suspension yielded a clear yellow solution which, however, soon turned cloudy again. The nature of the reaction is unknown but might involve addition of triethylamine to the double bond. Yields of distilled alkenyldiazenes from high-boiling reaction media were low. Solutions in solvents other than CH$_3$CN and DME were not extensively investigated.

2-Propenyldiazene. Procedures used for the generation and distillation of propenyldiazene were similar to those used for vinyldiazene, except that the carbonyl compound was chloroacetone. Since propenyldiazene was more reactive in the bimolecular reaction, measurements had to be carried out more quickly than for vinyldiazene.

Rate Measurements. The disappearance of the absorption band due to the $n \rightarrow \pi^*$ transition was followed with time using a cell in a thermostatted cell compartment (25°). Rate constants were calculated as previously described.[1]

Nmr Measurements. The major problem in preparing samples of alkenyldiazenes suitable for nmr studies was to attain sufficient concentrations of the alkenyldiazenes in the solvents used. The circumstance that benzoic acid could be used as a catalyst for acclerating hydrazone formation even in solutions which contained hydrazine was very helpful. Up to 0.3 *M* solutions of vinyldiazene and 2-propenyldiazene in *n*-heptane, DME, and CH$_3$CN were prepared and examined at various temperatures from -60 to $+25°$. Alkenyldiazenes were collected together with solvent by distillation into a receiver held at 77°K. The solvents were melted at the lowest possible temperature (DME, $-65°$; CH$_3$CN, $-40°$; *n*-hexane, $-95°$) and the solutions poured quickly through a side arm into an nmr tube sealed onto the apparatus. The solutions were frozen in liquid nitrogen, the nmr tube was sealed off and spectra were taken at various temperatures and times. In most cases, a small amount of tetramethylsilane was distilled into the solution or added to the original reaction medium.

1-Methyl-2-vinyldiazene was prepared in exactly the same manner as vinyldiazene from chloroacetaldehyde semihydrate and methylhydrazine. The nmr spectrum and the uv spectrum were consistent with the assigned structure. The compound was not further characterized. Data are recorded in Table I and in Figure 2.

Nmr Samples of Alkenyldiazenes. Vinyldiazene. Degassed hydrazine (80 μl in 1 ml of solvent) was distilled into a mixture of chloroacetaldehyde semihydrate (150 mg) and benzoic acid (100 mg) in a solvent (CH$_3$CN, 4 ml; or DME, 4 ml; or CD$_3$CN, 2 ml). The mixture was warmed to room temperature and stirred for 1.5–2 min, the yellow color of the vinyldiazene appearing rapidly. The mixture was then distilled into a receiver at 77°K, about 1 ml of distillate being collected. The frozen vinyldiazene solution was melted at the lowest possible temperature, the intensely yellow (or orange) solution transferred to an nmr tube, the solution frozen, and the tube sealed off. The nmr sample of **2-propenyldiazene** was prepared in exactly the same manner.

Solvent and Substituent Effects on the Thermal Isomerization of Substituted Azobenzenes. A Flash Spectroscopic Study

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Abstract: Thermal isomerization of some para-donor/para′-acceptor-substituted azobenzenes [for example, 4-(diethylamino)-4′-nitroazobenzene] was studied by observing relaxation to equilibrium following flash photolysis. Several of these dyes show much faster rates of thermal isomerization than those measured for azobenzene and its monosubstituted derivatives. The observation of sizable solvent effects on the rates and activation energies for thermal isomerization suggests that a rotational mechanism might be operative for these azobenzenes.

The thermal and photochemical isomerization of azobenzenes has been the subject of much investigation.[5–12] In contrast to the stilbenes which show sizable activation energies for thermal isomerization and thus exist as discrete, isolable isomers at ordinary temperatures, azobenzenes are readily isomerized (activation energies *ca.* 23 kcal/mol)[6] at room temperature. The mechanism of the facile thermal isomerization of azobenzene is still the subject of investigation. Schulte-Frohlinde suggested that azobenzenes isomerize thermally by rotation about the N=N bond;[8] however, since an N=N bond should have a higher barrier to rotation than a C=C bond[13,14] the explanation is less than satisfactory. Others have suggested that contributions from dipolar structures can lower the barrier to rotation in azobenzenes.[5–7] The lack of major solvent or substituent effects on the rate of isomerization of several azobenzenes has been cited as evidence against the rotational mechanism.[9,15] An alternative mechanism for thermal isomerization of azobenzenes is inversion of one or both of the nitrogens through a linear (sp hybridized) transition state in which the double bond is retained.[9,13] Evidence favoring this path includes the finding that imines, for which this path is possible, have rapid rates of isomerization,[16] but ole-

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[4] Alfred P. Sloan Foundation Fellow, 1970–1972.

