(mp 116–118°, 53% yield); N-benzyl-N-phenyl-2,4-dinitrobenzenesulfenamide (mp 134–136°, 75% yield).

N-Benzyltrifluoromethanesulfenamides (8). A cooled solution (−10°) of trifluoromethanesulfenyl chloride (0.016 mole) in toluene was added with stirring to a cooled toluene solution (−10°) of the appropriate amine (0.032 mole) in a flask equipped with a Dry Ice filled cold finger condenser. After stirring for 4 hr at −10°, the solution was allowed to warm to room temperature and stirred for an additional 20 hr. The amine hydrochloride was filtered, the filtrate successively washed with water, 10% aqueous sulfuric acid, 10% aqueous sodium bicarbonate water, and dried over magnesium sulfate. The solvent was removed *in vacuo* and the product distilled (**8a**, bp 46° (0.3 mm); **9b**, bp 119–120° (20 mm), $n^{24}\mathrm{D}$ 1.4738).

N-Trichloromethanesulfenyl-2,2-dimethylsuccinimide (13). A hexane solution of *n*-butyllithium (4.1 ml of a 23% solution) was added to a solution of 2,2-dimethylsuccinimide[37] (2.0 g, 0.15 mole) in 50 ml of dry dioxane. After stirring for an additional 30 min, a dioxane solution of trichloromethane–sulfenyl chloride was added dropwise. The reaction mixture was stirred for 20 hr, filtered, and the solvent evaporated *in vacuo*. Recrystallization from methanol afforded pure sulfenamide, mp 104–106°, yield 30%.

Acknowledgment. We thank Professor S. Wolfe and Professor I. Csizmadia for helpful and stimulating discussions.

[37] R. W. Stoughton, U. S. Patent 2,614,106 (1952); *Chem. Abstr.*, 47, 10000*h* (1953).

Internal Rotation in Olefins. I. Kinetic Investigation by Nuclear Magnetic Resonance

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Abstract: Two rotational processes which occur in the compounds listed in Table I have been detected and investigated by nmr spectroscopy. The first one was identified as a "low-energy" rotation about the carbon–carbon double bond ($\Delta G^* = 9.1$–19.4 kcal/mol), while the second as "high-energy" rotation about the nitrogen-to-sp^2 carbon bond ($\Delta G^* = 8.7$–13.3 kcal/mol). The above two processes which occur within a single molecule were found to be independent of each other. For most of the compounds, the rates under consideration are within nmr time scale. Activation parameters were determined from variable temperature nmr studies. Barriers for rotation about the carbon–carbon double bond are sensitive to structural variations. The relationship between structural parameters and activation energies was studied.

It has been frequently stated[2] that the rotation about a double bond is restricted. Such a restriction, generally referred to room-temperature measurements, is a consequence of the high activation energy (25–65 kcal/mol) for the thermal isomerization of olefins.[3] The phenomenological consequence of this situation is, of course, the thermal stability of olefins. This is usually allowed to contrast with the "free" rotation at room temperature about single bonds, which is associated with low activation energies, starting from *ca.* 1 kcal/mol[4] and extending to well over 20 kcal/mol.[5] The result of such a situation is the extremely low thermal stability of conformers and moderate stability of atropo isomers at room temperature. The above activation-energy ranges for rotation about formal single and double bonds approach, and in many cases actually overlap, each other. There are well-known examples of rotational processes about single bonds with relatively high energy barriers, exceeding 20 kcal/mol. These, among others, are the well-documented atropoisomerism phenomenon of biphenyls,[5] and the recent isolation of stable rotational isomers of amides.[6] On the other hand, systems which undergo thermal rotation about a carbon–carbon double bond at room temperature and even well below it ($\Delta G^* < 20$ kcal/mol) are rare.[7] Furthermore, no systematic studies of structure–reactivity relationship or of the mechanism of rotation are available.

In a previous investigation[8] we have measured by nmr the free energy of activation for rotation about a C=C bond in several conjugated enamines, and found values lower than 13 kcal/mol. Such low energy barriers preclude, of course, the isolation of stable stereoisomers (*cis* and *trans* isomers) at room temperature. However, the rotational rates are within nmr time scale, and can be conveniently measured by this technique. Consequently, such a system of olefins, equilibrating at room temperature, provides an excellent substrate to study the relationship between structural parameters and kinetic effects of the isomerization process. Furthermore, a study of these systems may also shed light on the mechanism of the rotational process, which may conceivably proceed *via* a biradical or dipolar transition state. The factors which govern the activation energy for rotation about bonds are manifold. The bond order is only one such factor, while steric interactions are by no means less important. In addition, the evaluation

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[1] H. Shanan-Atidi, M.S., Thesis, Tel-Aviv University, Tel-Aviv, Israel, 1967.

[2] (a) G. W. Wheland, "Advanced Organic Chemistry," 3rd ed, John Wiley & Sons, Inc., London, 1960, p 246; (b) K. Mislow, "Introduction to Stereochemistry," W. A. Benjamin, Inc., New York, N. Y., 1965, p 37.

[3] S. W. Benson, "The Foundation of Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, pp 254–256.

[4] J. Dale, *Tetrahedron*, 22, 3373 (1966).

