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The Electronic Interaction between the Methyl Group and Trigonal Carbon

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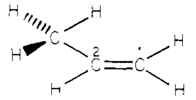
Abstract: The nature of the interaction between methyl and a trigonal carbon has been examined by the effect of substituents on the methyl rotational barrier. Barriers have been measured for para-substituted toluenes and for cis- and trans-substituted propenes by the motional effects of methyl rotation on dipole–dipole spin–lattice relaxation. The toluene barriers exhibit a fair correlation with σ_I and a very poor one with σ_R. Thus hyperconjugation cannot be a major factor in determining the methyl rotational barrier. The propene barriers, particularly in the cis series, also correlate with σ_I but have a better correlation with σ_R than do the toluenes. Examination of all the ^{13}C chemical shifts showed that the rotational barriers correlate only with the ortho carbon in the toluenes and with the 2-carbon (methyl substituted) in the propenes. These results suggest that the methyl rotational barrier is primarily sensitive to the nature of the ortho C–H bond in the toluenes and of the α-C–H bond in the propenes. The σ_R and σ_I correlations are in accord with this model, since the ortho toluene carbon cannot interact directly through resonance with the para substituent but must depend on polar interactions. In the propenes, on the other hand, electron density at the α-carbon is determined by both inductive and resonance effects. The major factor in determining these barriers is the electron density at the critical carbon center, which is the ortho carbon for the toluenes and the α-carbon for the propenes.

Whereas the conformational analysis of bonds connecting two sp^3 atoms has been very actively prosecuted, the study of bonds between sp^2 and sp^3 atoms has been rather more restricted.[2] In most such systems, the barrier is threefold and one bond to the sp^3 center is eclipsed with the double bond, as in **1**. Minor substitution at the 2-position, at the trans 1-position, or on the sp^3 atom probably does not alter this preference, but substitution at the cis 1-position may enhance the population of the alternative conformation **2**, in which one bond to the sp^3 center is eclipsed with the C–H bond at the 2-position. This change in conformational population has been interpreted in terms of steric effects alone.[2]



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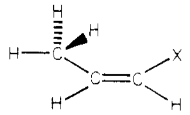

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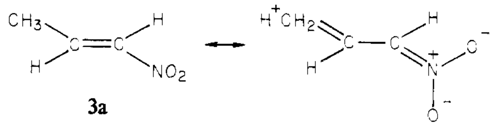
The electronic interaction of the saturated methyl group with the unsaturated center over the sp^3–sp^2 bond influences the barrier to rotation about this bond. The exact nature of this interaction has never been fully clarified. One mechanism of interaction is hyperconjugation, as depicted in **3**. Although hyperconjugation undoubtedly contributes to charged or radical systems (the sp^2 center would be a carbonium ion or free radical), the importance of such an interaction is not at all clear in closed shell, neutral systems such as these substituted propenes and toluenes. Dale has described the substituent effect as basically a polar interaction.[3] He attributes variations of the ethane barrier to electronic repulsion between orbitals. The sp^3–sp^2 barrier (1.98 kcal/mol in propene) is lower than the sp^3–sp^3 barrier (2.88 in ethane) because the double-bond orbitals are "bent back" and interact less with the orbitals on the saturated center.



3a **3b**

Although other theories can be described, most can be classified in terms of a dominant π (resonance) effect, as in hyperconjugation, or a dominant σ (inductive, polar) effect, as in the Dale theory. It would therefore seem reasonable that the problem could be clarified by comparison of rotational barriers with quantitative measures of resonance and inductive effects, specifically σ_I and σ_R. Microwave experiments have provided almost all the barriers in propene and toluene systems.[3,4] Although data are available for CH_3—CH═CH—X for H, CH_3, and halogen,[3] there are no electron-donating substituents, and only lower limits were set for the more strongly electron-withdrawing substituents (CN, NO_2).[4] Because of the lack of data for substituents at the electronic extremes, it has not been possible to make a clear choice between the resonance and inductive types of substituent interactions between CH_3 and a double bond.

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(1) This work was supported by the National Science Foundation (Grants CHE77-08384 and CHE79-05542 and a departmental equipment grant for the purchase of a Varian CFT-20 NMR spectrometer).

(2) For a review, see: Karabatsos, G. J.; Fenoglio, D. J. *Top. Stereochem.* **1970**, *5*, 167–203.

(3) Dale, J. *Tetrahedron* **1966**, *22*, 3373–3382.

(4) Ford, R. G. *J. Mol. Spectrosc.* **1974**, *49*, 117–123.

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We report herein the determination of methyl rotation barriers for a full series of substituted *cis*-propenes, *trans*-propenes, and *para*-toluenes, ranging from NO_2 on the electron-withdrawing end to NR_2 (R = H, CH_3) on the electron-donating end. We have measured these barriers from the effect of methyl rotation on the spin–lattice relaxation time of the methyl carbon. From these barriers, a distinction can be drawn in favor of a polar mechanism.

Methods

Most earlier barriers to methyl–carbon rotation in relatively unhindered systems were measured by microwave techniques.[3,4] Although these barriers are reasonably accurate, their determination is time consuming and often requires the synthesis of isotopic isomers. Furthermore, barriers much above 2.0 kcal/mol yield only lower limits. Woessner and co-workers[5] have described a method for extracting the barrier to methyl rotation from the dipole–dipole spin–lattice relaxation time T_1 (DD). The internal rotation of the methyl group, superimposed on the overall tumbling motion of the molecule, contributes to relaxation of the ^{13}C nucleus. Grant and co-workers have used this method extensively for the measurement of methyl rotation barriers,[6] and it is now coming into more general usage.[7]

The overall spin-lattice relaxation (T_1) and the nuclear Overhauser effect (η) are used to obtain the dipole–dipole contribution (T_1(DD)) by eq 1. The dipole–dipole relaxation time for CH_3

$$T_1(\mathrm{DD}) = T_1\ 1.988/\eta \qquad (1)$$

is related to the overall rotational diffusion constant D and the intramolecular methyl rotational diffusion constant D_i by eq 2,

$$\frac{1}{T_1^{\mathrm{CH_3}}(\mathrm{DD})} = \frac{3\gamma_{\mathrm{H}}^2\gamma_{\mathrm{C}}^2\hbar^2}{r_{\mathrm{CH}}^6}\left(\frac{A}{6D} + \frac{B}{6D + D_i} + \frac{C}{6D + rD_i}\right) \qquad (2)$$

in which the γ are gyromagnetic ratios for ^{13}C and ^1H and $r_{\mathrm{C-H}}$ is the methyl C–H bond length. The geometrical constants have been given in many different forms[6,7] such as $A = {}^1/_4(3\cos^2\theta - 1)^2$, $B = 3\sin^2\theta\cos^2\theta$, and $C = {}^3/_4\sin^4\theta$, in which θ is the angle between the CH bond and the principal axis of the top, usually taken to be 109.5°. Equation 2 assumes that the motion of the molecule in solution is isotropic, so that only a single overall diffusion constant D is required. If the methyl group reorients by a series of jumps (threefold or sixfold), the coefficient r is unity and the B and C terms combine; if the reorientation is by stochastic diffusion, r is 4. For the methyl jump model, D_i is $^3/_2$ of the methyl jump rate; for the stochastic diffusion model, D_i is the rate of methyl diffusion.