(5) G. S. Hartley, *Nature* (*London*), **140**, 281 (1937).

(6) R. J. W. Le Fevre and J. O. Northcott, *J. Chem. Soc.*, 867 (1953).

(7) H. H. Jaffé, *Chem. Rev.*, 53, 191 (1953).

(8) D. Schulte-Frohlinde, *Justus Liebigs Ann. Chem.*, **612**, 131, 138 (1958).

(9) E. R. Talaty and J. C. Fargo, *Chem. Commun.*, 65 (1967).

(10) D. Gegiou, K. A. Muszkat, and E. Fischer, *J. Amer. Chem. Soc.*, **90**, 3907 (1968), and references therein.

(11) P. P. Birnbaum and D. W. G. Style, *Trans. Farqday Soc.*, **50**, 1192 (1954).

(12) W. R. Brode, J. H. Gould, and G. M. Wyman, *J. Amer. Chem. Soc.*, 74, 4641 (1952).

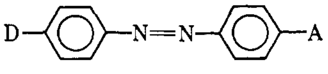
(13) See, for example, J. Binenboym, A. Burcat, A. Lifshitz, and J. Shamir, *J. Amer. Chem. Soc.*, **88**, 5039 (1966), and references therein.

(14) D. R. Kearns, *J. Phys. Chem.*, **69**, 1062 (1965).

(15) Reports that the isomerization rates of substituted azobenzenes follow a Hammett σp relationship[7] have been challenged by Talaty and Fargo,[9] who suggest that the lack of such a relationship argues against involvement of dipolar resonance structures.

fins, for which such a path is not possible, have reasonable activation energies for a rotational path. An inversion mechanism is also indicated by the finding that azobenzenes substituted with bulky groups, which might be expected to hinder rotation, are similar in kinetic behavior to unsubstituted azobenzene.[10]

In contrast to azobenzene and azobenzenes with a single substituent, certain azobenzenes of the type



(where D is an electron-donating group and A is an acceptor) have been isolated only as single isomers.[17] An example is the azo dye 4-(diethylamino)-4′-nitroazobenzene (**1**). Evidently, **1** is very stable under irradiation into its long-wavelength transitions; direct and sensitized photolysis of **1** at shorter wavelengths leads to various products but not to observable isomerization.[18,19] Since cis isomers of **1** and similar compounds are not readily detectable,[20] it has been assumed[18,19] that both photostationary states and thermal equilibrium are greater than 99% trans, or that there are very low barriers to isomerization and cis–trans isomerization rates (at room temperature) are very rapid.

In this paper we report an investigation of the thermal isomerization of **1** and other donor–acceptor-substituted azobenzenes by a flash spectroscopic technique. We found that these azobenzenes undergo both photochemical and thermal cis–trans isomerization. The rates of thermal isomerization of **1** and related compounds, measured by a relaxation technique, are much more rapid than those of previously studied azobenzenes. The presence of a significant solvent effect suggests that isomerization of these azobenzenes may involve a rotational mechanism in which dipolar structures are important.

Experimental Section

Materials. 4-(Diethylamino)-4′-nitroazobenzene and other dyes were prepared by methods previously described[22,23] and purified by recrystallizations from toluene.[24] Benzene (B & A reagent grade) was stirred over concentrated sulfuric acid for several days, washed with sodium bicarbonate solution, and then washed several times with water. The benzene was dried over anhydrous magnesium sulfate and then distilled through a column. The middle cut was retained. Hexane (James Hinton) was spectroquality. Other solvents were reagent grade, purified when necessary by distillation.