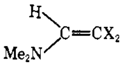
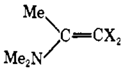
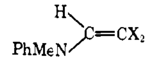
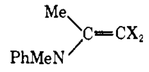
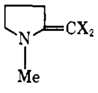
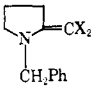
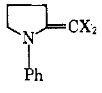
[5] F. H. Westheimer in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley & Sons, Inc., New York, N. Y., 1956, p 549.

[6] H. A. Staab and D. Lauer, *Tetrahedron Lett.*, 4593, (1966).

[7] G. Isaksson, J. Sandstrom, and I. Wennerbeck, *ibid.*, 2233 (1967); J. H. Crabtree and D. J. Bertelli, *J. Amer. Chem. Soc.*, 89, 5384 (1967); A. S. Kende, P. T. Izzo, and W. Fulmor, *Tetrahedron Lett.*, 3697 (1966).

[8] Y. Shvo, E. C. Tablor, and J. Bartulin, *ibid.*, 3259 (1967).

Table I. Nmr[a] and Activation Data for Rotation about the C=C Bond (CO_2Me Interchange)

Compd no.	Compound $X = CO_2Me$	$\Delta\nu$,[b] cps	Temp, °C	ΔG^*, kcal/mol	Solvent
1[c]		5.0	18.5	15.6	CH_2Cl_2
2		0	<−95	<9.1[d]	CH_2Cl_2 (−95°) $(CD_3)_2CO$ (−95°) $PhCH_3$ (−90°)
3[c]		7.2	90.0	19.4	CH_2Cl_2
4		14.0	−76.0	10.0	$(CD_3)_2CO$
5		12.5	−81.0	9.8	$(CD_3)_2CO$
6		32.0	−71.0	10.0	$(CD_3)_2CO$
7[e]		46.0	5.0	13.7	CH_2Cl_2

[a] Nmr data were obtained at a frequency of 100 Mc unless otherwise specified. [b] These values are maximum chemical shift separation of the carbomethoxy signals. [c] The data for this compound were taken from ref 8; nmr spectra were recorded at 60 Mc. [d] This limiting value was calculated taking $\Delta\nu$ of compound **1** and T_c as −95°. [e] Nmr spectrum was recorded at 60 Mc.

of the various factors must be applied to both the ground state and the transition state for rotation. It appears, therefore, that the activation energy for rotation about a bond does not necessarily reflect its order. Since a bond order is a ground-state property, no simple relationship between it and the activation energy may be anticipated.

Aside from the rotational process about the C=C bond in the conjugated enamines of Table I and in the previously studied compounds,[8] a second kinetic process has been detected in these compounds by nmr. Specifically, this process was identified as rotation about the nitrogen-to-sp^2 carbon bond (nitrogen rotation) which also occurs at rates measurable by nmr. This multiple isomerism is described in Figure 1. The kinetics of the rotational process about the C=C bond can be most conveniently investigated using a system of degenerate interconverting species ($X_1 = X_2$; $R_1 = R_2$), thus, I ≡ II ≡ III ≡ IV. Such a selection eliminates differences in the diastereomeric stability among the exchanging species which otherwise may, in some cases, prevent the observation of some of the species by nmr. In the present work we have investigated diesters ($X_1 = X_2 = CO_2CH_3$) with variable substitution on the double bond and on the tertiary nitrogen atom. In those compounds (Figure 1) where the nitrogen atom is nonsymmetrically substituted ($R_1 \neq R_2$; $X_1 = X_2$), the nitrogen rotation results in the exchange between diastereomeric species.

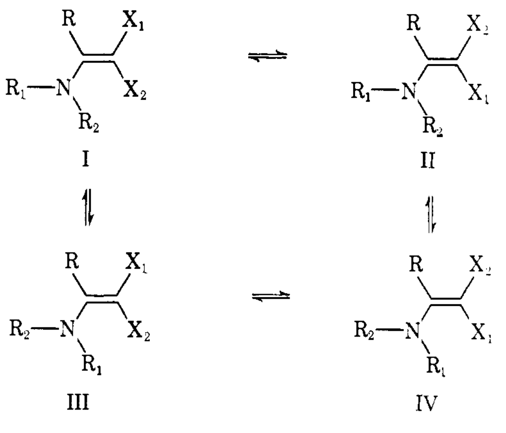


Figure 1. $X_1 = X_2 = CO_2CH_3$; R = H, CH_3; R_1, R_2 = Me, Ph.

The rotational process about the C=C bond has been investigated by observing the interchange of the two diastereotopic[9] methyls of the carbomethoxy groups, and the nitrogen rotation by observing the interchange of the N-methyl groups (Figure 1). Each process has been identified by studying the appropriate changes in the nmr spectra as a function of the temperature. No ambiguity exists in elucidating the nature of the kinetic process which is associated with the spectral changes. The fact that the diester compounds ($X_1 = X_2 = CO_2Me$) give rise to two *equal* intensity lines, unambiguously, indicates that the kinetic process which is being experimentally observed is rotation about the C=C bond. Conceivable conformational changes which are associated with rotation of the carbonyl groups of the esters should invariably lead to two *unequal* intensity lines, due to formation of diastereomers.

