1,2-dimesitylvinyl trimethylsilyl ether (isomer 1), 125640-51-9; 1,2-dimesitylvinyl trimethylsilyl ether (isome 2), 125640-52-0; methyl mesitylacetate, 41841-19-4; mesitylacetic acid, 4408-60-0; 2-mesityl-3-methylbutanoyl chloride, 125640-55-3; mesitylene, 108-67-8.

Supplementary Material Available: Tables S1-S4 giving bond lengths, bond angles, positional parameters, and thermal parameters for **3d**, Table S6 giving equilibration experiments, and Figures S1 (stereoscopic view of **3d**) and S2 (Meyer's cut of **3d** through the lower methyl group of the α-Mes ring) (16 pages); Table S5 giving observed and calculated structural factors for **3d** (14 pages). Ordering information is given on any current masthead page.

cis-Diazenes. Viscosity Effects, One-Bond Scission, and Cis-Trans Isomerization[1,2]

Robert C. Neuman, Jr.,* Richard H. Grow,[3a] Glen Al. Binegar,[3b] and Howard J. Gunderson

Department of Chemistry, University of California, Riverside, Riverside, California 92521

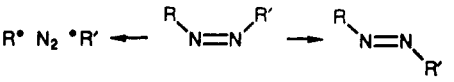
Received September 18, 1989

Effects of solvent viscosity on the rates of overall thermal decomposition, deazatization, and isomerization of several symmetric and unsymmetric *cis*-diazenes (*cis*-azoalkanes) have been determined in pure alkanes and mixtures of octane and mineral oil. Increasing viscosity decreases the overall decomposition and deazatization rates for all of these *cis*-diazenes. While isomerization rates also decrease with increasing viscosity for most of the diazenes, that for *cis*-*N*-*tert*-butyl-*N'*-1-norbornyldiazene (1) increases. These results are interpreted in terms of deazatization via one-bond scission and an intermediate diazenyl radical, isomerization via nonradical inversion, and the possibility of isomerization via a diazenyl radical for 1.

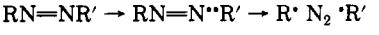
cis-Diazenes thermally decompose into radicals and molecular nitrogen in competition with isomerization to their trans isomers (Scheme I).[4] While it has been accepted for some time that highly unsymmetical diazenes (both cis and trans) undergo homolytic scission via one-bond scission to form an intermediate diazenyl radical that subsequently cleaves further to give a radical and molecular nitrogen (Scheme II),[4-6] our proposal[7] that this is also the mechanism for deazatization of symmetrical *cis*-diazenes (R = R') is relatively recent.

The pathway by which these *cis*-diazenes isomerize to their trans isomers has also been the subject of debate. Nonradical routes include rotation about the N=N bond, or inversion at nitrogen (semilinearization);[4,5] while recombination of the diazenyl radical and the R• radical formed by one-bond scission has also been suggested as a possible pathway.[7,8] It is generally accepted that rotation is a much higher energy process than inversion for alkyl diazenes and the latter seems to be the nonradical pathway.[4,5] However, the existence of a radical pathway for isomerization of *cis*-dialkyldiazenes has been controversial.

Scheme I



Scheme II



Scheme III

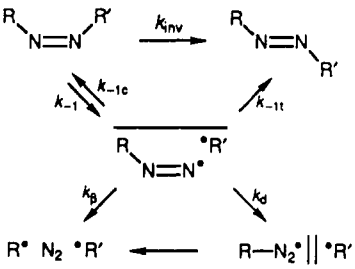
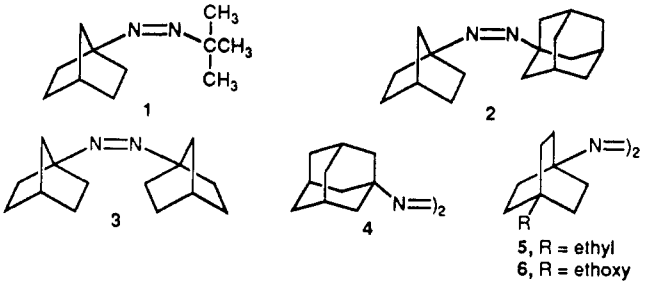


Chart I



The results of a detailed study of a series of bridgehead *cis*-diazenes has been interpreted as support for the inversion mechanism and against the radical pathway.[5]

A kinetic scheme including these possibilities is shown as Scheme III. This scheme includes recombination steps (k_{-1c} and k_{-1t}) to form both the *cis*- and *trans*-diazene from the proposed intermediate diazenyl radical-R• pair. They would compete with loss of molecular nitrogen (k_β) and separative diffusion (k_d). As a direct consequence of the

(1) Support by the National Science Foundation is greatly appreciated. This paper is dedicated to the memory of my friend and colleague Professor Morton Gibian.

(2) Presented at the following. (a) Pacific Conference on Chemistry and Spectroscopy, Pasadena, CA, October, 1983 by Neuman, R. C., Jr.; Binegar, G. A. (b) Fourth International Symposium on Organic Free Radicals, St. Andrews, Scotland, July 1984, poster by Neuman, R. C., Jr.; Binegar, G. A.; Adam, W.; Nishizawa, Y. (c) "Free Radicals in Perspective", A Symposium in Honor of Professor C. Walling, Park City, UT, April 1986, by Neuman, R. C., Jr. (d) Pacific Conference on Chemistry and Spectroscopy, San Francisco, CA, October 1988 by Neuman, R. C., Jr.; Grow, R.; Gunderson, H. (e) Northwest Regional Meeting of the American Chemical Society, Symposium on Free Radical Chemistry, Reno, NV, June 1989, by Neuman, R. C., Jr.

(3) (a) Grow, R. Ph.D. Dissertation, University of California, Riverside, June, 1989; studies of *cis*-diazenes **1-3**. (b) Binegar, G. Ph.D. Dissertation, University of California, Riverside, December, 1984; original observations of *cis*-diazene viscosity dependence.

(4) Chae, W.-K.; Baughman, S. A.; Engel, P. S.; Bruch, M.; Özmeral, C.; Szilagyi, S.; Timberlake, J. W. *J. Am. Chem. Soc.* **1981**, *103*, 4824.

(5) Schmittel, M.; Rüchardt, C. *J. Am. Chem. Soc.* **1987**, *109*, 2750.

(6) Engel, P. S. *Chem. Rev.* **1980**, *80*, 99.

(7) Neuman, R. C., Jr.; Binegar, G. A. *J. Am. Chem. Soc.* **1983**, *105*, 134.

(8) Engel, P.; Gerth, D. B. *J. Am. Chem. Soc.* **1983**, *105*, 6849.