Preparation of Solutions. Solutions having equal concentrations of dye in various solvents were prepared by diluting a stock benzene solution 1:100 in the desired solvent. For kinetic measurements using the flash photolysis technique, solutions approximately 1×10^{-5} M in dye were used; for measurements with the conventional spectrophotometer 3×10^{-4} M solutions were used. Solutions of different dyes in benzene or acetone were prepared to approximate concentrations adjusted to have optical densities at λ_{max} equal to a 1×10^{-5} or 3×10^{-4} M solution of **1**. Nondegassed solutions, solutions degassed by flushing with argon, and solutions degassed by five freeze–pump–thaw cycles and sealed under vacuum all yielded the same results.

Kinetic Measurements. Fast decay times were measured by a flask spectroscopic technique. The solutions were placed in a cylindridal quartz cell 2.5 cm long and 2 cm i.d. The cell was surrounded by an insulated brass heating block for measurements above room temperature and was fixed at one focus of an elliptical sample cavity of polished aluminum with a Xe–Hg flash tube (10% to 10% time = 15 μsec) at the other focus. A steady monitoring light beam was passed through the cell perpendicular to the direction of the flash from an 18-Å tungsten projective lamp (GE type CPG). The monitoring light was passed through a Bausch and Lomb high-intensity grating monochromator before the sample cell, then through a Bausch and Lomb 500 mm grating monochromator after passing through the sample, and finally was detected by an RCA 1P-28 phototube. Transient signals were displayed on a Tektronix 585 oscilloscope and photographed on Polaroid Type 47 film. Corning glass filters were interposed between the sample and the flash tube.

Excitation of the dye solutions by the sharp pulse of light from the flash tube caused trans to cis isomerization of the dye. The isomerization could be seen as a change in absorbance of the solution at a convenient wavelength; the decay of ΔA back to the original absorbance could be observed as a function of time on the oscilloscope.

All of the dyes were stable under the flash-photolysis conditions; identical spectra were obtained for the original solutions and those subjected to several flashes.

For slower decay rates a Unicam SP 800 B spectrophotometer with an SP 820 constant wavelength scan control was used. The solutions were placed in 1-cm cuvettes and bleached by an unfiltered 500-W tungsten lamp, then placed in the spectrophotometer and the change in absorbance with time at a suitable wavelength measured.

Low-temperature spectra of *cis*- and *trans*-**1** in methylcyclo hexane and in EPA were measured on a Cary 14 spectrophotometer. The sample solutions were held in a 1-mm quartz cell suspended in a Dewar flask having quartz windows and containing Dry Ice in acetone above the sample cell.

Results and Discussion

Figure 1 is an absorption spectrum of 4-(diethylamino)-4′-nitroazobenzene (**1**) in benzene. The spectrum is qualitatively similar to those of trans isomers of other azobenzenes.[12,26] The absorption spectrum of **1** shifts to longer wavelengths with increases in solvent polarity; the shifts in λ_{max} of the long wavelength band have been found[25] to correlate well with the Bayliss–McRae equation.[27] The magnitude of the shift agrees with that expected for an intramolecular charge transfer band.[25] When **1** is irradiated with visible light in benzene solution, a short-lived bleaching can be observed. Return of the photobleached solution to the original spectrum can be followed on a conventional spectrophotometer. In more polar solvents such bleaching occurs but its duration is so short that a flash spectroscopic technique must be employed to follow the kinetics of relaxation.[28] Approximate spectra of the photobleached solutions can be obtained by monitoring the changes in the absorption spectrum of solutions of **1** immediately following flash excitation. In cooled EPA (ether–pentane–ethanol 5:5:2) and methylcyclo-

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[16] D. Y. Curtin, E. J. Grubbs, and C. G. McCarty, *J. Amer. Chem. Soc.*, **88**, 2775 (1966).

[17] An apparent exception is 4-methoxy-4′-nitroazobenzene.[10]

[18] G. Irick, Jr., and J. G. Pacifici, *Tetrahedron Lett.*, 1303 (1969); J. G. Pacifici and G. Irick, Jr., *ibid.*, 2207 (1969).

[19] J. G. Pacifici, G. Irick, Jr., and C. G. Anderson, *J. Amer. Chem. Soc.*, **91**, 5654 (1969).