The overall diffusion constant D can be evaluated from the relaxation time of any nucleus α that is not subject to internal rotation (eq 3, in which n = 1 for a CH group and 2 for a CH_2

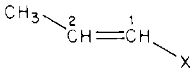
$$\frac{1}{T_1^{\alpha}(\mathrm{DD})} = \frac{n\gamma_{\mathrm{H}}^2\gamma_{\mathrm{C}}^2\hbar^2}{6r_{\mathrm{CH}}^6 D} \qquad (3)$$

group). Thus measurement of $T_1^{\mathrm{CH_3}}(\mathrm{DD})$ and of $T_1^{\alpha}(\mathrm{DD})$ gives D_i from eq 2 and 3. This rate is subject to the usual Arrhenius temperature dependence of the type in eq 4, in which D_{i0} is the

$$D_i = D_{i0}e^{-V_0/RT} \qquad (4)$$

rate of free methyl reorientation in the gas phase (multiplied by $^3/_2$ for a threefold jump mechanism) and V_0 is the activation energy to methyl rotation. The value of D_{i0} for the methyl jump mechanism has been generally taken to be 1.33 × 10^{13} s^{-1} at 40 °C ($^3/_2(kT/I)^{1/2}$) and $^2/_3$ of this value for the stochastic diffusion model.[8] With all the factors determined, the activation energy V_0 can be calculated. The limitations and approximations in this procedure will be considered in the first discussion section.

Table I. Relaxation Data and 90% Confidence Limits for the *trans*-Propenes

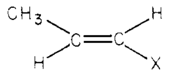


X	carbon	T_1, s	NOE	T_1(DD), s	T_1^{α}(DD),[a] s
NO_2	1	18.2 ± 0.8	2.52 ± 0.04[b]	23.8 ± 1.7	24.2 ± 1.4
	2	18.7 ± 0.3		24.5 ± 1.0	
	CH_3	13.8 ± 0.2	2.85 ± 0.02	15.0 ± 1.0	
CN	1	11.9 ± 1.2	1.85 ± 0.05	26.6 ± 3.5	27.2 ± 2.6
	2	14.6 ± 0.4	2.05 ± 0.03	27.7 ± 1.6	
	CH_3	13.1 ± 0.4	2.80 ± 0.04	14.6 ± 0.6	
Br	1	12.9 ± 0.3	1.26 ± 0.03	100.0 ± 1.2	56.4 ± 6.2
	2	5.5 ± 0.2	1.85 ± 0.01	12.9 ± 0.6	
	CH_3	17.1 ± 0.2	2.32 ± 0.02	25.9 ± 0.8	
SCH_3	1	13.4 ± 0.3	2.41 ± 0.11	19.0 ± 2.0	20.2 ± 1.5
	2	13.3 ± 0.3	2.23 ± 0.02	21.4 ± 0.9	
	CH_3	12.2 ± 0.2	2.73 ± 0.07	14.1 ± 0.6	
CH_3	1, 2	16.8 ± 1.2	1.33 ± 0.01	101.2 ± 9.9	101.2 ± 9.9
	CH_3	24.2 ± 1.4	2.16 ± 0.03	43.4 ± 2.7	
OCH_3	1	22.2 ± 0.2	2.01 ± 0.03	43.9 ± 1.7	41.6 ± 2.4
	2	22.9 ± 0.8	2.17 ± 0.05	39.2 ± 3.0	
	CH_3	17.5 ± 0.1	2.77 ± 0.08	19.8 ± 1.1	
NMe_2	1	4.9 ± 0.1	2.33 ± 0.02	7.3 ± 0.3	14.4 ± 0.6
	2	10.8 ± 0.2	2.00 ± 0.02	21.5 ± 0.8	
	CH_3	12.2 ± 0.3	2.56 ± 0.01	15.6 ± 0.5	

[a] Average of T_1 (DD) for C1 and C2. [b] Average value, because peaks are not well resolved.

Results

In this study, we have examined three series of compounds containing methyl groups attached to a carbon–carbon double bond, the *trans*-propenes (**4**), the *cis*-propenes (**5**), and the *para*-toluenes (**6**). All of the *para*-toluenes were commercially



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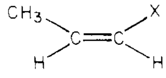

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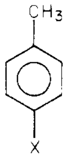

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available. In the propene series, the nitriles, bromides, and 2-butenes were commercially available, although only the 2-butenes were available as separate isomers. The methoxy-, methylthio-, and (dimethylamino)propenes were prepared by the procedure given in eq 5 (X = O, S, NCH_3). The nitropropenes were prepared

$$\mathrm{CH_3CHO + 2CH_3XH \rightarrow CH_3CH_2CH(XCH_3)_2 \xrightarrow{\Delta} CH_3CH{=}CXCH_3} \qquad (5)$$

by the sequence given in eq 6. In each case, products were

$$\mathrm{CH_3CHO + CH_3NO_2 \rightarrow CH_3CH(OH)CH_2NO_2 \xrightarrow{CH_3C({=}O)Cl} CH_3CH(OAc)CH_2NO_2 \xrightarrow[Ni]{200\ ^\circ C} CH_3CH{=}CHNO_2} \qquad (6)$$

stereoisomeric mixtures. Conditions were developed to produce substantial proportions of both cis and trans materials. The nitropropene synthesis was particularly successful in achieving

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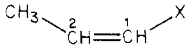
(5) Woessner, D. E. *J. Chem. Phys.* **1962**, *37*, 647–654. Woessner, D. E.; Snowden, B. S., Jr.; Meyer, G. H. Ibid. **1969**, *50*, 719–721.

(6) (a) Kuhlmann, K. F.; Grant, D. M. *J. Chem. Phys.* **1971**, *55*, 2998–3007. (b) Alger, T. D.; Grant, D. M.; Harris, R. K. *J. Phys. Chem.* **1972**, *76*, 281–282. (c) Lyerla, J. R., Jr.; Grant, D. M. *Ibid.* **1972**, *76*, 3213–3216. (d) Collins, S. W.; Alger, T. D.; Grant, D. M.; Kuhlmann, K. F.; Smith, J. C. *Ibid.* **1975**, *79*, 2031–2037. (e) Ladner, K. H.; Dalling, D. K.; Grant, D. M. *Ibid.* **1976**, *80*, 1783–1786.