0022-3263/90/1955-2682$02.50/0

Table I. Viscosity Dependence of the Decomposition Rate Constants of *cis*-Diazenes 1–6

diazene[a]	solvent[b]	vis(cp)[c]	10^4k(O)[d]	10^4k(N)[d]	10^4k(I)[d]	k(I)/k(N)
1 (20)[e]	hexane	0.250	1.87 (0.02)[f]	1.55 (0.01)[f]	0.32 (0.02)[f]	0.2
	octane	0.490	1.67 (0.03)	1.33 (0.02)	0.34 (0.04)	0.3
	dodecane	1.30	1.39 (0.03)	0.96 (0.04)	0.43 (0.02)	0.3
	1 to 2	1.44	1.41 (0.02)	1.01 (0.07)	0.40 (0.05)	0.4
	1 to 1	2.76	1.23 (0.02)	0.86 (0.03)	0.37 (0.03)	0.4
	2 to 1	6.50	1.13 (0.04)	0.74 (0.02)	0.39 (0.01)	0.5
	5 to 1	21.4	0.99 (0.03)	0.63 (0.01)	0.36 (0.01)	0.6
	10 to 1	38.4	0.95 (0.01)	0.59 (0.01)	0.36 (0.01)	0.6
	mineral oil	106	0.90 (0.03)	0.53 (0.02)	0.37 (0.01)	0.7
2 (40)	octane	0.440	1.15 (0.04)	0.04 (0.04)	1.11 (0.04)	28
	tetradecane	1.55	1.05 (0.05)	0.03 (0.05)	1.02 (0.05)	34
	mineral oil	61	0.96 (0.04)	0.00 (0.04)	0.96 (0.04)	
3 (85.7)	octane	0.287	1.39 (0.03)	*g*	1.39 (0.03)	
	tetradecane	0.815	1.28 (0.06)	*g*	1.28 (0.06)	
	mineral oil	10.5	1.20 (0.04)	*g*	1.20 (0.04)	
4 (21)	hexane	0.311	6.18 (0.09)	3.82 (0.08)	2.36 (0.05)	0.6
	decane	0.882	5.11 (0.06)	3.22 (0.04)	1.88 (0.03)	0.6
	hexadecane	3.12	4.58 (0.04)	2.81 (0.03)	1.77 (0.01)	0.6
	9 to 1	16.4	4.16 (0.04)	2.34 (0.02)	1.80 (0.02)	0.8
4 (20)	hexane	0.312	5.40 (0.06)	2.97 (0.20)	2.43 (0.15)	0.8
	dodecane	1.50	4.28 (0.10)	2.24 (0.06)	2.04 (0.05)	0.9
	mineral oil	190	3.56 (0.06)	1.74 (0.06)	1.82 (0.08)	1.0
5 (35.7)	hexane	0.273	4.23 (0.14)	0.24 (0.01)	4.00 (0.14)	17
	decane	0.734	3.86	0.22	3.64	17
	hexadecane	2.37	3.70 (0.01)	0.20 (0.01)	3.50 (0.02)	18
	9 to 1	25.2	3.45 (0.01)	0.17 (0.01)	3.28 (0.01)	19
6 (30.5)	hexane	0.288	2.64 (0.15)	*g*	2.64 (0.15)	
	decane	0.793	2.35 (0.07)	*g*	2.35 (0.07)	
6 (30.0)	hexane	0.288	2.46	*g*	2.46	
	hexadecane	2.67	2.07	*g*	2.07	

[a] Compound number followed by kinetics temperature in °C. [b] 1 to 2 means one part mineral oil to two parts octane by volume, etc. [c] Viscosity temperature corresponds to the kinetics temperature unless otherwise noted. [d] Units of s^{-1}. [e] Viscosities at 30 °C. [f] Numbers in parentheses are standard deviations. [g] No evidence of deazatization.

separative diffusion step (k_d), the rates of both deazatization and radical isomerization could show a viscosity dependence. An increase in medium viscosity would cause k_d to decrease, leading to an increase in the lifetime of the radical pair. This increased lifetime would be expected to lead to an overall reduction in rate of loss of the cis isomer since the fraction of return to the starting cis isomer would increase. Paradoxically, the rate of isomerization by the radical path might be expected to increase because separative diffusion, which would be retarded by increasing viscosity, virtually always leads to deazatization.

Although this is our first published account of these observations, we have known for some time that *cis*-diazene thermal decomposition rates are significantly retarded by increasing solvent viscosity in nonpolar hydrocarbon solvents.[2] Since the overall decomposition rate constant for a *cis*-diazene (k(O)) is the sum[4,5] of those for deazatization (k(N)) and isomerization (k(I)), we have been particularly concerned with dissecting the viscosity dependence of k(O) into those of k(N) and k(I).

We have consistently observed that increasing solvent viscosity slows deazatization, and until recently we had only observed similar, but smaller, decreases in rates for isomerization.[2a-c] Now, however, we have seen a strikingly different result. While both k(O) for k(N) for **1** show the typical decrease with increasing solvent viscosity, there is a definite increase in k(I) with viscosity increase.[2d,e] This is the behavior that we had hoped to find to support isomerization via a radical pathway.[2a-c]

Results

We have studied the effects of solvent viscosity on the rates of thermal decomposition of the series of symmetrical and unsymmetrical *cis*-diazenes **1–6** (Chart I). Values of their apparent rate constants k(O), k(N), and k(I) are given in Table I.

Pure samples of the *trans*-diazenes were dissolved in the reaction solvent containing a trace amount of triethylamine or tert-butylamine to inhibit acid-catalyzed reactions,[4] the solutions were vacuum degassed, and a fraction of the trans isomer was photoisomerized to the *cis*-diazene. The substantially different λ_{max} values for the cis and trans isomers permitted simultaneous monitoring by UV spectroscopy of loss of the cis isomer and reformation of the trans isomer. This allowed the determination of the three rate constants as described below and in the Experimental Section.[4,7] The substantially greater activation energy[4-6] for thermal decomposition of each *trans*-diazene compared to its cis isomer permitted *cis*-diazene to be thermolyzed in the presence of *trans*-diazene without any thermolysis of the latter compound. Although formation of molecular nitrogen was not monitored, previous work leaves little doubt that *cis*-diazene, which did not isomerize to the trans isomer, decomposed by deazatization.[4,5] In most cases, deazatization was competitive with isomerization. However, for compounds **3** and **6** there was no observable loss of trans isomer after photoisomerization to the cis isomer and subsequent thermolysis.