[20] Short-lived cis isomers of a similar compound, 4-dimethylamino-4′-nitroazobenzene, have been previously detected.[21]

[21] E. Fischer, private communication.

[22] E. Baumberger, *Ber.*, **28**, 843 (1895).

[23] E. Ziegler and G. Snatzke, *Monatsh.*, **84**, 610 (1953).

[24] Physical properties of compounds **2**–**12** as well as a study of substituent effects on the absorption spectra of these dyes are reported elsewhere.[25]

[25] J. G. Pacifici and G. Irick, Jr., in preparation.

[26] E. Fischer and Y. Frei, *J. Chem. Phys.*, **27**, 328 (1957).

[27] E. G. McRae, *J. Phys. Chem.*, **61**, 563 (1957).

[28] A similar flash spectroscopic technique has been used to measure isomerization rates for imines[29] and *o*-hydroxyazobenzenes.[30]

[29] G. Wettermark and L. Dogliotti, *J. Chem. Phys.*, **40**, 1486 (1964); D. G. Anderson and G. Wettermark, *J. Amer. Chem. Soc.*, **87**, 1433 (1965).

[30] G. Wettermark, M. E. Langmuir, and D. G. Anderson, *ibid.*, **87**, 476 (1965).

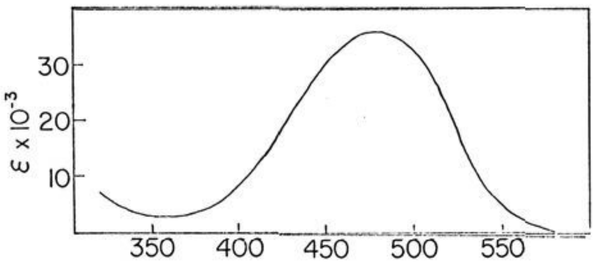

Figure 1. Absorption spectrum of 4-(diethylamino)-4′-nitroazobenzene in benzene at 25°.

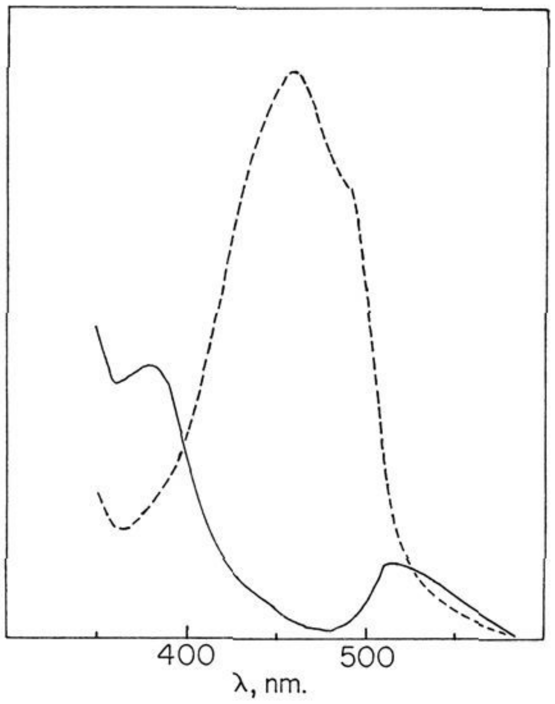

Figure 2. Absorption spectra of *cis*- (solid line) and *trans*- (dashed line) 4-(diethylamino)-4′-nitroazobenzene in methylcyclohexane at −50°. The absorption spectrum of the cis isomer was extrapolated from the spectrum of a mixture of cis and trans produced from irradiation of pure trans.