(7) (a) ApSimon, J. W.; Beierbeck, H.; Saunders, J. K. *Can. J. Chem.* **1975**, *53*, 338–342. (b) Axelson, D. E.; Holloway, C. E. *Ibid.* **1976**, *54*, 2820–2826. (c) Blunt, J. W.; Stothers, J. B. *J. Magn. Reson.* **1977**, *27*, 515–519. (d) Baldo, M.; Forchioni, A.; Irgolic, K. J.; Pappalardo, G. C. *J. Am. Chem. Soc.* **1978**, *100*, 97–100. (e) Platzer, N. *Org. Magn. Reson.* **1978**, *11*, 350–356.

(8) The Woessner dipolar derivations of V_0, with one exception, have always used one temperature, because of the immense amount of instrument time required for the T_1 and NOE measurements. The uniformity of D_{i0}, rather than its absolute accuracy, is critical for our serial comparisons. For the exception, see: Ericsson, A.; Kowalewski, J.; Liljefors, T.; Stilbs, P. *J. Magn. Reson.* **1980**, *38*, 9–22.

Table II. Relaxation Data and 90% Confidence Limits for the *cis*-Propenes



X	carbon	T_1, s	NOE	T_1(DD), s	$T_1{}^\alpha$(DD),[a] s
NO_2	1	19.6 ± 0.2	2.18 ± 0.01	33.1 ± 0.1	38.8 ± 0.8
	2	19.7 ± 0.1	1.88 ± 0.02	44.5 ± 1.0	
	CH_3	18.2 ± 0.2	2.28 ± 0.01	28.3 ± 0.6	
CN	1	12.9 ± 0.9	2.28 ± 0.03	19.6 ± 0.7	23.2 ± 2.0
	2	17.2 ± 1.5	2.30 ± 0.08	26.7 ± 3.2	
	CH_3	13.1 ± 0.3	2.60 ± 0.07	16.6 ± 1.1	
Br	1	17.6 ± 0.8	1.42 ± 0.02	83.5 ± 7.6	50.5 ± 4.3
	2	6.8 ± 0.3	1.77 ± 0.01	17.6 ± 1.0	
	CH_3	17.8 ± 0.2	1.81 ± 0.01	43.9 ± 1.0	
SCH_3	1	15.1 ± 0.4	2.41 ± 0.02	21.4 ± 0.9	23.3 ± 1.6
	2	15.4 ± 0.8	2.21 ± 0.04	25.2 ± 2.2	
	CH_3	17.4 ± 0.4	2.26 ± 0.06	27.6 ± 1.8	
CH_3	1,2	26.8 ± 0.7	1.57 ± 0.02	93.9 ± 5.7	94.0 ± 5.7
	CH_3	23.2 ± 0.4	1.58 ± 0.03	79.7 ± 5.3	
OCH_3	1	18.5 ± 0.8	2.24 ± 0.04	29.7 ± 2.3	37.5 ± 4.1
	2	25.3 ± 0.5	2.15 ± 0.11	45.2 ± 5.9	
	CH_3	18.2 ± 0.2	1.90 ± 0.02	40.1 ± 1.4	
NMe_2	1	5.8 ± 0.2	1.82 ± 0.03	14.1 ± 1.0	17.8 ± 0.7
	2	14.8 ± 0.1	2.37 ± 0.02	21.5 ± 0.4	
	CH_3	17.0 ± 0.2	2.21 ± 0.02	27.9 ± 0.7	

[a] Average of T_1(DD) for C1 and C2.

this objective, since the 45% cis content was considerably better than the 10% previously reported.[9] The isomeric mixtures were separated by preparative gas chromatography or by distillation, with exceptions noted in the Experimental Section.

Tables I–III give the relaxation data and Tables IV–V the chemical shift data. The values of $T_1{}^\alpha$ for eq 3 were taken as the average of the ortho and meta carbon values for the toluene series and as the average of the C1 and C2 values for the propene series. For the most part, the ortho/meta and the C1/C2 values are not very different. Particularly deviant cases such as the 2-bromopropenes will be discussed later.

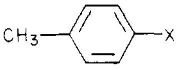
The NOE's are above 2.2 for most cases, so that dipole–dipole relaxation is dominant. For toluene and *cis*-2-butene, the lower values probably indicate contributions from spin-rotation relaxation.

We have calculated the methyl rotation barriers for both the stochastic diffusion and the methyl jump models. The results and the 90% confidence limits are given in Tables VI and VII. In order to test the legitimacy of the assumption of isotropic molecular motion, we also calculated barriers for toluene by using an anisotropic model developed by Platzer.[7e] The anisotropic-model barriers were slightly lower.[10]

Discussion of Approximations, Limitations, and Assumptions

Our primary aim in this study was to explore the electronic interaction between the methyl group and trigonal carbon. Determination of the barriers to methyl rotation was a means to this end. Because the microwave method had given only lower limits to barriers[3,4] for the upper range of numbers and because the method is not easily applicable to complex molecules, we chose to measure barriers by their effect on NMR dipole–dipole relaxation. Application of the exact Woessner equations[5] for anisotropic motion is generally not possible, because molecules do not offer enough pieces of independent data to determine all the requisite diffusion constants. The method has proved useful because the isotropic approximation appears to be reasonable in many instances. Since we wanted to focus on the systematic errors of the method, we essayed to minimize the experimental errors. Each spin–lattice relaxation time and nuclear Overhauser enhancement were measured four or five times in order to reduce the 90% error bars to less than 5%. Accuracy of the NOE's is more difficult to achieve, because each determination is based on only two intensity measurements. To optimize NOE accuracy, we reduced the spectral width to 1 kHz, rather than the usual 4–5 kHz for ^{13}C measurements, thereby producing more data points per hertz. The cost of course was in spectrometer time,

Table III. Relaxation Data and 90% Confidence Limits for the *para*-Toluenes



X	carbon	T_1, s	NOE	T_1(DD), s	$T_1{}^\alpha$(DD),[a] s
NO_2	ortho	4.6 ± 0.1	2.89 ± 0.07	4.8 ± 0.3	4.9 ± 0.3
	meta	4.7 ± 0.1	2.91 ± 0.06	4.9 ± 0.3	
	CH_3	7.2 ± 0.4	2.38 ± 0.03	10.6 ± 0.6	
$C(O)CH_3$	ortho	3.4 ± 0.1	2.96 ± 0.04	3.5 ± 0.1	3.6 ± 0.1
	meta	3.4 ± 0.1	2.78 ± 0.06	3.7 ± 0.1	
	CH_3	6.0 ± 0.0	2.39 ± 0.06	8.7 ± 0.6	
Cl	ortho	10.8 ± 0.1	2.71 ± 0. 12	12.7 ± 1.0	11.7 ± 1.0
	meta	9.5 ± 0.6	2.78 ± 0.03	10.6 ± 0.9	
	CH_3	10.9 ± 0.3	2.20 ± 0.05	18.3 ± 1.3	
H(lit)	ortho	16.4 ± 0.2	2.50 ± 0.02[b]	21.7 ± 0.5	21.3 ± 0.7
	meta	15.9 ± 0.4		20.9 ± 0.8	
	CH_3	14.1 ± 0.5	1.71 ± 0.03	39.7 ± 3.0	
OCH_3	ortho	6.9 ± 0.5	2.93 ± 0.11	7.3 ± 0.9	7.4 ± 0.8
	meta	7.2 ± 0.4	2.96 ± 0.06	7.4 ± 0.6	
	CH_3	9.4 ± 0.1	2.22 ± 0.04	15.3 ± 0.6	
NH_2	ortho	4.6 ± 0.0	2.51 ± 0.04	6.1 ± 0.2	5.7 ± 0.8
	meta	4.1 ± 0.1	2.53 ± 0.03	5.4 ± 0.2	
	CH_3	8.5 ± 0.2	2.30 ± 0.02	13.1 ± 0.2	