Discussion

Deazatization. An examination of Table I will show that the values of k(O) consistently decrease with increasing solvent viscosity for all of the *cis*-diazenes. This is graphically represented for compounds **1**, **4**, and **5** in Figure 1. Since the absolute values of rate constants for the various diazenes differ significantly, relative rate constants ($k_{rel} = k(\text{solv } 1)/k(\text{solv } n)$) are used in all figures. Some data for (phenylazo)triphenylmethane (PAT) have also been included in this figure.[9,10]

(9) (a) Pryor, W. A.; Smith, K. *J. Am. Chem. Soc.* **1970**, *92*, 5403. (b) All of the $k(O)_{rel}$ values for PAT have been displaced downward by 0.1 unit in Figures 1 and 2 for ease of observation.

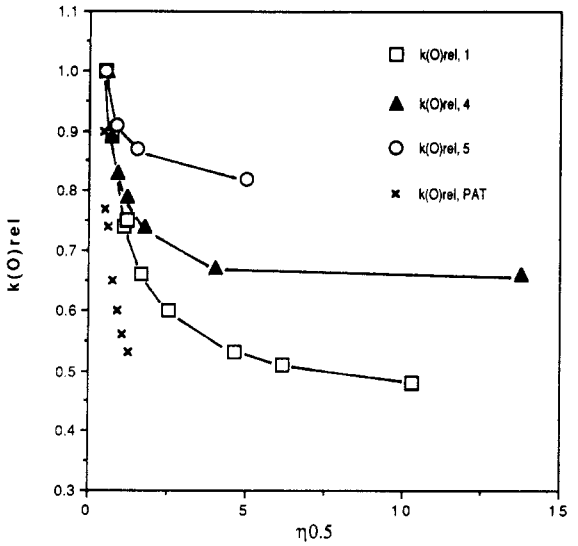


Figure 1. $k(O)_{rel}$ versus square root of viscosity.

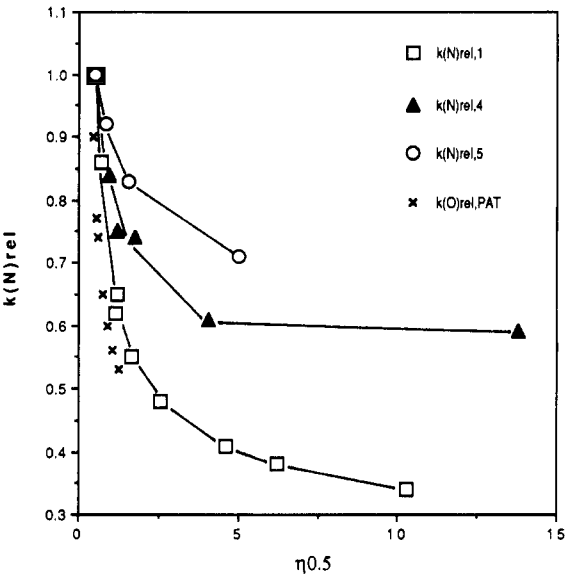
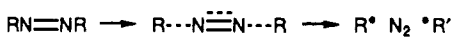


Figure 2. $k(N)_{rel}$ versus square root of viscosity.

Scheme IV

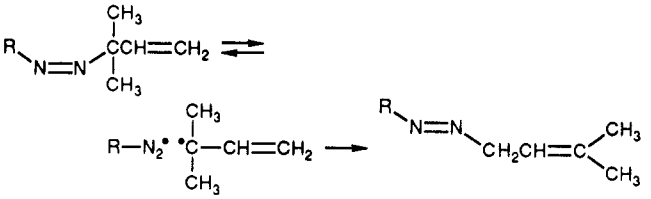


It is obvious that the viscosity dependence for thermolysis of PAT is analogous[9b] to those of the *cis*-diazenes shown. In the case of PAT, the overall decomposition rate constant $k(O)$ is exclusively that for deazatization $k(N)$.[9] However the values of $k(O)$ for compounds **1**, **4**, and **5** are the sums of rate constants for both deazatization ($k(N)$) and isomerization ($k(I)$) (Table I). Thus, the relative values of $k(N)$ for compounds **1**, **4**, and **5** ($k(N)_{rel}$) have been plotted in Figure 2 along with the values of $k(O)_{rel}$ for PAT[9b] in order to provide a comparison of the viscosity dependence specifically for deazatization of these diazenes.

PAT is a classical example of a diazene that is accepted to decompose by one-bond scission.[9] Thus we feel that the similarity in the viscosity dependence for deazatization of all compounds in Figure 2 provides strong support for the one-bond scission mechanism (Scheme III) for compounds **1**, **4**, and **5**. Of particular interest is the fact that both compounds **4** and **5** are symmetric *cis*-diazenes. For years, it was generally thought that symmetric diazenes underwent deazatization by simultaneous two-bond scission aided by the large stabilization energy expected for the developing nitrogen molecule in the activated complex (Scheme IV).[6] Crawford,[11a] however, presented evidence in 1972 that this might not be generally true for *trans*-diazenes and our results suggest that this reasoning is not necessarily justified for *cis*-diazenes.[11b]

Isomerization. Because symmetric *cis*-diazenes appear to undergo homolysis by one-bond scission, it has seemed attractive to us to consider the possibility that their isomerization to *trans*-diazenes, competitive with deazatization, might also proceed, at least in part, via the intermediate diazenyl radical-R• pair (Scheme III).[2,7] This is certainly not an original concept. Using CIDNP experiments, Porter proposed that unsymmetrical *cis*-diazenes isomerized to their trans isomers by a radical pair mechanism.[12] More recently Engel reached similar conclusions by studying several unsymmetrical *cis*-diazenes of the type shown in Scheme V.[8]

Scheme V



However, our proposal that such a mechanism might compete with the generally accepted nonradical inversion (semilinearization) pathway, particularly for symmetric *cis*-diazenes, has been controversial.[5,13] We argued[7] that effects of pressure on the isomerization rates of some *cis*-diazenes supported such a mechanism, but this reasoning was severely undermined when Rüchardt and coworkers[13] showed that the isomerization activation volume for azonorbornane (**3**) was identical with isomerization activation volumes determined by us[7] for other *cis*-diazenes. It is most certain that isomerization of **3** occurs only by a nonradical path since no hint of deazatization has ever been detected for this compound,[4,5,13] and 1-norbornyldiazenyl radicals are known to lose molecular nitrogen.[12] Although we suggested that activation volumes for isomerization by radical and nonradical inversion might be fortuitously identical,[2] this could hardly be considered support for a radical path.

Thinking that some information about isomerization mechanism might be found in the viscosity dependence of $k(I)$, we investigated this for the *cis*-diazenes **1**–**6**. Our results prior to the study of **1** consistently showed a decrease in values of $k(I)$ with increasing viscosity (Figure 3). Since these data parallel those for **3** (which must undergo isomerization by inversion), it seems likely that all of these compounds isomerize by inversion. Such rate decreases are consistent with an inversion mechanism since the movement of a bulky R group through the solvent should be retarded by an increase in solvent viscosity.[14]

(10) Neuman, R. C., Jr.; Lockyer, G. D. *J. Am. Chem. Soc.* **1983**, *105*, 3982.