The two said rotational processes about the C=C and C—N bonds occur around the axis of σ bonds which are part of *one* conjugated system. It is a relevant question, therefore, whether the two processes are coupled or independent of each other. The unique feature of a coupled mode of rotation is a *simultaneous* interchange of

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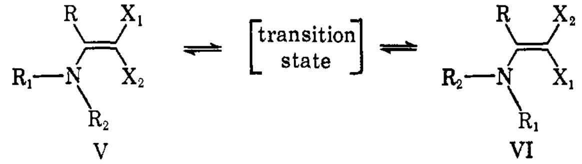
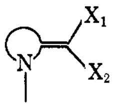
(9) K. Mislow and M. Raban in "Topics in Stereochemistry," Vol. 1, N. L. Allinger and E. L. Eliel, Ed., Interscience Publishers, New York, N. Y., 1967, p 19.

the two X and the two R groups as depicted in V $\rightleftharpoons$ VI. The transition state which is formed by the synchronous conrotatory motion of the nitrogen and the carbon



V VI

p orbitals would be energetically more favorable than at least one of the two transition states which are associated with the two independent modes of rotation. One way to detect such a process would consist of a total line-shape analysis of the two separate nmr phenomena, one involving the interchange of X_1 and X_2 and the other of R_1 and R_2. If, indeed, the two rotational processes are synchronous, identical enthalpies of activation should be found. Even though such an investigation is now being undertaken, we would like to report



VII, $X_1 = X_2 = CO_2Me$
$R = CH_3; CH_2Ph; Ph$

here the results of an indirect approach to this problem. In such an approach, the effect of restricting the rotational motion of the nitrogen atom on the rotational rates about the C=C bond is being investigated. This can be achieved by tying the nitrogen atom to the trigonal carbon, and thereby locking it in a small ring as depicted in VII. The electronic properties of the conjugated system in such a structure have not been modified and may be considered to be similar to those of the acyclic system of Figure 1. While the mechanical interchange of the two X groups in VII is still possible, the rotation of the nitrogen atom by 180° is prevented. Since the rotation of the nitrogen atom is a necessary requirement for a coupled mode of rotation, the interchange of the two X groups will now be prohibited and this can readily be established by nmr. If, on the other hand, it will be evident from nmr study that the two X groups in VII are still interchanging, it would be concluded that the rotation of the nitrogen atom *does not constitute a requirement* for the rotational process about the C=C bond. This does not explicitly rule out a coupled rotational process in acyclic systems of Figure 1.

Results and Discussion

The compounds which were prepared, and the corresponding free energies of activation for rotation about the C=C bond are listed in Table I. The ΔG^* values for the nitrogen rotational process are presented in Table II, and the chemical shifts of all the compounds are listed in Table III. All values of free energy of activation for the processes under consideration have been determined at the coalescence temperature (T_c) of the two equal intensity signals, using Eyring activation function and taking the transmission coefficient as unity. The rate at T_c was determined from the Gutowsky-Holm relationship[10] $({}^1/_2\tau = {}^{\Delta\nu\pi}/_{\sqrt{2}})$.

Table II. Nmr and Activation Data for Rotation about the C-N Bond (NMe_2 Interchange)

Compd no.	$\Delta\nu$,[a] cps	Temp, °C	ΔG^*, kcal/mol	Solvent
1[b]	22.8	−9.0	13.3	CH_2Cl_2
2[c]	~22[d]	−96.5	~8.7[d]	CH_2Cl_2

[a] This value is the maximum chemical shift separation of the NMe_2 signals. [b] All data were taken from ref 8, and recorded at 60 Mc. [c] Nmr spectra were recorded at 100 Mc. [d] This is an estimated value since at −100° $\Delta\nu$ = 20 cps and the lines are still broad.

Table III. Chemical Shift Data at Room Temperature

		Chemical shifts δ, ppm			
Compd no.	Solvent	CO_2Me	NMe	C-3 Me or H	Pyrrolidine protons[a]
1	$CDCl_3$	3.69	2.98	7.47	
2	$CDCl_3$	3.69	3.03	2.32	
	CH_2Cl_2	3.61	2.95	2.25	
3	$CDCl_3$	3.74; 3.60	3.37	7.85	
4	$CDCl_3$	3.62	3.24	2.18	
5	$CDCl_3$	3.67	2.85		3.58; 3.15; 1.97
	CH_2Cl_2	3.69	2.82		3.54; 3.12; 1.95
6	$CDCl_3$	3.55	4.39 (*CH*$_2$Ph)		3.35; 3.21; 1.92
7	$CDCl_3$	3.30			3.84; 3.37; 2.08
	CH_2Cl_2	3.69; 2.91 (at −40°)			

[a] Each signal integrated for 2 protons; the two low-field signals in each compound appear as triplets, the high-field signal as a multiplet.