[a] Average of T_1(DD) for ortho and meta carbons. [b] Average value, because peaks are not well resolved.

Table IV. Carbon-13 Chemical Shifts[a] for the *cis*- and *trans*-Propenes

	trans			cis		
X	CH_3-	$CH=$	CH-	CH_3-	$CH=$	CH-
NO_2	13.6	140.9	138.6	17.0	170.5	118.4
CN	19.0	151.9	101.2	19.0	160.0	101.4
Br	18.2	132.8	104.7	15.4	129.4	109.1
SCH_3	18.4	125.5	121.7	14.4	128.5	122.7
CH_3	18.0	126.2	126.2	12.4	125.0	125.0
OCH_3	12.6	148.3	96.8	9.1	147.6	100.8
$N(CH_3)_2$	11.6	127.4	86.3	8.9	132.1	93.4

[a] In ppm (δ) downfield from Me_4Si; C_6D_6 solvent.

Table V. Carbon-13 Chemical Shifts[a] for the *para*-Toluenes

X	ipso	ortho	meta	para	CH_3
NO_2	146.4	130.2	123.7	146.7	21.4
$C(O)CH_3$	145.0	130.1	130.9	136.6	22.8
Cl	136.1	130.4	128.3	131.2	20.7
H	136.7	129.1	128.4	126.0	21.8
OCH_3	130.0	129.7	114.3	158.2	20.9
NH_2	126.4	129.3	114.8	144.2	20.8

[a] In ppm (δ) downfield from Me_4Si; C_6D_6 solvent.

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(9) Melton, J.; McMurry, J. E. *J. Org. Chem.* **1975**, *40*, 2138–2139.

(10) Lambert, J. B.; Nienhuis, R. J.; Finzel, R. B., unpublished results.

Table VI. Methyl Rotational Barriers (kcal/mol) and 90% Confidence Limits for the *cis*- and *trans*-Propenes

X	stochastic diffusion model	methyl jump model	lit.[a]
trans-NO_2	1.78 ± 0.08	1.89 ± 0.09	>2.25
-CN	1.93 ± 0.16	2.34 ± 0.10	>2.10
-SCH_3	1.72 ± 0.11	1.83 ± 0.11	
-CH_3	1.60 ± 0.30	1.89 ± 0.46	>1.95
-OCH_3	1.88 ± 0.17	2.04 ± 0.21	
-$N(CH_3)_2$	1.37 ± 0.06	1.50 ± 0.06	
cis-NO_2	1.27 ± 0.04	1.39 ± 0.04	
-CN	1.60 ± 0.15	1.72 ± 0.14	1.4
-SCH_3	0.96 ± 0.13	1.10 ± 0.12	
-CH_3	0.55 ± 0.04	0.67 ± 0.04	0.75
-OCH_3	0.80 ± 0.11	0.93 ± 0.11	
-$N(CH_3)_2$	0.75 ± 0.07	0.89 ± 0.07	

[a] Literature values, measured by the microwave method and taken from ref 3 and 4.

Table VII. Methyl Rotational Barriers (kcal/mol) and 90% Confidence Limits for the *para*-Toluenes

X	stochastic diffusion model	methyl jump model
NO_2	0.91 ± 0.25	1.06 ± 0.25
$C(O)CH_3$	0.88 ± 0.18	1.03 ± 0.18
Cl	0.99 ± 0.17	1.14 ± 0.17
H	0.36 ± 0.17	0.51 ± 0.17
OCH_3	0.75 ± 0.25	0.90 ± 0.25
NH_2	0.71 ± 0.18	0.87 ± 0.17

since a 1-kHz sweep might incorporate only half or a third of the resonances of a given compound. The result of repetitive measurements and smaller sweep widths was reasonably accurate data, given in Tables I–III.

Use of eq 2 for the determination of the internal diffusion constant for methyl rotation, D_i, requires that the overall motion of the molecule be described by a single diffusion constant, D. In the absence of anisotropic overall motion, all values of nT_1(DD) for carbons not undergoing internal rotation should be the same. Since the methinyl carbons possess the same number of directly bonded protons, their values of T_1(DD) may be compared directly. As can be seen from Table III for the toluenes, the ortho and meta carbons have values that are equal within experimental error, with the possible exception of X = NH_2. The agreement between T_1(DD) for C1 and C2 is excellent for the *trans*-propenes, with the flagrant exception of X = Br and the lesser exception of $N(CH_3)_2$ (Table I). Differences for the *cis*-propenes are larger but only flagrant again for X = Br (Table II). For this reason, we have not determined V_0 for either bromopropene. Using the Platzer method,[7c] we carried out an anisotropic analysis for toluene and found a slight lowering of the barrier.[10] The procedure is not possible in the other systems, because two C–H vectors are insufficient to determine the unknowns.

There has been no general agreement in preference for the stochastic diffusion or the methyl jump models. Two groups have used the stochastic method,[6e,7c] whereas the remaining studies have used the methyl jump model[6,7] and one group reported both.[7b] This last group pointed out that the methyl jump model loses accuracy below about 0.8 kcal/mol and above 2.8 kcal/mol.[7b] Other authors have suggested that the methyl jump model should be preferred above about 1.4 kcal/mol.[7c] As the barrier gets very low, the dipole–dipole relaxation time becomes increasingly less sensitive to methyl rotation, since it is governed primarily by the slowest motion.[6e] We have carried out the full analysis for both models.

Blunt and Stothers[7c] have also pointed out that the calculation is dependent on the exact value of the angle θ in the calculation of the geometrical constants A, B, and C in eq 2. Tetrahedral symmetry is usually assumed. Deviation of θ from 109.5° by as little as 3°, however, can have a major impact on the value of V_0.[7c] When the ratio $T_1^{CH_3}(DD)/T_1^{\alpha}(DD)$ is between 0.4 and 2.4, the assumption of tetrahedral symmetry is reasonable. This ratio varies from 0.43 to 1.08 for the *trans*-propenes, from 0.72 to 1.57 for the *cis*-propenes, and from 1.6 to 2.4 for the *para*-toluenes (Tables I–III). The higher values for the toluenes reflect lower barriers on the average. Nonetheless, it appears that our systems are not in the extreme regions in which the assumption of tetrahedral geometry is poor.