(11) (a) Crawford, R. J.; Takagi, K. *J. Am. Chem. Soc.* **1972**, *94*, 7406. (b) For presentation of a theoretical prediction that both *cis*- and *trans*-diazenes thermally decompose via one-bond scission, see: Dannenberg; et al. *J. Org. Chem.* **1982**, *47*, 4529; *J. Am. Chem. Soc.* **1985**, *107*, 671.

(12) (a) Porter, N. A.; Dubay, G. R.; Green, J. G. *J. Am. Chem. Soc.* **1978**, *100*, 920 and references therein. (b) In RN_2R', R was phenyl or norbornyl, while R' was trityl, cumyl, or cyanoisopropyl.

(13) Van Eldik, R.; Kelm, H.; Schmittel, M.; Rüchardt, C. *J. Org. Chem.* **1985**, *50*, 2998.

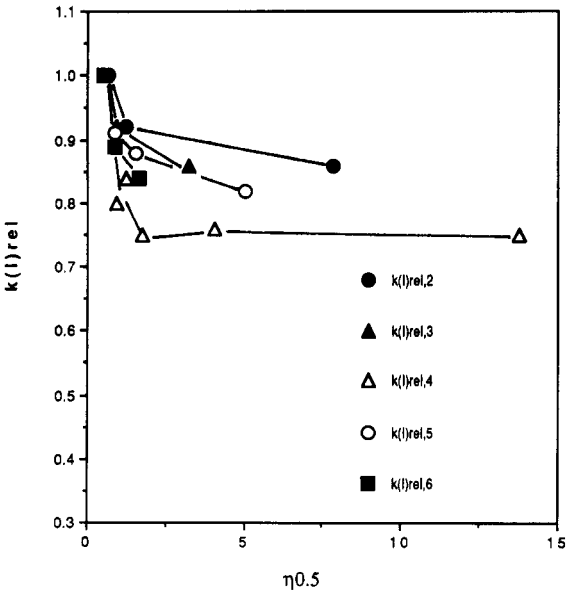


Figure 3. $k(I)_{rel}$ versus square root of viscosity.

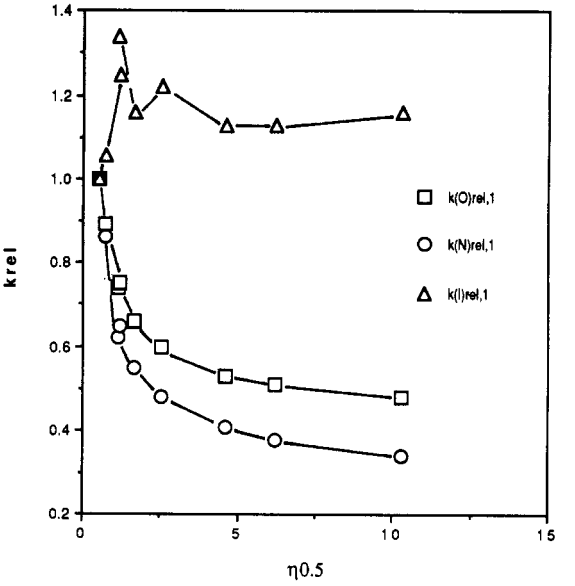


Figure 4. k_{rel} for 1 versus square root of viscosity.

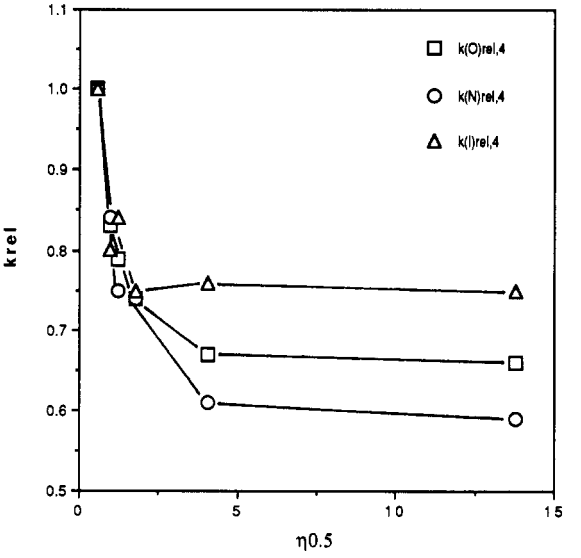


Figure 5. k_{rel} for 4 versus square root of viscosity.

However, the notion that a fraction of the diazenyl radical-R• pairs from such diazenes should be able to combine to give the trans isomer as well as the cis isomer (Scheme III) continued to intrigue us. We reasoned that this would be most probable for a *cis*-diazene that underwent substantial deazatization and therefore gave a large amount of radical intermediates, but one in which an intermediate diazenyl radical would also be relatively stable. That led to the study of compounds 1 and 2 because the relatively stable *tert*-butyl and adamantyl radicals might promote their initial radical scission (k_1, Scheme III) while the low stability of a norbornyl radical would stabilize the resulting norbornyldiazenyl radical.

In the case of the adamantylnorbornyldiazene 2, deazatization was only a minor contributor to overall decomposition (Table I; $k(I)/k(N) \cong 30$). However, deazatization was much more significant for the *tert*-butylnorbornyldiazene 1 (Table I; hexane, $k(I)/k(N) \cong 0.2$). While the effects of solvent viscosity variation on $k(O)$ and $k(N)$ for 1 were similar to those for the other diazenes studied (Figures 1 and 2), the viscosity dependence of $k(I)$ was found to be dramatically different. Instead of decreasing with increasing viscosity, $k(I)$ *increased.* This can be seen from a plot of each of the relative rate constants for 1 shown in Figure 4. For comparison, a comparable plot for the diadamantyldiazene 4 is shown in Figure 5.

Because of this unusual result we carefully considered all aspects of analysis of the experimental data. The decrease in absorbance at λ_{max} for each cis isomer is cleanly translated into the overall decomposition rate constant $k(O)$.[4] However, the other two rate constants must be extracted from $k(O)$ by using experimental values of the ratio $k(I)/k(O)$ and the relationship $k(O) = k(N) + k(I)$.[4] The ratio $k(I)/k(O)$ is obtained from the amount of *cis*-diazene that returns to the trans isomer and is more prone to error than the value of $k(O)$.