The temperature dependence of the carbomethoxy signals of the three pyrrolidine derivatives **5–7** of Table I indicates unambiguously that the two diastereotopic carbomethoxy groups do undergo a kinetic exchange process. The usual pattern of broadening and the eventual coalescence of the two equal intensity signals have been observed in the nmr spectra of the above three compounds. These experimental findings clearly establish that the rotational freedom of the nitrogen atom *does not constitute a requirement* for the process of esters interchange. As mentioned before, this does not explicity exclude a synchronous process within the series of the acyclic compounds **1–4** in Table I. However, from the following deductive argument, based on experimental observations, it may be concluded that the rotational process about the C=C bond in compounds **1–4** is also independent of the nitrogen rotational process. For the sake of argument, accepting a synchronous mechanism, which is depicted in V $\rightleftharpoons$ VI the two X and the two R groups, regardless of their nature, should interchange *simultaneously*. Consider now a case when the two R groups are constitutionally different, while the two X are identical. Then, V and VI are actually diastereomers and in each, the two X groups are diastereotopic. Thus, in the case where there is no exchange between the above two diastereomers, X_1 and X_2 should give rise to a total of four chemically shifted signals (two sets of two equal-intensity signals, each set having a different total integrated intensity which is determined by the population distribution of the two diastereomers). When a rapid exchange ensues, the four lines should coalesce to a two-line system, and should not further coalesce with increase in the rate of rotation.

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[10] H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 1228 (1956).

This follows from the fact that X_1 in V exchanges (synchronously) only with X_1 in VI, while X_2 in V exchanges only with X_2 in VI. Therefore, for compounds with the above pattern of substitution ($X_1 = X_2$; $R_1 \neq R_2$) an unequal doublet for the two X groups should always persist in their nmr spectra. This behavior has *not* been encountered with the relevent compounds **3** and **4** in Table I, and additional ones reported in ref 8; in all cases the two carbomethoxy signals coalesce to a singlet. The same argument also holds for those cases where X_1 and X_2 are constitutionally different while R_1 and R_2 are equivalent. Thus, the signals of the latter groups (NMe_2) should coalesce from a four-line system at slow exchange to a two-line system at fast exchange. It is noted in the following publication that in all compounds which satisfy the above substitution requirements the NMe_2 signals always do coalesce to a singlet. It seems unreasonable to invoke an accidentally identical chemical-shift argument for the above behavior which was found to be consistent within relatively large number of compounds of different nature. In conclusion, it appears certain that even though the two rotational processes are occurring within one conjugated system, they follow two different energy paths.

We now wish to examine the dependence of ΔG^* values for the rotational process about the carbon–carbon double bond on the various structural parameters. The determination of ΔG^* values at T_c by nmr provides a route for the fast surveying of large numbers of compounds. However, in the absence of detailed kinetic studies, we are forced to compare ΔG^* values at different temperatures which strictly is not legitimate inasmuch as the above parameters may be temperature dependent. It should be noted that our prime interest lies in the magnitude of the difference in ΔG^* between pairs of compounds which result from single structural modification. Thus, examination of Table I reveals a pronounced depression in the energy barrier due to substitution of H by CH_3 on C-3. Comparison of the activation data of the relevent pairs of compounds, **1** and **2** and **3** and **4** yields differences of >6.5 and 9.4 kcal/mol, respectively. Only an upper limit could be calculated for the activation value of **2** (*cf.* footnote *d* in Table I), since the carbomethoxy signal in the nmr spectrum of this compound persists as a singlet even at −95° (this behavior was encountered in a variety of solvents, thus excluding the possibility of accidentally identical chemical shifts of the two signals). Now, it is necessary to determine to what extent the above mentioned $\Delta\Delta G^*$ values are meaningful. Obviously our experimental ΔG^* values are related to different $T_c\Delta S^*$ terms. We have carried out trial calculations for E_a values using the relationship $E_a = \Delta G^* + T_c\,(\Delta S^* - R)$, with the purpose of finding the dependence of $E_a(\mathbf{3}) - E_a(\mathbf{4})$ on various hypothetical combinations of ΔS^* values for the above two compounds. The results of such calculations clearly indicate that there is only one range of ΔS^* combinations where $E_a(\mathbf{3})$ approaches $E_a(\mathbf{4})$, namely when $\Delta S^*(\mathbf{3}) \approx -15$ eu and $\Delta S^*(\mathbf{4}) = +15$ eu. When the difference between the above two ΔS^* values diminishes, it turns out that $E_a(\mathbf{3}) > E_a(\mathbf{4})$; thus when $\Delta S^*(\mathbf{3}) = -5$ eu and $\Delta S^*(\mathbf{4}) = +5$ eu, $E_a(\mathbf{3}) - E_a(\mathbf{4}) = 6.0$ kcal/mol. For all other possible combinations tested (varying ΔS^* from 0 to 30 eu) the difference $E_a(\mathbf{3}) - E_a(\mathbf{4})$ is positive and larger than 5 kcal/mol. Speculating on the entropy relationship of **3** and **4**, it seems logical to assume that $\Delta S^*(\mathbf{4}) > \Delta S^*(\mathbf{3})$. This follows since more entropy would be gained in proceeding from the more rigid planar ground state of **4** to the orthogonal transition state, than in the corresponding transition of **3**. Appropriate analogies in olefinic systems could not be traced in the literature. However, the geometrical relationship between the ground and the transition states in the rotational process about the C=C bond in the compounds under consideration is equivalent to such a relationship in the rotational process about the C–N bond in amides. The structural relationship between compounds **3** and **4** is analogous to N,N-dimethylformamide ($\Delta S^* = -1$ eu)[11] and N,N dimethylacetamide ($\Delta S^* = +2.7$ eu),[12] indicating an increase in entropy upon Me substitution, as was previously predicted. Thus, if it is granted that $\Delta S^*(\mathbf{4}) > \Delta S^*(\mathbf{3})$, there is only one range, as previously argued, where the value of $E_a(\mathbf{3})$ approaches that of $E_a(\mathbf{4})$, namely when $\Delta S^*(\mathbf{3}) = -15$ eu and $\Delta S^*(\mathbf{4}) = +15$ eu. It would indeed be illogical to assume such a large difference between the ΔS^* values of **3** and **4**, which differ only by Me substitution, especially when such values possess opposite signs. In conclusion, it seems that there are sufficient grounds to consider the differences in ΔG^* values of **3** and **4** (9.4 kcal/mol) and also of **1** and **2** as arising, mainly, from changes in the E_a rather than in ΔS^* terms. Furthermore, as a first approximation, the various ΔG^* values may be treated additively whenever the magnitude of the difference is relatively large. These conclusions will be further corroborated by the forthcoming results.