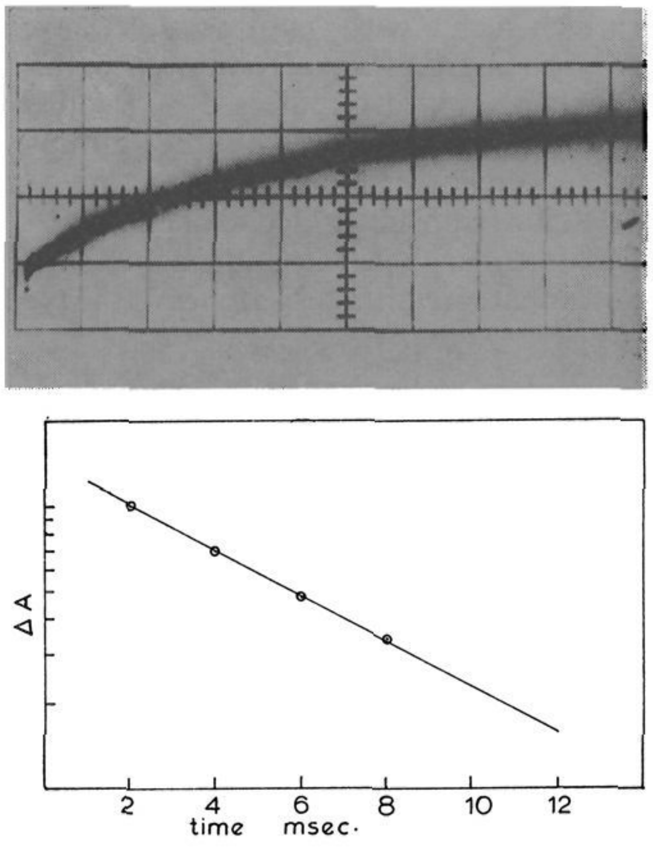

Figure 3. Upper part: oscilloscope trace showing return of absorption of *trans*-4-(diethylamino)-4′-nitroazobenzene in *N,N*-dimethylformamide following flash excitation. The vertical deflection is inversely proportional to the intensity of light transmitted. Monitoring wavelength = 480 nm; time base is 2 msec/cm. Lower part: logarithmic plot of ΔA *vs.* time, data taken from oscilloscope trace above.

hexane solutions recovery of the bleached solution was slowed so that a spectrum of the photoproduct could be obtained (Figure 2). In all cases the changes were similar; excitation of **1** into its long-wavelength band leads to decreases in absorption near the λ_{max} and concurrent increases in absorption on either side of this band.[31] The isosbestic points expected for a simple isomerization were observed during photobleaching and recovery in each case; for example, in benzene solution isosbestic points were measured at 400 and 560 nm while in *N,N*-dimethylformamide they were found at 410 and 595 nm.

Approximate spectra for the cis and trans isomers of 4-(diethylamino)azobenzene in benzene have been determined by using a shutter technique[12] and in methylcyclohexane by irradiation of the trans isomer at low temperatures.[26] In both cases, the cis isomer showed two absorption bands, one on the long-wavelength edge of the visible absorption band of the trans isomer and one between the visible and uv bands of the trans. The low-temperature spectrum presented in Figure 2 and the approximate spectra determined following flash excitation bear the same relationship to the spectrum of the starting *trans*-**1** in each case as for the monosubstituted azobenzenes and indicate that the short-lived photoproduct is *cis*-**1**. The results are in accord with the interpretation that the solution before flashing is nearly all trans. The flash induces photoisomerization to *cis*-**1** and the relaxation back to the initial composition is caused by rapid thermal isomerization of *cis*-**1** to trans.

The rate of return from cis to trans for **1** in several solvents was measured; in each case the return showed the expected first-order kinetics. Figure 3 shows a typical curve for return of absorption of *trans*-**1** following flash photobleaching along with a plot from which $k_{c\to t}$ was obtained. In all systems a Corning 3-72 filter was used to activate most of the visible band of the dye and changes of absorbance were monitored near the λ_{max} of the unexcited solution. As shown in Table I, the rate is strongly solvent dependent, in-

Table I. Solvent Effects on Thermal Isomerization Rates of 4-(Diethylamino)-4′-nitroazobenzene (**1**) and 4-Amino-4′-(diethylamino)azobenzene (**12**)

Solvent	Dielectric constant, ε	$k_{c\to t}$, sec^{-1} **1**	**12**
Hexane	1.89[a]	0.007	
Benzene	2.28[a]	0.03	0.003
Carbon tetrachloride	2.24[a]	0.009	
Triethylamine	2.42[a]	0.024	
Chloroform	5.05[b]	1.0	
o-Dichlorobenzene	9.93[a]	2.0	0.01
Pyridine	12.3[a]	30	
Isopropyl alcohol	18.3[a]	17	0.02
Acetone	20.7[a]	20	0.003
N,N-Dimethylformamide	36.7[b]	190	
Dimethyl sulfoxide	48.9[b]	440	0.009
N-Methylformamide	180[c]	600	