Thus, we substantially increased the number of solvents that were utilized for 1 compared to the other diazenes. Additionally, we employed several different methods[3a] to extract the $k(I)/k(O)$ ratios from the spectral data (see Experimental Section). All of these methods, however, gave the same basic results: $k(I)_{rel}$ for 1 initially showed a steep increase with increasing viscosity followed by a levelling off of the curve. All of the methods used to analyze the spectral data for 1 were also used on new data collected for 4. The continuous decrease in $k(I)$ for 4 with increasing viscosity occurred in all cases. The new results for 4 using the same method employed for 1[3a] are included with previous data[3b] for 4 in Table I and Figure 5. The consistency of all of these results, along with those presently being obtained[15] in a detailed study of solvent effects on the decomposition of 4, satisfies us that the trends in $k(I)$ for 1 are different than those for 4.

With several of these diazenes, high viscosity data points have been obtained by using mineral oil and mineral oil/octane mixtures. To check for unexpected problems[9,10,16] in comparing such mixtures with pure lower viscosity hydrocarbon solvents, we attempted to overlap the viscosity values of these two solvent types in our

(14) See, for example, effects of solvent viscosity on intramolecular rotations: Sharafy, S.; Muszkat, K. A. *J. Am. Chem. Soc.* **1971**, *93*, 4119. Liu, R. S. H.; Asato, A. E.; Denny, M. *J. Am. Chem. Soc.* **1983**, *105*, 4829.

(15) Gunderson, H. Unpublished observations.

(16) Simple alkane and mineral oil/alkane mixtures have been used successfully in single scales of viscosity by several workers; see ref 9a, 10, and 16a,b. (a) Kiefer, H.; Traylor, T. *J. Am. Chem. Soc.* **1967**, *89*, 6667. (b) Neuman, R. C., Jr.; Bussey, R. J. *J. Am. Chem. Soc.* **1970**, *92*, 2440.

studies of 1. This was approximately accomplished with the solvent dodecane and a 1 to 2 by volume mixture of mineral oil and octane (Table I). While the data points for the values of k(O) and k(N) overlap satisfactorily in these two solvents, there is a discontinuity in the k(I) plot (Figure 4) where these two solvents meet.

This may reflect the larger error associated with the smaller values of k(I) compared to k(O), or could indicate some microscopic solvent effect not adequately accounted for by macroscopic viscosity values. One might also conclude that the overall trend in k(I) for 1 in mineral oil mixtures is downward like that for k(I) in all of the other systems. However, irrespective of these possibilities with the mineral oil mixtures, it is clear that the values of k(I) for 1 *increase*, while those for all of the other diazenes *decrease*, in the pure hydrocarbon solvents.

Kinetics. Kinetic rate laws for k(N) and k(I) based on Scheme III (excluding k_{inv} for the nonradical path) are reproduced below (eqs 1 and 2) in the forms that are most

$$1/k(\mathrm{N}) = (1/k_1)[1 + k_{-1c}/(k_\beta + k_d) + k_{-1t}/(k_\beta + k_d)] \quad (1)$$

$$1/k(\mathrm{I}) = (1/k_1)[1 + k_{-1c}/k_{-1t} + (k_\beta + k_d)/k_{-1t}] \quad (2)$$

convenient for analysis. The rate constant that should be most dependent on viscosity variation is k_d and it should decrease with increasing viscosity.

The decrease in k_d will cause the quantity $1/k$(N) to increase, and therefore the rate constant k(N) to decrease. This behavior characterizes all of the *cis*-diazenes that we have studied and is our rationale for saying that the decrease in k(N) supports a one-bond scission mechanism. This conclusion remains valid *irrespective of the isomerization mechanism*. If isomerization is nonradical (e.g. inversion), the last term in eq 1 will disappear but the same conclusions will be reached for the viscosity dependence of k(N) based on the remaining terms in the equation. The same viscosity dependence of k_d will cause the last term of eq 2 to decrease. Thus, if isomerization occurs by the radical mechanism, this would lead to a decrease in $1/k$(I) and the *increase* in k(I) that we have noted for *cis*-diazene 1.

Viscosity increases could also have an effect on k_{-1t}. Rotational diffusion[17] within the solvent cage is necessary for combination to give the trans isomer (k_{-1t}) and this would be expected to be retarded by increasing viscosity. Viscosity effects on rotational diffusion should be significantly less than on separative diffusion, however, and some support for this comes from the viscosity dependence of the ratio k(I)/k(N). Based on Scheme III (excluding k_{inv}), this ratio is defined by eq 3. Its increase with in-

$$k(\mathrm{I})/k(\mathrm{N}) = k_{-1t}/(k_\beta + k_d) \quad (3)$$

creasing viscosity for 1 (Table I) is consistent with the predicted effects on k_d and k_{-1t}. The only other diazene that has sufficient deazatization to make values of k(I)/k(N) meaningful is 4. The fact that this ratio is more constant for 4 is the result of the decreases in both k(I) and k(N) with increasing viscosity consistent with an inversion mechanism.[4,5]

Although we have not obtained evidence that shows a radical isomerization pathway for a truly symmetric *cis*-diazene, we feel that the asymmetry in 1 is less than that in some other diazenes for which radical isomerization has been proposed.[8,12] The contrasting behavior of the k(I) dependence on viscosity for 1 and the other systems warrants further study as a mechanistic probe.

(17) Inversion of the R group on the diazenyl radical would also permit recombination of the diazenyl radical and R'• to form the trans isomer. This process might also be expected to be retarded by increasing solvent viscosity.[14]

Experimental Section[3]

Synthesis of *trans*-Diazenes. The *cis*-diazenes **1–6** were synthesized in situ by photoisomerization[4] of their corresponding trans isomers **1'–6'** (vide infra). All of the *trans*-diazenes were prepared in this laboratory by following known procedures in the literature except for **5'** and **6'**, which were gifts from Professor W. Adam and Dr. Y. Nishizawa.[18]

***trans*-*N*-*tert*-Butyl-*N'*-1-norbornyldiazene (1'). 2-Bromonorbornane-1-carboxylic Acid.**[3b,19] A 28-g (0.20 mol) sample of norbornane-2-carboxylic acid (Alfa), 18 mL (0.23 mol) of bromine, and 2 mL of fresh phosphorus trichloride were reacted to give 2-bromonorbornane-1-carboxylic acid: yield 12.9 g (30%); mp 147–148 °C; lit.[19] mp 151 °C; NMR ($CDCl_3$) δ 10.66 (1 H, s), 4.16 (1 H, m), 2.30 (1 H, m), and 1.71 (8 H, m) (lit.[16a] NMR ($CDCl_3$) δ 10.66 (s), 4.16 (m), 2.30 (m), 1.71 (m)).