The compounds under investigation must possess an essentially planar geometry in the ground state. Such an arrangement will maximize electron delocalization along the conjugated π system. Indeed, compounds **1–7** of Table I exhibit intense uv absorption bands ($\log \epsilon > 4$) in the region of 281–305 mμ which may be assigned to the $\pi \rightarrow \pi^*$ transition. The interchange of the two carbomethoxy groups, which was detected by nmr, must proceed through a conformation in which the two rotating parts of the molecule and also the two carbon p orbitals are orthogonal. Such a conformation can be identified with the thermal transition state for the rotation process about the C=C bond, since it most probably possesses maximum energy due to the minimal overlap of the carbon p orbitals. It is not possible to to decide *a priori* whether such a transition state is of a biradical or dipolar nature. Thermal isomerizations of simple olefins are considered to proceed *via* a twisted biradical transition state.[13] However, the magnitude of the decrements in ΔG^* values found by us for the rotation about the C=C bond upon substitution of H by CH_3 on C-3, strongly suggests a dipolar rather than biradical transition state. The argument is based on the differential capacity of a methyl group to stabilize an adjacent free radical with respect to a carbonium ion. While the upper limit of stabilization in the former case is *ca.* 3 kcal/mol[14] the latter is noted for values reaching 8.5 kcal/mol in limiting solvolytic reactions.[15] Our

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[11] Calculated from available data in ref 12.

[12] R. C. Neuman and V. Jonas, *J. Amer. Chem. Soc.*, 90, 1970 (1968).

[13] M. S. Lin and K. J. Laidler, *Can. J. Chem.*, 46, 973 (1967).

[14] E. M. Kosower, "Physical Organic Chemistry," John Wiley & Sons, Inc., New York, N. Y., 1968, pp 86–89.

relevent experimental parameters of >6.5 and 9.4 kcal/mol may therefore be considered in support of a dipolar transition state for rotation about the C=C bond in the systems under investigation. It is realized that the decrement in ΔG^*, which is associated with methylation of C-3, is composed of the methyl stabilization effect and steric energy term. The latter must necessarily be operative in the eclipsed ground state rather than in the orthogonal transition state and should contribute to the acceleration of the rotational rate about the C=C bond. This effect was recently demonstrated in a similar nmr investigation of conjugated enol ethers.[16] The magnitude of the steric energy term is estimated at *ca.* 2 kcal/mol.[16] Thus, even after accounting for the above term, the net magnitude of stabilization due to the methyl substitution on the double bond is still well out of the energy range for stabilization of a radical.

The generally low energy barriers for the process under consideration in the compounds listed in Table I, when compared for example to the same process in *cis*-methyl crotonate[13] (E_a = 57.8 kcal/mol), must be attributed mainly to extra stabilization of the transition state for rotation, where charge separation is developed. Thus, in the compounds of Table I, the malonate residue resonatively disperses the developed negative charge on C-2, while the nitrogen atom and alkyl substituents are responsible for resonative stabilization of the positive charge on C-3 in the transition state for rotation. Such a description implies that the effects of the substituents on the rates of rotation are operatively mainly in the transition state of rotation rather then in the ground state of the molecule. Thus, there seems to be no mechanism operative in the ground state which can be invoked to explain the above pronounced changes in ΔG^* upon methylation of C-3. On the other hand, the magnitude of the energy changes due to methyl substitution do indicate that we are observing rate effects associated with the stabilization of a positive charge, which is developed in the heteropolar *transition state*. This brings us to the conclusion that ground-state properties such as bond orders or dipole moments cannot be obviously correlated with activation energy for rotation about the bond under consideration. Such properties do not necessarily reflect the energy of the transition state for rotation which, according to the above argument, seems to be most important in determining the value of ΔG^*.