[a] "Handbook of Chemistry and Physics," 42nd ed, C. D. Hodgman, Ed., Chemical Rubber Publishing Co., Cleveland, Ohio, 1960. [b] Data from ref 25. [c] G. R. Leader and J. F. Gormley, *J. Amer. Chem. Soc.*, **73**, 5731 (1951).

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(31) Generally excitation of **1** into its short wavelength bands led to the same results. In isopropyl alcohol where "permanent" photodegradation occurs,[18] no such transient photobleaching could be detected on short wavelength irradiation.

creasing sharply for polar solvents such as dimethyl sulfoxide or *N*-methylformamide. Free energies of activation for isomerization of **1** range from 14 to 20 kcal/mol in the various solvents. Arrhenius activation energies were obtained by studying the temperature dependence of isomerization rates. Figure 4 shows Arrhenius plots for **1** in different solvents.

Kinetic measurements on a similar compound, 4-(diethylamino)-4′-nitroazobenzene, were considered unreliable because of acid–base-catalyzed isomerization.[10] Details regarding the nature of this phenomenon and the experimental procedure were not reported, however, so it is difficult to assess these results. Although we find a sizable increase in the isomerization rate of **1** in the presence of acid, we believe the rapid rates of isomerization observed in this study cannot be due simply to catalytic effects. Rates of isomerization observed in triethylamine and pyridine, bases which might be expected to remove adventitious acid impurities or, alternatively, catalyze isomerization, were comparable to those in other solvents of similar polarity. Addition of water to acetone or dimethyl sulfoxide solutions of **1** also increases relaxation rates; the effect is noticable only after the water content increases to measureable (*ca.* 1 %) levels.[32]

Rate constants for several similar dyes in benzene and acetone solution were measured to assess the effect of varying the donor and acceptor substituents (Table II). The change in absorbance near the λ_{max} of the unexcited solution was monitored after flashing with light filtered only by a Corning O-51 filter, which permitted all light of λ >360 nm to pass. In all systems, the absorbance decreased, indicating displacement of the starting trans to cis. Most of the dyes showed rate increases on changing solvent from benzene to acetone. The changes are qualitatively what one would expect for slight differences in the importance of dipolar resonance forms. As expected, when additional acceptors are added to the ring as in compounds **10** and **11**, the rates are significantly faster.

Table II. Thermal Isomerization Rate Constants for Para-Donor/Para′-Acceptor-Substituted Azobenzenes in Benzene and Acetone

	Para	Para′	Ortho′	$k_{c\rightarrow t}$,[b] sec^{-1}	
Compd[a]	Donor	Acceptor	Acceptor	Benzene	Acetone
1	$N(C_2H_5)_2$	NO_2		0.03	20
2	NH_2	NO_2		0.004	2.75
3	$NH(C_2H_5)$	NO_2		0.01	15.7
4	$N(CH_3)_2$	NO_2		0.02	8.9
5	$NH(C_6H_5)$	NO_2		0.002	2.7
6	$N(C_2H_5)(C_6H_5)$	NO_2		0.044	18.6
7	$N(C_2H_5)_2$	SO_2CH_3		0.002	0.02
8	$N(CH_2CH_2CN)_2$	NO_2		0.002	0.05
9	$N(CH_3)_2$	COOH		0.002	0.002
10	$N(C_2H_5)_2$	NO_2	CF_3	28	
11	$N(C_2H_5)_2$	NO_2	SO_2CH_3	144	

[a] Concentration ~3 × 10^{-4} to 1 × 10^{-5} *M*. [d] Estimated precision ±5%.