Norbornane-1-carboxylic Acid.[3b,19] A 14-g (0.0064 mol) sample of of 2-bromonorbornane-1-carboxylic acid was reacted with 19.5 mL of tri-*n*-butyltin hydride to give 5.5 g (0.039 mol) of norbornane-1-carboxylic acid (61%): mp 105–107 °C (lit.[3b,19] 111–112 °C); NMR ($CDCl_3$) δ 10.45 (1 H, s), 2.30 (1 H, s), and 1.60 (10 H, m) (lit.[20] NMR ($CDCl_3$) δ 10.44 (s), 2.30 (m), and 1.60 (m)).

***N*-*tert*-Butyl-*N'*-1-norbornylurea.**[20] An 11.4-g (0.081 mol) sample of norbornane-1-carboxylic acid in chloroform was reacted with 76 mL of concentrated sulfuric acid and 8.2 g of sodium azide to give 1-norbornylamine. This was reacted with a total of 16 mL (0.14 mol) of *tert*-butyl isocyanate (Aldrich), yielding 16.9 g (0.081 mol) (99%) of solid urea: mp 285–287 °C dec (lit.[20] mp 285 °C dec; NMR ($CDCl_3$) δ 2.30 (1 H, s), 1.80 (4 H, m), 1.62 (2 H, m), 1.50 (4 H, m), and 1.40 (9 H, s).

***trans*-*N*-*tert*-Butyl-*N'*-1-norbornyldiazene (1').**[20] A 6.0-g (0.029 mol) sample of *N*-*tert*-butyl-*N'*-1-norbornyl urea in 45 mL of anhydrous *tert*-butyl alcohol was reacted with a 6.6-mL sample of fresh *tert*-butyl hypochlorite[21] and then reacted with a mixture of 6.0 g of potassium *tert*-butoxide in 50 mL of anhydrous *tert*-butyl alcohol. The resulting 4.5 g of crude diaziridone (75% yield) was added slowly to a stirred solution of 100 mL of 1 N hydrochloric acid ultimately yielding an oily yellow residue. After chromatography and sublimation, a 0.48-g (0.0027 mol) (62%) sample of *N*-*tert*-butyl-*N'*-1-norbornyldiazene, a yellow liquid,[20] was obtained, which solidified when placed in the freezer overnight: NMR ($CDCl_3$) δ 2.30 (1 H, s), 1.80 (4 H, m), 1.62 (2 H, m), 1.47 (4 H, m), and 1.18 (9 H, s); mass spectrum 180 (6, M^+), 95 (100, norbornyl group), 123 (3, due to the loss of a *tert*-butyl group from the parent compound), 57 (86, *tert*-butyl group); UV λ_{max} (octane) 368 nm (ϵ = 9.6) (lit.[20] (cyclohexane) 370 nm (ϵ = 9.6)).

***trans*-*N*-1-Adamantyl-*N'*-1-norbornyldiazene (2'). *N*-1-Adamantyl-*N'*-1-norbornylurea.**[20] A 3.0-g sample of norbornane-1-carboxylic acid[22] was converted to its acid chloride and reacted with a 1.2-g sample of potassium azide to give 1-norbornyl isocyanate, which was not isolated. This was then reacted with 2.3 g (0.015 mol) of 1-adamantylamine (Aldrich) to give the desired urea: yield 2.27 g (0.0087 mol) (87%); mp sublimed at 327 °C (lit.[20] sublimed at ca. 305 °C).

***trans*-*N*-1-Adamantyl-*N'*-1-norbornyldiazene (2').**[20] A 2.4-g (0.0090 mol) sample of adamantylnorbornylurea was reacted with 3 mL of *tert*-butyl hypochlorite[21] to give 1.06 g (0.037 mol) (41%) of 1-adamantyl-1-norbornyldiaziridone. A 0.8-g (0.028 mol) sample of this material was then converted into the corresponding diazene

(18) We are indebted to Professor Waldemar Adam, Institut Für Organishce Chemie, Universität Wurzburg, FDR, for sending us samples of compounds **5'** and **6'**, which were synthesized in his laboratory by Dr. Y. Nishizawa.

(19) Kwart, H.; Null, G. *J. Am. Chem. Soc.* **1959**, *81*, 2765.

(20) Golzke, V.; Groeger, F.; Oberlinner, A.; Rüchardt, C. *Nouv. J. Chim.* **1978**, *2*, 169.

(21) (a) *Organic Syntheses*, Collect. Vol. IV; J. Wiley and Sons: New York, 1963; p 125. (b) The *tert*-butyl hypochlorite was stored for no longer than 1 week in a refrigerator in a foil-covered flask before its use.

(22) In this particular synthesis a commercial sample from Alfa was utilized.

as described for 1′: yield 0.33 g (0.0013 mol, 45%); mp 167–169 °C (lit.[20] mp 170–171 °C); mass spectrum 258 (2, M^+), 135 (100, adamantyl group), 95 (26, norbornyl group); UV λ_{max} (octane) 372 nm (ϵ = 19.4).

***trans*-*N*,*N*′-Di(1-norbornyl)diazene (3′). Di(1-norbornyl)sulfamide.** 1-Norbornylamine was synthesized starting with 7.7 g (0.055 mol) of norbornane-1-carboxylic acid (vide supra) and the resulting petroleum ether solution of amine was reacted with 1 mL (0.0012 mol) of sulfuryl chloride to give the sulfamide: yield 2.3 g (0.00086 mol, 72%); mp 177–179 °C (lit.[20] mp 176–178 °C).

***trans*-*N*,*N*′-Di(1-norbornyl)diazene (3′).[20]** A 0.96-g (0.0036 mol) sample of di(1-norbornyl)sulfamide, 0.25 g of powdered sodium hydroxide, and 22 mL of Clorox bleach (5% sodium hypochlorite solution) were reacted in low boiling petroleum ether to give 3′: yield 0.30 g (0.0014 mol, 38%); mp 164–165.5 °C (lit.[20] mp 164 °C); UV λ_{max} 369 nm (ϵ = 15.1); NMR ($CDCl_3$) δ 2.30 (1 H, s), 1.50 (4 H, m), 1.62 (2 H, m), and 1.80 (4 H, m); mass spectrum 218 (9, M^+), 95 (100, norbornyl group).

***trans*-*N*,*N*′-Di(1-adamantyl)diazene (4′). Di(1-adamantyl)sulfamide.[3b]** An 18-g (0.12 mol) sample of 1-adamantylamine was reacted with 4.8 mL (0.059 mol) of sulfuryl chloride, yielding 3.8 g (17%) of sulfamide; mp 238–240 °C (lit.[20] mp 239 °C).