Turning now to the pyrrolidine derivatives **5–7** in Table I the net effect of ring closure on the activation energy for rotation about the C=C bond can be evaluated. This can be achieved by comparing ΔG^* values of the pyrrolidine derivatives with those of compounds having Me substitution on C-3, and of course identical substitution on the nitrogen atom. Such a comparison accounts for the previously observed decrement in ΔG^* upon alkylation of C-3 and thus presumably yields the net effect of cyclization on the free energy of activation for the process under consideration. Comparison of **2** and **5** yields a minimal difference of 0.7 kcal/mol while that of **4** and **7** yields a difference of 3.7 kcal/mol. Both values represent an increment in ΔG^* upon cyclization. The fact that the β position of the double bond in the pyrrolidine derivatives is substituted by a methylene rather than by a methyl group may possibly account for just a small fraction of the above difference in the activation energy. A rough estimate of this fraction may be obtained by considering the σ_R values of CH_3 and CH_3CH_2 which are −0.102 and −0.094, respectively,[17] and therefore may account only for a fraction of a kilocalorie. The origin of the rest of the difference may possibly be attributed to interplay of entropy terms and its clarification must await a detailed kinetic study.

Regarding variations in ΔG^* values for rotation about the C=C bond as a function of the nitrogen atom substitutes, it has already been noted[8] that electron-withdrawing substituents are capable of increasing the activation energy for the above process. In terms of a dipolar transition state, stabilization involving the nitrogen atom can be considered as bonding between the empty carbon p orbital and the occupied nitrogen p orbital in the transition state for rotation. Structural modifications of the substituents on the nitrogen atom which would result in a new electronic interaction of the nitrogen lone pair with an adjacent π system are bound to create new molecular orbitals having nodal planes between the nitrogen and the carbon. Such a situation is indeed expected to destabilize the thermal transition state for rotation about the C=C bond inasmuch as the above type of bonding is less effective and consequently would bring about an increase in ΔG^* for the above process. Two measurable energy contributions due to substitution of a methyl by phenyl on the nitrogen atom can be extracted from Table I: $\Delta G^*(\mathbf{3}) - \Delta G^*(\mathbf{1})$ = 3.8 kcal/mol and $\Delta G^*(\mathbf{7}) - \Delta G^*(\mathbf{5})$ = 3.9 kcal/mol.[18] The agreement between these values is satisfactory and they can be exploited to estimate the ΔG^* value of **2**, for which only an upper limit of 9.1 kcal/mol could be assigned (Table I). Thus, $\Delta G^*(\mathbf{2}) = \Delta G^*(\mathbf{4}) - 3.8 = 10 - 3.8 = 6.2$ kcal/mol. Alternatively, $\Delta G^*(\mathbf{2})$ can also be approximated by exploiting the previously observed contribution (9.4 kcal/mol) of the C-3 methyl to the activation energy for the process under consideration. Thus, $\Delta G^*(\mathbf{2}) = \Delta G^*(\mathbf{1}) - 9.4 = 15.6 - 9.4 = 6.2$ kcal/mol. The agreement between the two values, which were obtained independently, is indeed gratifying. If such a compatibility is indeed not a result of fortuitous interplay of entropy terms, it must indicate limited dependence of ΔG^* on temperature. This observation corroborates our previous argument claiming additivity of ΔG^* values which were determined at different temperatures. However, the striking result is the above calculated extremely low energy barrier when it is considered to be related to a rotational process about a carbon–carbon double bond which is restricted formally. Actually, the magnitude of this barrier approaches those for rotation about σ bonds in saturated hydrocarbons.

Compound **7** represents one more variation in the nitrogen atom substituents. The replacement of the NCH_3 group in **5** by NCH_2Ph to give **6** virtually does not affect the barrier for rotation about the C=C bond (Table I). This is understandable in view of the fact that the phenyl group in **6** is not conjugated with the nitrogen lone pair. However, the differential chemical shift

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(15) A. Streitwieser, "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 72.

(16) Y. Shvo, *Tetrahedron Lett.*, 5923 (1968).

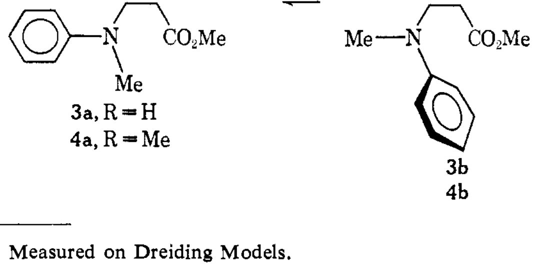
(17) R. W. Taft and I. C. Lewis, *Tetrahedron*, **5**, 211 (1959).

(18) Two analogous energy differences amounting to 3.5 and 3.1 kcal/mol are recorded in the subsequent publication.

of the carbomethoxy signals is increased by a factor of *ca.* 2.5 due to such a replacement. The significance of this change will be discussed later.

