) Molecular elimination of hydrogen is not considered because gas evolution was not observed during photolysis.

(7) Identified as the acid,[8] mp 123.5–125.5°; satisfactory elemental analysis was obtained for the ester.

(8) Literature value 123–124°: H. De Konig, K. Wiedhaup, U. K. Pandit, and H. O. Huisman, *Recl. Trav. Chim. Pays-Bas*, **83**, 364 (1964).

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_3OH; 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_3OH) 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_6D_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.