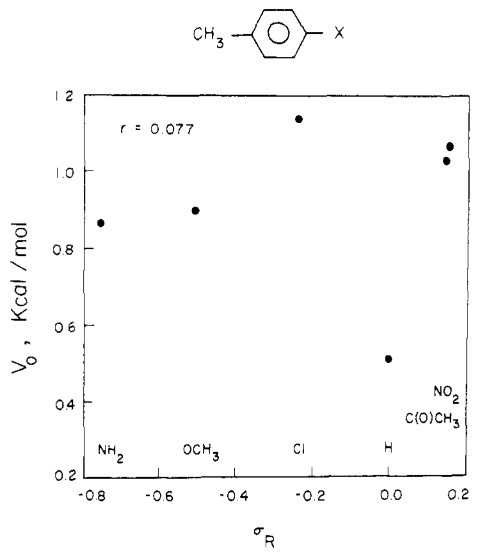

Figure 1. The methyl rotational barrier V_0 as a function of the resonance substituent parameter σ_R for para-substituted toluenes.

Agreement between the barriers calculated for the propenes and the literature values in Table VI is reasonably good.[3,4] In the toluenes, only the parent value is known, and it is thought to be smaller (0.012 kcal/mol) than that calculated by the NMR method. By a completely different NMR method, Woessner et al. have measured the toluene barrier to be 0.9 kcal/mol.[11] We believe that the higher NMR barrier results from the assumption of isotropic motion. Our anisotropic calculation for toluene brings V_0 down to below 0.1 kcal/mol,[10] in excellent agreement with the microwave result.

The *trans*-propenes have the highest values, which fall in the region to which spin–lattice relaxation is more sensitive. Consequently, it is expected that the *trans*-propene barriers are more accurate. Methyl rotation in the *cis*-propenes and the toluenes may tend toward a free rotor in the extreme cases. The NMR method appears to overestimate these barriers. Nonetheless, this method correctly shows the much lower barrier for the *cis*-propenes than for the *trans*-propenes for a given substituent. The average difference in barrier between isomers in Table VI is 0.75 kcal/mol, a number which is in line with expectations from known barriers.[3,4] Intermolecular interactions should be small, since our samples were almost neat (80% substrate, 20% C_6D_6). Either highly basic or highly acidic solvents are required for observation of intermolecular effects.

The effects that we want to examine are not based on absolute values of methyl rotational barriers but on their relative order with respect to substituent. The known electronic nature of substituents, based on resonance and inductive principles, has predictable effects on rotation. The systematic errors that influence the barriers in Tables VI and VII should not alter the order of electron-donating and electron-withdrawing effects. For this reason, comparison of the barriers, in terms of resonance and induction, should yield valid conclusions concerning the nature of the interaction of the methyl group with trigonal centers.

Electronic Effects on Methyl Rotation

We chose the substituent parameters σ_I and σ_R as the monitors for inductively based and resonance-based mechanisms for the interaction between the methyl group and the trigonal center. We also looked at a host of other substituent constants but decided that the pure resonance and pure induction parameters provided

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[11] Woessner, D. E.; Snowden, B. S., Jr. *Adv. Mol. Relaxation Processes* **1972**, *3*, 181–197.

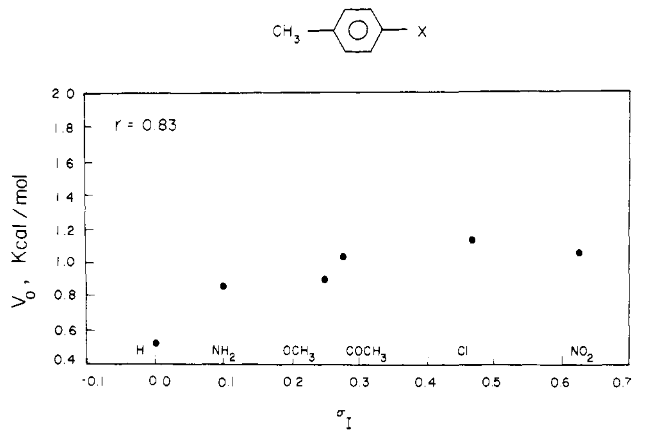


Figure 2. The methyl rotational barrier V_0 as a function of the inductive substituent parameter σ_I for para-substituted toluenes.

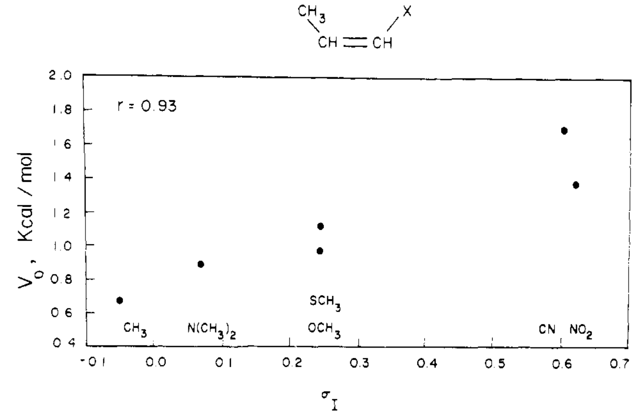
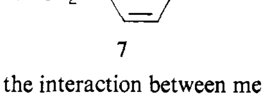


Figure 3. The methyl rotational barrier V_0 as a function of the inductive substituent parameter σ_I for cis 2-substituted propenes.

the clearest measure of the interaction mechanism.

Figure 1 shows a plot of the methyl barriers (methyl jump model) in the *para*-toluenes as a function of σ_R. The plot is badly scattered (correlation coefficient of 0.077 for a linear fit). The point for hydrogen is critical, and use of the lower anisotropic barrier would only worsen the correlation. Figure 2 shows a similar plot for σ_I. The plot is vastly improved, and the correlation coefficient is 0.83. The sensitivity of the barrier to substitution is rather low, so the role of H is critical. It clearly has the lowest barrier. By the resonance monitor, H is in the middle; by the inductive monitor, it is at an extreme. This factor provides the major reason for the very different correlation coefficients.

The poor correlation with the resonance monitor suggests that hyperconjugation (7) and other resonance-based effects are not a direct influence on the interaction between methyl and a trigonal carbon. It is possible, however, that hyperconjugation is present but has no effect on the barrier, because of its peculiar angular properties. Induction does appear to have an important influence on the methyl rotation barrier (Figure 2). Although a correlation coefficient of 0.83 is not excellent, it is still considerably better than the values with σ_p (0.43) and σ_R (0.077).