Regarding changes in the magnitude of the energy barrier for the process of nitrogen rotation as a function of structural parameters, only two measurable values could be obtained, namely that of **1** and **2** (Table II). By comparing the magnitude of these two parameters, it is evident that substitution of H by CH_3 on C-3 is accompanied by a decrease (4.6 kcal/mol) in the energy barrier for the above process. In fact, the nitrogen rotational process within the compounds under the present investigation may be considered to be analogous to the corresponding process in amides. It is therefore appropriate to compare qualitatively our activation data with that of the structurally analogous N,N-dimethylformamide (E_a = 22.0 kcal/mol; $\Delta G^*_{298.2}$ = 21.7 kcal/mol; ΔS^* = -1 eu[11]) and N,N-dimethylacetamide (E_a = 19.6 kcal/mol; $\Delta G^*_{298.2}$ = 18.2 kcal/mol; ΔS^* = 2.7 eu).[12] From the above data it is evident that both E_a and ΔG^* decrease upon substituting H by CH_3, and the magnitude of the difference in ΔG^* (3.5 kcal/mol is similar to the observed difference between **1** and **2** (4.6 kcal/mol). Part of this decrement in proceeding from compound **1** to **2** (Table II) may be attributed to steric interaction of the NCH_3 with CCH_3. The distance[19] between the hydrogens of the above two methyl groups (in a cogwheel conformation) in **2** is 2 Å, and is identical with the corresponding distance in N,N-dimethylacetamide and smaller than the sum of the van der Waals radii of two hydrogen atoms (2.4 Å). Such an interaction would operate to raise the ground state of **2** with respect to **1** and thus lower the energy barrier for the rotational process of the nitrogen atom.

Regarding the N-phenyl substituted compounds **3** and **4**, only one set of signals was observed with respect to the nitrogen rotational process. The observation of separate nmr signals from the individual conformers of **3** and **4** depends on both the rational rates and the relative diastereomeric stability of the exchanging conformers. Obviously, in these compounds, the two conformers resulting from the nitrogen rotational process differ energetically and are, therefore, not expected to be equally populated. On the basis of the experimental results it is impossible to decide whether the lack of multiplicity of the signals is due to fast exchange rates or to a low concentration level of one of the exchanging diastereomers, or to a combination of both factors. However, on the basis of chemical-shift arguments it is concluded that regardless of the rate of rotation, the predominating conformations of **3** and **4**, with respect to the nitrogen atom substituents, are **3a** and **4a**, respectively, in which the phenyl group is in a *s-trans* position with respect to the double bond. It can be readily verified from examination of Table III, that the average chemical shift of the two carbomethoxy groups in compounds having no phenyl substituent (**1**, **2**, and **5**) is extremely constant (3.67–3.69 ppm). However, the average shift of two carbomethoxy groups of **7** is 3.30 ppm which represents an upfield shift of almost 0.4 ppm with respect to the above range (Table III). In the pyrrolidine derivative (**7**) the phenyl group is necessarily locked in a *s-cis* conformation with respect to the double bond. Therefore, the above upfield shift of 0.4 ppm must result from shielding of one or both carbomethoxy groups due to the diamagnetic component generated by the phenyl ring. That indeed it is only the carbomethoxy group situated *cis* to the nitrogen which is being shielded can be deduced from the chemical shifts of the individual carbomethoxy groups of **7** which are 3.69 and 2.91 ppm (Table III). While the first value is within the above mentioned spectral range for compounds having no phenyl substituent, the second value represents an upfield shift of 0.78 ppm. In view of this striking shielding effect it must be concluded that the phenyl ring in **7** is twisted with respect to the plane of the rest of the molecule. Only in such a conformation may the carbomethoxy group be affected by the diamagnetic field component of the adjacent phenyl ring. Analogous phenomena were recognized in amides and were recently subjected to nmr investigations.[20] Indeed, model examination of **7** reveals a large steric congestion in an all planar structure, and the same holds true for the acyclic conformations **3b** and **4b**. From the above argument the presence of the conformations **3b** and **4b** in the respective equilibrium systems should result in shielding of the carbomethoxy groups and consequently in an upfield shift of the corresponding nmr signals. The average chemical shifts of the above groups in **3** and **4** are 3.67 and 3.62 ppm, respectively (Table III), and the differential chemical shifts are 0.12 and 0.14 ppm, respectively (Table I). It follows that both the average and the differential chemical shifts of the two carbomethoxy groups in **3** and **4** exclude the presence of the *s-cis* conformations **3b** and **4b**. Thus in conclusion, regardless of the rates of exchange between the *s-cis* and *s-trans* conformations, **3a** and **4a** are the species which predominate in solution.



3a, R = H
4a, R = Me

3b
4b

Experimental Section

General. The chemical shifts reported in Table III were obtained from measurements of the spectra on a Varian A-60A or HR-100 spectrometer employing solutions of approximately 10–20% by volume, using TMS as internal standard (the solvents are indicated in Table III). The spectrometers were equipped with variable-temperature probes. The coalescence temperatures are accurate to 2°, $\Delta\nu$ values are averages of at least three tracings and are accurate 0.1 cps, chemical shifts are accurate to 1 cps. Ultraviolet spectra were recorded on a Cary 14 spectrometer, and infrared spectra on Perkin-Elmer grating spectrometer, Model No. 337.