***trans*-*N*,*N*′-Di(1-adamantyl)diazene (4′).** A mixture of 15 mL of Clorox bleach, 4 mL of water, 0.9 g of sodium hydroxide, and 3.8 g of di(1-adamantyl)sulfamide were reacted to give 4′: yield 0.44 g (0.0015 mol, 14%); mp 283–285 °C (lit.[20] mp 280–284 °C); NMR ($CDCl_3$) δ 2.10 (s), 1.70 (d), 1.50 (s) (lit.[3b] δ 2.10 (s), 1.70 (d), 1.50 (s)); UV λ_{max} (octane) 368 nm (ϵ = 14.1) (lit.[3b] 368 nm (ϵ = 14.1)).

***trans*-*N*,*N*′-Bis(1-(4-ethylbicyclo[2.2.2]octyl))diazene (5′).** This compound was synthesized by Adam and Nishizawa:[18] NMR: ($CDCl_3$) δ 1.53 (m), 1.18 (q), 0.78 (t). Mass spectrum: 302 (2, M^+), 137 (100, 4-ethylbicyclooctyl ion). UV: 368 nm.

***trans*-*N*,*N*′-Bis(1-(4-ethoxybicyclo[2.2.2]octyl))diazene (6′).** This compound was synthesized by Adam and Nishizawa.[18] NMR: ($CDCl_3$) δ 3.40 (q), 1.70 (m), 1.15 (t). Mass spectrum: 334 (2.8, M^+), 153 (100, 4-ethoxybicyclooctyl ion). UV: 369 nm.

Materials Used in Kinetic Studies. Solvents. The alkane solvents were purified by being stirred over sulfuric acid for 24 to 48 h, washed with water and 10% aqueous sodium bicarbonate, then distilled from phosphorus pentoxide, and stored over potassium carbonate. Mineral oil/octane mixtures were made by using purified octane and heavy mineral oil purchased from The Thrifty Drug Co. The mixtures were prepared in ratios of 1:2, 1:1, 2:1, 5:1, 10:1, and 15:1 mineral oil to octane by volume.

Triethylamine and *tert*-Butylamine. These amines, used to eliminate traces of acid in the reaction mixtures,[3b,4] were stirred over potassium hydroxide for 12 h, distilled in vacuo, and stored in brown bottles.

Viscosity Measurements. Viscosities of the solvents were determined by using a laminar flow viscometer immersed in a thermostatted temperature bath. Densities of the same solvents were determined at the temperatures used for the viscometer measurements by filling volumetric flasks with the solvents at the appropriate temperatures and then carefully weighing the full and empty flasks. Literature values[23] for octane were used as reference points for calculating the viscosities of the other solvents.

Kinetics. General. All glassware, reaction cells, droppers, and syringes that came in contact with the diazene reaction mixtures were carefully washed with dilute ammonium hydroxide and oven dried. Solutions of *trans*-diazenes 1′–6′ were prepared by dissolving 25–30 mg of the diazene in 3 mL of the solvent containing about 0.012 M triethylamine or *tert*-butylamine.[3b,4] These solutions were injected into specially prepared sample cells that fit into the cell compartment of a Cary 2390 UV–vis–NIR spectrometer (Varian Techtron Ltd.). The cells were rectangular cuvettes prepared from T08 commercial glass (Amersil Inc. Optics) fitted with an Ace stopcock connected to a joint for attachment to a vacuum line. The diazene solutions were vacuum degassed on a vacuum line by standard freeze–thaw procedures.

(23) Rossini, F. D. "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds", American Petroleum Institute Research Project 44, Carnegie Press, 1953.

Table II. Values of $\epsilon_{trans}/\epsilon_{cis}$ Determined Using Eq 6

solvent	$\epsilon_{trans}/\epsilon_{cis}$ 1	4
hexane	0.20	0.20
octane	0.25	
dodecane	0.19	0.19
1 to 2	0.19	
1 to 1	0.19	
2 to 1	0.18	
5 to 1	0.19	
10 to 1	0.20	
mineral oil	0.21	0.18
average	0.20 (0.02)	0.19 (0.01)

The temperature of the thermostatted cell compartment in the spectrometer was maintained by using a Neslab RTE-8 circulating temperature bath. The temperature of the circulating fluid was monitored close to the outlet from the spectrometer by using both digital and conventional mercury thermometers inserted into special in-line adapters. The base line for each series of kinetic runs on a particular diazene sample was programmed into the spectrometer by using two UV cells (the actual sample cell to be used for the diazene solution and a sealed reference cell) containing the solvent/amine solution to be used in the kinetic run about to be performed. The solvent in the sample cell was the solvent that was used to prepare the diazene solution for the kinetic study.

Kinetic Studies of *cis*-Diazene Decompositions. The procedure outlined here was specifically used for studies of 1 and 4.[3a] Similar procedures were used for the other *cis*-diazenes.[3,15] The degassed sample cell was thermostatted at the photolysis temperature (0.5 °C) but was quickly removed before photolysis, placed in the Cary 2390 spectrophotometer, and its spectrum taken from 500 to 280 nm to provide prephotolysis spectral data. The sample cell was then warmed to the kinetic temperature and another spectrum taken. The UV cell was then removed from the spectrometer, brought to the photolysis temperature, photolyzed at approximately 360 nm (Osram HBO-200 W Super Pressure mercury lamp in conjunction with a Schott Model UG-1-S-5085 G546, UV filter) for 15 min, and quickly returned to the spectrophotometer where collection of spectral data was immediately initiated. Spectra were recorded from 500 to 280 nm at a specified interval (usually every 2 or 5 min). The absorbance values were printed at specific wavelengths to a precision of 0.0001 absorbance unit. The readings were taken through a period of 4 to 5 half-lives and the spectrophotometer was then placed in a stand-by mode until 10 half-lives had passed. "Infinite time" (10 half-lives or greater) spectral data were collected at the kinetics temperature and subsequently at the photolysis temperature. Three complete photolysis and reaction cycles were performed on each sample. Values of k(O) were calculated from the decrease with time in the *cis*-diazene absorbance at λ_{max}, using standard procedures and appropriate base-line corrections.