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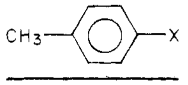
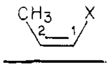
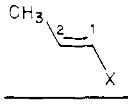
The *cis*-propenes respond in a very similar fashion. Correlation with σ_I ($r = 0.93$) is stronger than with σ_R (0.61). The inductive plot is given in Figure 3. We again conclude that inductive effects are more important than resonance effects in the methyl/trigonal carbon interaction, but resonance effects appear to have gained some importance in comparison to the toluene series.

The *trans*-propene series is similar to the *cis*-propene series. Although the resonance correlation is no better than for the *cis*-propenes ($r = 0.65$), the inductive correlation is slightly worse (0.55). Contributions from the two sources appear to be similar, and in fact the correlation with σ_p (0.68) is better than that with either. The modification by Collins et al. of the methyl jump model[6d] does suggest a stronger inductive (0.83) than resonance (0.41) correlation. Without judging one model to be superior to another, however, we can conclude that inductive effects are somewhat less important than in the trans series, but that resonance effects are similar for the cis and trans compounds.

Table VIII. Correlation Coefficients for V_0 and δ vs. Substituent Parameters for *cis*-Propenes, *trans*-Propenes, and *para*-Toluenes

						
	σ_I	σ_R	σ_I	σ_R	σ_I	σ_R
V_0, stochastic diffusion	0.83	0.09	0.93	0.63	0.67	0.60
V_0, methyl jump	0.83	0.08	0.93	0.61	0.55	0.65
$\delta(C')$[a]	0.58	0.96	0.07	0.54	0.22	0.71
$\delta(C'')$[b]	0.90	0.40	0.78	0.55	0.67	0.06

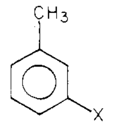
[a] The ^{13}C chemical shift (ppm) of the carbon ipso to CH_3 in the toluenes and C1 in the propenes. [b] The ^{13}C shifts (ppm) of the carbons ortho to CH_3 in the toluenes and C2 in the propenes.

Table VIII summarizes the correlation coefficients for all three systems. A particularly remarkable result apparent from the table is that in all three systems the correlation coefficients are essentially independent of whether the stochastic diffusion or the methyl jump model is chosen. This result serves to confirm our earlier statement that the measured barriers have relative, though not absolute reliability.

If the barriers depend most strongly on inductive effects, then what carbon centers most closely mirror these effects and hence may have an influence on the barriers? The ^{13}C chemical shifts provide one measure of electron density in these unsaturated systems. Consequently, we examined correlations between ^{13}C shifts and σ_I and σ_R. The carbon that is ipso to methyl in the toluenes and the C1 carbon (attached to X) in the propenes correlate better with the resonance parameter σ_R ($r = 0.96, 0.54, 0.71$) (see Table VIII) than with the induction parameter σ_I ($r = 0.58, 0.07, 0.22$). Hence these carbons do not parallel the V_0 correlations. Conversely for the ortho carbon in the toluenes and for the C2 carbon (attached to CH_3) in the propenes, the chemical shift correlates worse with σ_R (0.40, 0.55, 0.06) than with σ_I (0.90, 0.78, 0.67), in line with the barriers themselves. As a result, the chemical shifts of the ipso/C1 carbons must correlate poorly with V_0 (0.31, 0.16, 0.03), whereas the chemical shifts of the ortho/C2 carbons must correlate well with V_0 (0.92, 0.78, 0.78). The correlation is best with the toluene series, in which resonance effects appeared to be relatively less important than in the propenes. The correlation of the ortho carbons with V_0 is illustrated in Figure 4. Only these carbons (ortho/C2) and not even CH_3 gave good correlations with V_0. The trend is that the methyl rotational barrier increases as the ortho/C2 carbons are deshielded (shifted downfield).

One intriguing explanation of these chemical shift correlations is that the toluene barrier is controlled principally by the electronic environment of the ortho C–H bond and not by that of the CH_3–C bond. Electron withdrawal by substitution at the position para to methyl both deshields the ortho carbon and increases the methyl rotation barrier. Because the substituent is meta with respect to the ortho carbon, the major interaction between the substituent and the methyl rotational barrier is inductive, in agreement with the observed correlation with σ_I. A para substituent naturally cannot have a direct resonance interaction with an ortho carbon; hence the σ_R correlation is poor. This analysis yields the interesting prediction that the methyl rotation barrier in meta-substituted toluenes (8) should have a stronger correlation with σ_R than do these para-substituted toluenes.

In the propenes, correlation of V_0 with the chemical shift of the C2 carbon suggests that the critical interactions are with the



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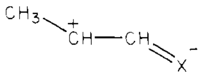

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C2–H bond, which does not exist in the toluene series. This carbon can conjugate directly with the substituent, as in **9**, in contrast to the situation in the toluenes. As a result, the methyl barrier depends on a mix of resonance and inductive effects and exhibits a good correlation with both σ_I and σ_R. These resonance effects are not hyperconjugative. They serve primarily to alter the electron density at C2, an effect that cannot occur in the less resonance-controlled para-substituted toluene series.

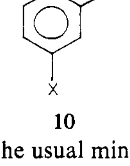
The conclusions deduced from the correlations of V_0 with chemical shifts are entirely hypothetical, although they offer a complete explanation of the experimental results. The prediction that V_0 for meta-substituted toluenes should have a higher resonance component offers a viable test of the hypothesis.

Summary and Conclusions

We have measured the barriers to rotation about the methyl–carbon bond in *para*-toluenes, *trans*-propenes, and *cis*-propenes by the effect of the methyl rotation process on the dipole–dipole spin–lattice relaxation time. The trans barriers on the average are 0.75 kcal/mol higher than the cis barriers, in agreement with the pattern established in the literature. The barriers of the toluenes may be systematically somewhat high, because the sensitivity of dipole–dipole relaxation to the methyl motion drops off as the barrier decreases. Nonetheless, we can use the relative order of the barriers as a function of substitution in all three systems to probe the nature of the electronic interaction between the methyl group and the trigonal carbon to which it is attached.

The toluenes exhibit a reasonably linear correlation between barrier height and σ_I, which measures sensitivity to inductive effects. At the same time, they have a very poor correlation with σ_R, the corresponding measure of resonance effects. Consequently, the substituents at the para position must have very little direct resonance influence on the methyl rotational barrier, as in hyperconjugation. The propenes show similar sensitivity to the inductive monitor but a somewhat better correlation with the resonance monitor. These observations are independent of the choice of rotational mechanism (methyl jump or stochastic diffusion).

In comparing chemical shift trends with the electronic monitors, we found that the rotational barrier, the chemical shift of the carbon that is ortho to methyl in the toluenes, and the chemical shift of the carbon attached to methyl (C2) in the propenes show similar dependencies on σ_I and σ_R. As a result, these ^{13}C chemical shifts (ortho and C2), and no others, gave fair to good correlations with V_0 (0.92 for *para*-toluenes, 0.78 for both propene series). These results point to particular sensitivity of the barrier height to the nature of the C–H bonds at the ortho positions in the toluenes (**10**) and at the position α to methyl in the propenes (**11**).