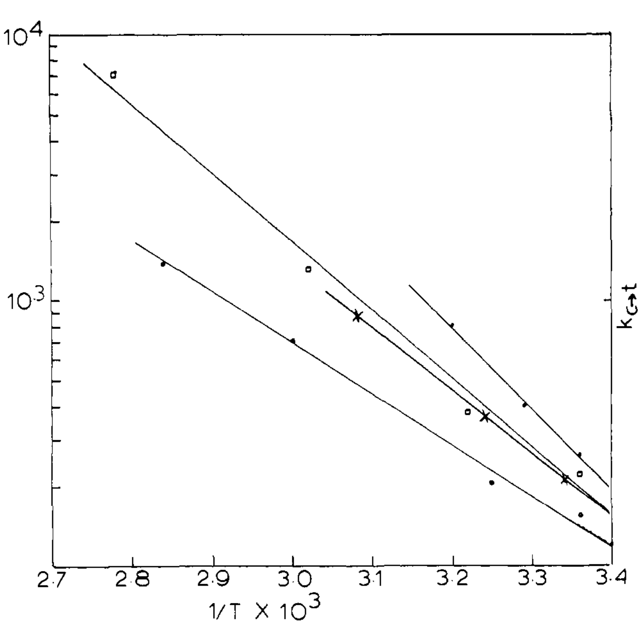

Figure 4. Arrhenius plot of log $k_{c\rightarrow t}$ *vs.* 1/*T* for 4-(diethylamino)-4′-nitroazobenzene in different solvents: ●, data for benzene solutions, *k* × 10^4; □, *o*-dichlorobenzene solutions, *k* × 10^2; ×, acetone solutions, *k* × 10; ○, *N*,*N*-dimethylformamide solutions, *k* × 1.

Rates of thermal isomerization of *cis*-4-amino-4′-(diethylamino)azobenzene (**12**) were also measured in several solvents and $k_{c\rightarrow t}$ values for **12** are listed in Table I. Rates of isomerization for this doubly donor-substituted dye were "normal" [12] for donor-substituted azobenzenes and showed little solvent effect. The fact that **12** and other azobenzenes substituted with free amino groups do not show rapid rates for relaxation in polar solvents indicates that the observed phenomena cannot be ascribed to tautomerism of the azohydrazone type previously observed with 2-hydroxyazobenzenes.[12,30]

It is difficult to conclude what type of mechanism is responsible for the thermal isomerization of compounds **1–11**. The energies of activation (Table III) for **1** measured in this study are considerably lower than those reported for monosubstituted azobenzenes.[6] However, the E_a value for **1** in benzene (14 kcal/mol) is not much lower than the value of 16–17 kcal/mol of E_a for syn–anti isomerization of the anil of benzaldehyde where an inversion or "lateral shift" mechanism is almost certainly operating.[16] An inversion mechanism surely operates for monosubstituted azobenzenes and for compound **12**; therefore one might expect that an inversion mechanism having comparable activation energy could operate for **1–11**. However, the compounds previously shown to isomerize by an inversion mechanism show little solvent or substituent effect such as is observed for **1–11**.[34] The observed solvent and

Table III. Arrhenius Activation Energies (E_a) for Thermal Isomerization of **1** in Various Solvents

Solvent	E_a, kcal/mol
Benzene	14
o-Dichlorobenzene	12
Acetone	10
N,*N*-Dimethylformamide	9

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(32) Although excited states of simple azobenzenes are stronger bases than the ground states,[33] the effects observed here are likely simply due to increased solvent polarity.

(33) D. L. Beveridge and H. H. Jaffé, *J. Amer. Chem. Soc.*, **88**, 1948 (1966); H. H. Jaffé, D. L. Beveridge, and H. L. Jones, *ibid.*, **86**, 2932 (1964).

substituent effects clearly argue in favor of a polar or dipolar transition state. It is difficult to envision how contribution of a dipolar form with presumably increased ring carbon–nitrogen bond strength could lower the activation energy to the extent observed in this study. Although no experimental data or calculations are available, it might be argued that the hydridization and ring carbon–nitrogen bonding changes required on going from starting material to transition state in an inversion mechanism could become energetically more difficult as contributions from a dipolar structure increased. All of the present data are in accord with an internal rotation mechanism in which contribution from dipolar resonance structures has reduced the nitrogen–nitrogen double bond strength and consequently the torsional barrier to rotation. Perhaps the one major argument in opposition to the internal rotation mechanism for **1–11** is the fact that similarly substituted stilbenes do not undergo facile thermal isomerization.[35]