Values of the ratio $k(I)/k(O)$ were obtained as the other experimental quantity, using both eqs 4 and 5 shown below.

$$k(I)/k(O) = [A_{trans(t=\infty)} - A_{trans(t=0)}]/[A_{trans(pre-h\nu)} - A_{trans(t=0)}] \quad (4)$$

$$k(I)/k(O) = [A_{trans(t=\infty)} - A_{trans(t=x)}]/[(A_{cis(t=x)})(\epsilon_{trans}/\epsilon_{cis})] \quad (5)$$

Equation 4 permits the calculation of only one value of $k(I)/k(O)$ per kinetic run, using data before photolysis (pre-$h\nu$), after photolysis, but before thermal decomposition of *cis*-diazene (t = 0), and at the end of thermal decomposition of *cis*-diazene (t = ∞). Equation 5, however, allows several determinations of $k(I)/k(O)$ per run since values of A_{cis} and A_{trans} can be determined at various times (t = x) during thermolysis of the *cis*-diazene. This latter equation also precludes the necessity of accurately determining the value of $A_{trans(t=0)}$ corresponding to the beginning of thermal decomposition *at the thermal decomposition temperature*. Values of $\epsilon_{trans}/\epsilon_{cis}$ for the different diazenes and solvent systems were determined using eq 6 since pure samples of the

$$\epsilon_{trans}/\epsilon_{cis} = [A_{trans(pre-h\nu)} - A_{trans(t=0)}]/[A_{cis(t=0)} - A_{cis(pre-h\nu)}] \quad (6)$$

cis-diazene were never isolated. While this equation does require careful measurements of both $A_{cis(t=0)}$ and $A_{trans(t=0)}$, these mea-

surements can be made under conditions where no significant amount of *cis*-diazene is decomposing (i.e., at temperatures below those for decomposition) and hence are more reliable than the $A_{trans(t=0)}$ value required in eq 4. Values of $\epsilon_{trans}/\epsilon_{cis}$ using eq 6 were determined prior to each kinetic run (three per diazene–solvent mixture) and the results are outlined in Table II for diazenes 1 and 4.

Values of $k(I)/k(O)$ were calculated from eq 5, using the individual average values of $\epsilon_{trans}/\epsilon_{cis}$ for each solvent and diazene, and also using the overall average value of $\epsilon_{trans}/\epsilon_{cis}$ from all solvents for each of the diazenes. In addition, the ratios $k(I)/k(O)$ were calculated, using eq 4. Although the values of $k(I)/k(O)$ varied with the choice of method for both 1 and 4, the apparent increase in $k(I)$ with increasing viscosity for 1 and the decrease in $k(I)$ for 4 was consistently observed independent of the calculation procedure.

Because there was no clearcut trend in variation of $\epsilon_{trans}/\epsilon_{cis}$ as a function of solvent, the data resulting from the use of the overall average value of this ratio for each of the diazenes were used to obtain the values of $k(I)$ reported in Table I for 1 and 4. Values of $k(N)$ were determined by subtracting values of $k(I)$ from values of $k(O)$.

Supplementary Material Available: Full experimental details of the compounds described in this study (4 pages). Ordering information is given on any current masthead page.

New Records for Sterically Congested Stilbenes: (*E*)- and (*Z*)-1-(2,2-Dimethyl-1-tetralinylidene)-2,2-dimethyltetralin†

James E. Gano,* Bong-Ser Park, and A. Alan Pinkerton

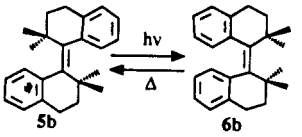
Department of Chemistry, University of Toledo, Toledo, Ohio 43606

Dieter Lenoir*

Chair of Ecological Chemistry and Geochemistry, University of Bayreuth, Bayreuth D-8580, West Germany

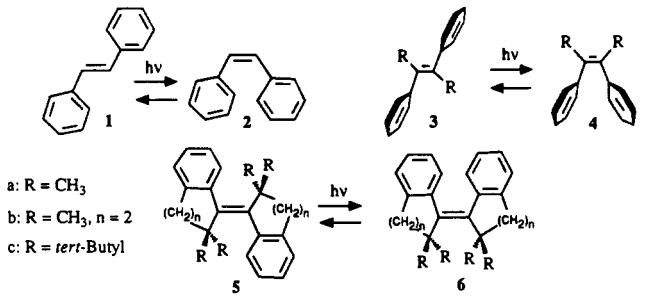
Received October 16, 1989

The synthesis and characterization of the isomeric, highly distorted stilbenes **5b** and **6b**, are reported. X-ray analysis showed **5b** to be twisted 36.7° at the central double bond. Isomer **6b** was unstable at room temperature,



isomerizing back to **5b** with $E_a = 21 \pm 1.8$ kcal/mol. MMP2 calculations, supported by direct observations, suggested **6b** was an unsymmetrical structure twisted 73° about the central double bond.

Distortion of normally planar carbon–carbon double bonds has frequently produced strained materials with significantly altered chemical and physical properties.[1] Sterically demanding groups can introduce such structural modifications.[2] Because potential reaction channels are blocked, steric congestion frequently reduces kinetic reactivity while increasing strain energy. The important places held by (*E*)- (1) and (*Z*)-stilbene (2) in the development of photochemistry and in the evolution of many new chemical techniques make them particularly attractive for structural elaboration.[3] *E* to *Z* isomerization is particularly useful for photochemical introduction of further strain. This approach has been successful with stilbenes substituted on the carbon–carbon double bond such as (*E*)- (**3c**) and (*Z*)-di-*tert*-butylstilbene (**4c**).[3,4] The resulting steric congestion in **3c** and **4c** created novel, twisted π systems. The *Z* to *E* isomerization barrier was reduced from 42.8 (stilbene) to 32.0 kcal/mol by the *tert*-butyl substitution, the lowest recorded barrier for any symmetrically substituted stilbene.[3-5] In the cases of **3c** and **4c**, the molecule responded to the steric congestion introduced by the *tert*-butyl groups by rotation of the phenyl groups. This led to complete loss of conjugation of the phenyl rings from the central double bond. The central double bond, however, remained planar.[6] If the phenyl rings had been



† This paper, which was made possible by the combination of experiment and force field calculations, is dedicated to Paul von Ragué Schleyer on the occasion of his 60th birthday.

(1) (a) Wiberg, K. B. *Angew. Chem., Int. Ed. Engl.* **1986**, *254*, 312. (b) Liebman, J. F.; Greenberg, A. *Strained Organic Molecules*; Academic: New York, 1978.

(2) Sandstroem, J. *Top. Stereochem.* **1983**, *14*, 83.

(3) Saltiel, J.; Charlton, J. L. *Rearrangements in the Ground and Excited State*; DeMayo, P., Ed.; Academic: New York, 1980; p 25.

(4) (a) Lenoir, D.; Gano, J. E.; McTague, J. A. *Tetrahedron Lett.* **1986**, *27*, 5339. (b) Gano, J. E.; Park, B.-S.; Subramaniam, G.; Lenoir, D.; Gleiter, R. *J. Am. Chem. Soc.*, submitted.

(5) A push–pull substitution pattern on alkenes dramatically lowers the $Z \rightarrow E$ isomerization barrier. In contrast to 1–6, however, the barrier in push–pull substituted systems is lowered by reducing the π bond strength electronically rather than increasing the energy in the reactant.

0022-3263/90/1955-2688$02.50/0