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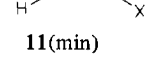
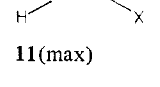


11(min)



11(max)

In the usual minimum conformation of propenes (**11**(min)), the methyl group avoids an eclipsing interaction with the α-C–H bond, and in the rotational transition state (**11**(max)) such an eclipsing occurs. Interactions of the methyl group with this C–H bond appear to be critical in determining the barrier height for propenes. In the toluenes, the α-C–H bond is replaced by the aromatic C–C bond, which is present on either side of the CH_3–C bond. This structural difference changes the key interaction to the ortho C–H bond (**10**).

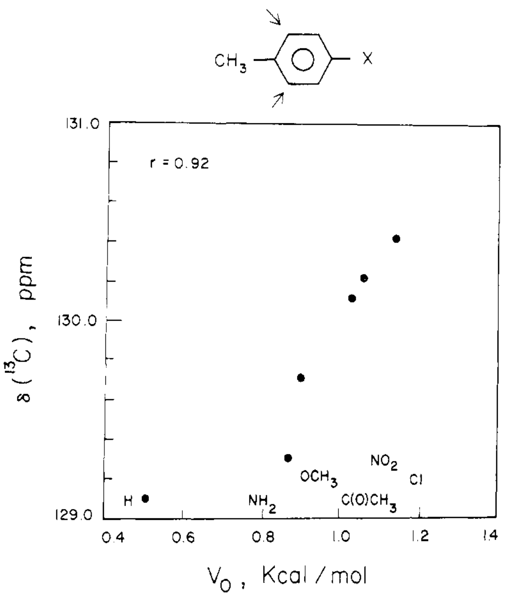


Figure 4. The ^{13}C chemical shift (δ) for the carbons ortho to CH_3 as a function of the methyl rotational barrier for para-substituted toluene.

If these explanations are valid (they are offered only as an hypothesis), then the relative sensitivities of the toluene and propene barriers to resonance (σ_R) and inductive (σ_I) effects of the para and β substituents become understandable. The substituent that is para to methyl is also meta to the ortho C–H bond that appears to influence the barrier height the most in the toluenes. The meta relationship between the substituent X and the critical C–H bond precludes any large resonance effect ($r = 0.08$) on the barrier and leaves only a strong inductive effect (0.83). In the propenes, resonance can affect the charge density at the critical α-C–H bond (**9**), so that resonance effects become more significant (about 0.62 for both cis and trans), although inductive effects are still important (0.93 for cis, 0.55–0.67 for trans).

Although these explanations rationalize all the V_0 and ^{13}C chemical shift dependencies on electronic effects and they are in agreement with the conformational preferences of trigonal systems,[2] they are presented as a theory that must be subjected to further experimental test.

Experimental Part

NMR Measurements. The ^{13}C spin–lattice relaxation times were determined on a Varian CFT-20 equipped with 16K of core or on a Varian FT-80 equipped with 24K of core.[12] Both spectrometers were also equipped with a Sykes 120 Compu/Corder. The ^{13}C resonance frequency was 20 MHz. The T_1's were measured by using the IRFT 180°–τ–90° pulse sequence. Each T_1 was the average of at least four separate measurements and was computed by the program RNTICAL, which is a least-squares exponential fit.[13] Each τ value represents the accumulation of at least 20 180°–τ–90° pulse sequences with a delay of $5T_1$ or more between sequences. The nuclear Overhauser enhancement factors η_{CH}, NOE-1, were determined for the methyl carbons by using the NOE-suppress gated decoupling technique. No significant radio-frequency heating of the sample occurred, as evidenced by probe temperature measurements during both decoupler modes. All of the temperature measurements were made with a calibrated digital thermocouple. All T_1 and NOE measurements were done at ambient probe temperature, which was measured to be 27 ± 0.5 °C. The intensity of each carbon resonance was measured as the peak height. This method was found to be more reliable than measurement by planimeter, computer integration, or intensity printout. The FT-80 was used for fewer than 3% of the measurements, and all of these were also done on the CFT-20. No significant differences in T_1 and NOE were observed with the FT-80, even though its probe temperature was 35 °C. The spin rate of the sample tube was always ≤20 Hz to preclude problems associated with vortexing.

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(12) This instrument is located at Loyola University, Chicago, IL. We thank Professor David Crumrine for the opportunity to use this instrument.

(13) Program RNTICAL is a modification of DNTICAL found in: Netzel, D. A., Ph.D. Dissertation, Northwestern University, Evanston, IL, 1975.

Sample Preparation. All samples were degassed thoroughly prior to preparation and were prepared as an 80% v/v solution in C_6D_6. This procedure provided an internal deuterium lock while also affording high concentration and therefore high sensitivity. At least five freeze–pump–thaw cycles were carried out in all cases with a Sargent-Welch Model 1392 oil diffusion vacuum pump. Obtainable vacuum was typically 10^{-3} mm as measured by a McLeod mercury manometer. All of the sample tubes were sealed while under vacuum in order to exclude subsequent diffusion of oxygen into the sample. It was found that the T_1's of a sample in an unsealed tube would decrease by as much as 40% over a 2-week period, as oxygen diffused through a rubber septum cap or parafilm wrapping.

General Synthetic Procedures. All melting points and boiling points are uncorrected. Melting points were measured on a Hirschberg apparatus. Proton NMR spectra were obtained at 60 MHz with Varian T-60 and Perkin-Elmer R-20B spectrometers. Signal-averaged ^1H and ^{13}C NMR spectra were obtained at 80 and 20 MHz, respectively, with a Varian CFT-20 spectrometer. All ^1H chemical shifts (δ) are reported in parts per million downfield from tetramethylsilane (Me_4Si), and ^{13}C chemical shifts (δ) are also reported with respect to Me_4Si (0.0 ppm) (some are converted from C_6D_6 at 128.17 ppm, the center spike of the triplet). The ^{13}C shifts are collected in Tables IV and V. All infrared spectra were recorded with a Perkin-Elmer model 283 spectrometer. Analytical and preparative gas chromatography was performed on Hewlett-Packard F & M Model 900 gas chromatographs with thermal conductivity detectors. GC–MS measurements were obtained on a Hewlett-Packard 5700A gas chromatograph coupled to a Hewlett-Packard 5930A mass spectrometer. Data were accumulated and spectra recorded through the use of the HP/Nova GC/MS data computer program. This Nova computer was also used to calculate the ^{13}C T_1's from the experimental data. Infrared and mass spectral results are reported herein for cis/trans mixtures; NMR data are for pure isomers. Elemental analyses were obtained from Micro-Tech Laboratories, Skokie, IL. Pyrolyses were carried out by utilizing a vertical tube furnace and flow system that limited the contact time of reactant and pyrolysis tube to the order of seconds. The *para*-toluenes, the cyanopropenes, the bromopropenes, and the 2-butenes were commercially available.