Information regarding the mechanism of the photochemical isomerization of these dyes has proved somewhat elusive. We have been unable to detect any transient absorbance changes other than those associated with cis–trans isomerization following flash excitation. Experiments with most "triplet sensitizers" give inconclusive results since singlet sensitization[36] cannot be excluded and since quantum yields could not be measured. However, we find that etioporphyrin I, $E_T \sim 40$ kcal/mol,[37] does sensitize trans to cis isomerization of **1**. Etioporphyrin I can be excited by red light $\lambda > 600$ nm, which excludes any possibility of direct excitation of **1**. Normal singlet energy transfer is excluded by energy considerations and **1** does not quench etioporphyrin I fluorescence. Although we have found that nitrostilbenes quench metalloporphyrin triplet states and undergo cis to trans isomerization from an exciplex,[37] trans to cis isomerization from the exciplex is usually unimportant. Consequently we conclude that the observed results indicate triplet energy transfer from etioporphyrin I to **1** and subsequent isomerization *via* a low-lying triplet of **1**. Whether this is the only path for photoisomerization of **1** remains uncertain.

Acknowledgment. We are grateful to Professor E. Fischer for helpful discussion and suggestions. Support for the portion of this work carried out at the University of North Carolina, in part from the Research Corporation, in part from the National Institutes of Health (Grant No. GM 15,238), in part from the U. S. Army Research Office, Durham (Grant DA-ARO-D-31-124-G1097), and in part from the University of North Carolina Materials Research Center in conjunction with the Advanced Projects Agency (Contract SD-100), is gratefully acknowledged.

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(34) Compound **9** also shows no solvent effect and compounds **7** and **8** show only a slight solvent effect; probably these compounds also isomerize by an inversion mechanism.

(35) D. Schulte-Frohlinde, H. Blume, and H. Güsten, *J. Phys. Chem.*, **66**, 2486 (1962), and references therein.

(36) A. B. Smith, III, and W. C. Agosta, *Chem. Commun.*, 466 (1970).

(37) I. G. Lopp, R. W. Hendren, P. D. Wildes, and D. G. Whitten, *J. Amer. Chem. Soc*, **92**, 6440 (1970).

Hydrogen Abstractions from Arylmethanes[1]

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Corvallis, Oregon 97331. Received August 14, 1970

Abstract: The relative rates of hydrogen abstraction from a series of 13 arylmethanes by the trichloromethyl radical were determined at 70°. An excellent correlation, with a coefficient of 0.977, was obtained when the data were correlated with the change in π-binding energies between the incipient radicals and the arylmethanes, if the π-binding energies were calculated by the SCF approach. When the data were correlated with the change in π-binding energies as calculated by the HMO approach, the correlation was poor with the coefficient of 0.855. A possible explanation for this difference might be the Hückel method's complete neglect of electron interactions. The kinetic data were also plotted against various ground-state properties such as free valence, atom–atom self-polarizability, and $\Sigma 1/r_{ij}$. In all cases only very poor correlations were obtained. The relative rates of hydrogen abstraction from a series of nine arylmethanes by the *tert*-butoxy radical were also determined at 70°. A satisfactory correlation was obtained with none of the above quantities. It is felt that the transition state for hydrogen abstraction by the trichloromethyl radical must strongly resemble the intermediate free radical. That for abstraction by the *tert*-butoxy radical probably has a structure between the ground state and the intermediate.

We have reported in an earlier communication that delocalization effects are important in the abstraction of hydrogen atoms from a series of arylmethanes by the trichloromethyl radical.[3] We would now like to discuss more fully correlations obtained in the above systems and to augment the study further with a discussion of the hydrogen abstraction reaction by the more reactive *tert*-butoxy radical.

In the past decade, attempts to correlate the rates of formation of arylmethyl carbonium ions[4,5] and car-

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(1) Taken from the Ph.D. Thesis of J. D. Unruh.

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(4) M. J. S. Dewar and R. J. Sampson, *J. Chem. Soc.*, 2789 (1956); 2946, 2952 (1957).