Methyl Propenyl Ether. Propionaldehyde dimethyl acetal[14] (10.4 g, 0.1 mol) was pyrolyzed at 300 °C over 3 g of Ni ore dispersed in glass wool. The N_2 carrier gas flow rate was 33 mL/min. The product was washed three times with dilute, aqueous Na_2CO_3 and dried (K_2CO_3). Distillation yielded 6.41 g (89%) of the product (cis/trans ratio of 3/2): bp 45–47 °C (lit.[15,16] 45–46 °C); ^1H NMR (CCl_4) cis δ 5.75 (m, 1, CH), 4.40 (m, 1, CH), 3.20 (s, 3, OCH_3), 1.65 (m, 3, CH_3); ^1H NMR (CCl_4) trans δ 6.25 (m, 1, CH), 4.65 (m, 1, CH), 3.15 (s, 3, OCH_3), 1.45 (m, 3, CH_3).

Methyl Propenyl Sulfide. Propionaldehyde dimethyl thioacetal (13.6 g, 0.1 mol) was pyrolyzed at 300 °C over Ni ore and glass wool by the method described above. The acetal was added at a rate of one drop every 4–5 s. A flow rate of 30 mL/min of N_2 was used. Exhaust tubing was run from the exit of the last trap directly into a bath of saturated, aqueous NaOH. By this method all vapors of the byproduct CH_3SH were quenched. The product mixture was twice-distilled to yield 5.8 g (67%) of the product (cis/trans ratio of 1/2): bp 101–102 °C (lit.[15,16] 102–103 °C); ^1H NMR ($CDCl_3$) cis δ 5.90–5.15 (m, ^3J = 7.63 Hz, 2, CH=CH), 1.81 (s, 3, SCH_3), 1.65 (d, 3, CH_3); ^1H NMR trans δ 6.05–4.95 (m, ^3J = 12.50 Hz, 2, CH=CH), 1.83 (s, 3, SCH_3), 1.55 (d, 3, CH_3): IR (film) (cis/trans mixture) 2970 (m), 2910 (s), 1730 (m), 1710 (s), 1700 (m), 1445 (m), 1436 (m), 960 (w), 935 (w); mass spectrum (70 eV) (cis/trans mixture), *m/e* (relative intensity) 88 (M^+, 1012), 73 (725), 45 (121). Anal. (cis/trans mixture) Calcd for C_4H_8S: C, 54.49; H 9.14; S, 36.36. Found: C, 53.78; H, 9.12; S, 34.97.

Dimethylpropenylamine was prepared by a variation of the method of Hall and Ykman.[17] In a 200-mL pyrolysis tube was placed 60 g (88 mL, 1.33 mol) of dimethylamine by condensation at −78 °C. Propionaldehyde (39 g, 0.67 mol) and anhydrous K_2CO_3 (46 g) were cooled at dry-ice temperature and added. The pyrolysis tube was sealed and spun for 100 h by a mechanical stirrer at ambient temperature. This spinning was accomplished by supporting the pyrolysis tube in a horizontal position with two ring clamps. The tube was opened, and the reaction mixture was filtered to remove the precipitate. The precipitate was washed thoroughly with two 70-mL portions of ethyl ether. The filtrates were combined and distilled to yield 12.4 g (20%) of the product (cis/trans ratio of 1/2): bp 68–71 °C; ^1H NMR (C_6D_6) cis δ 5.30 (d, 1, CH), 4.30 (m, 1, CH), 2.35 (s, 6, $N(CH_3)_2$), 1.68 (d, 3, CH_3); ^1H NMR (C_6D_6) trans δ 5.76 (d, 1, CH), 4.10 (m, 1, CH), 2.42 (s, 6, $N(CH_3)_2$), 1.59 (d, 3, CH_3) (the cis and trans resonances were distinguished by their vicinal ^1H–^1H coupling constants: $^3J_{CH=CH}$(trans) = 13.6 Hz and $^3J_{CH=CH}$ (cis) = 8.8 Hz); IR (film) (cis/trans mixture) 2940 (vs), 2814 (s), 2770 (s), 1690 (s), 1650 (s), 1450 (s); mass spectrum (70 eV) (cis/trans mixture), *m/e* (relative intensity) 85 (M^+, 84), 84 (100), 70 (53), 42 (53).

1-Nitropropene. The pyrolysis of 1-nitro-2-propyl acetate[18] to form the nitroalkene was attempted by several methods. It was found that with the flow pyrolysis method, the alkene could be obtained in high yield and in a cis/trans ratio of nearly 1/1. With a N_2 flow rate of 80 cm^3/min and the tube furnace at 200 °C, 7.0 g (0.048 mol) of freshly distilled acetate was added at a rate of 1 drop/10 s. The product was trapped at liquid N_2 temperature and distilled to give 3.30 g (79%) of the product (cis/trans ratio of 45/55): bp 55 °C (20mm Hg) (lit.[17] 37–42 °C (10mm Hg)); ^1H NMR (C_6D_6) cis δ 7.1-6.7 (m, 2, CH=CH), 1.80 (d, 3, CH_3); ^1H NMR (C_6D_6) trans δ 7.2-6.3 (m, 2, CH=CH), 1.39 (d, 3, CH_3); IR (film) (cis/trans mixture) 3140 (m), 3020 (w), 1665 (s), 1530 (vs), 1370 (vs), 940 (s), 835 (m). Anal. (cis/trans mixture) Calcd for $C_3H_5NO_2$: C, 41.39; H, 5.74; N, 16.09. Found: C, 41.24; H, 5.87; N, 15.99.

Separation of the Cis and Trans Isomers. With the exception of the 2-butenes and the dimethylpropenylamines, all of the cis and trans isomers of the propene series were separated by preparative gas chromatography. The conditions for these separations have been detailed elsewhere.[10] The methyl propenyl ethers were also separated by fractional distillation with a Nester/Faust spinning band column. The distillation and the VPC methods of separation were both found to be satisfactory. For the nitropropenes, the trans isomer was isolated by VPC in >95% purity and was used in this form for the ^{13}C studies. Isolation of the cis isomer by VPC was precluded by isomerization of cis to trans in the vpc columns. The data for the trans isomer in the mixture and for the pure sample were found to be identical, within experimental error. Consequently, T_1 measurements of the cis isomer were carried out on the mixture. The enamines decomposed on all VPC columns tried. The trans form was purified by distillation, but relaxation measurements for the cis form had to be taken on the mixture. Again, control runs on the purified trans form and on trans form in the mixture showed no medium effects on the T_1 and NOE.

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