Methyl 2-Carbomethoxy-3-dimethylaminoacrylate (1). A solution of 10.0 g (0.0575 mol) of methyl 2-carbomethoxy-3-methoxyacrylate[21] and 6.5 ml of 41% methanolic dimethylamine solution (0.059 mol) in 40 ml of ether was left overnight at room temperature. The residue which was left after evaporation of the solvent was distilled (7 g; 65% yield), bp 115° (0.5 mm). The distillate which solidified was crystallized from ethyl acetate–hexane, mp 65–67°; uv max (isooctane) 281 (ϵ 18,900), 225 mμ (ϵ 7000); ir ($CHCl_3$) 1685 (ester C=O) and 1604 cm^{-1} (C=C). *Anal.* Calcd

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[19] Measured on Dreiding Models.

[20] Y. Shvo, E. C. Taylor, K. Mislow, and M. Raban, *J. Amer. Chem. Soc.*, 89, 4910 (1967), and references cited therein.

[21] L. Claisen, *Anal. Chem.*, 297, 1 (1897).

for $C_{18}H_{13}NO_4$: C, 51.33; H, 7.00; N, 7.48. Found: C, 51.39; H, 7.25; N, 7.61.

Methyl 2-Carbomethoxy-3-dimethylaminocrotonate (2). A mixture of 39.9 g (0.3 mol) of dimethylacetamide dimethyl acetal[22] and 39.6 g (0.3 mol) of dimethyl malonate was left for 1 week at room temperature. The solution was concentrated and the residue distilled (36.2 g; 60%), bp 94–96° (0.01 mm). The distillate which solidified was crystallized twice from ethyl acetate–hexane, mp 62–63.5°; uv max (isooctane) 297 (ϵ 13,900), 236 mμ (ϵ 5300); ir ($CHCl_3$) 1670 (ester C=O) and 1548 cm^{-1} (C=C). *Anal.* Calcd for $C_9H_{15}NO_4$: C, 53.72; H, 7.51; N, 6.96. Found: C, 53.68; H, 7.38; N, 6.92.

Methyl 2-Carbomethoxy-3-(N-methylanilino)acrylate (3). A mixture of 8.70 g (0.05 mol) of methyl 2-carbomethoxy-3-methoxyacrylate[21] and 5.35 g (0.055 mol) of N-methylaniline was kept in an oil bath at 110–120° for 1 hr. The resulting oil was distilled twice (8.3 g; 65%), bp 128° (10^{-3} mm); uv max (isooctane) 298 (ϵ 27,100), 221 mμ (ϵ 10,100); ir 1703 cm^{-1} (ester C=O). *Anal.* Calcd for $C_{13}H_{15}NO_4$: C, 62.64; H, 6.07; N, 5.62. Found: C, 62.67; H, 6.11; N, 5.81.

Methyl 2-Carbomethoxy-3-(N-methylanilino)crotonate (4). A mixture of 9.4 g (0.0357 mol) of methyl 2-carbomethoxy-3-methoxycrotonate[23] and 5.35 g (0.0525 mol) of N-methylaniline was kept in an oil bath at 180° for 1.5 hr. Distillation at 132–133° (10^{-3} mm) gave a yellow oil (3 g; 32%) which was redistilled, bp 129–131° (5×10^{-3} mm); uv max (isooctane) 305 (ϵ 21,500), 235 mμ (ϵ 14,100); ir ($CHCl_3$) 1681 cm^{-1} (ester C=O). *Anal.* Calcd for $C_{14}H_{17}NO_4$: C, 54.75; H, 6.46; N, 5.32. Found: C, 54.81; H, 6.72; N, 5.43.

1-Methyl-2-bis(carbomethoxy)methylenpyrrolidine (5). This compound was prepared in 52% yield according to the procedure given in ref 24 for the preparation of the corresponding bis(carboethoxy) derivative, crystallized from ethyl acetate–hexane, mp 47–48°; uv max (isooctane) 281 (ϵ 17,900), 233 mμ (ϵ 5100); ir ($CHCl_3$) 1672 (ester C=O), 1568 cm^{-1} (C=C). *Anal.* Calcd for $C_{10}H_{15}NO_4$: C, 56.32; H, 6.57; N, 7.09. Found: C, 56.46; H, 6.30; N, 7.20.

1-Benzyl-2-bis(carbomethoxy)methylenpyrrolidine (6). A mixture of 1-benzylpyrrolidine (3.5 g; 0.2 mol) and dimethyl sulfate (25.2 g; 0.2 mol) was heated in an oil bath at 90–100° for 2 hr. To the cold reaction mixture was added a solution of sodium methoxide in 70 ml of methanol (prepared from 4.6 g of sodium) with stirring during 15 min. After keeping the reaction mixture overnight at room temperature the salt was filtered, the methanol was evaporated *in vacuo*, and the residue was distilled at 84° (0.01 mm) to give 1-benzyl-2-pyrrolidone dimethyl acetal (13.5 g; 30%). The above compound (4.57 g; 0.02 mol), 2.64 g (0.02 mol) of dimethyl malonate, and 5 ml of methanol were heated under reflux for 36 hr. Distillation, bp 144–146° (10^{-3} mm), yielded 5.0 g (87%) of product which was crystallized from ethyl acetate–hexane, mp 41–42°; uv max (isooctane) 282 mμ (ϵ 19,500); ir ($CHCl_3$) 1681 cm^{-1} (ester C=O). *Anal.* Calcd for $C_{16}H_{19}NO_4$: C, 66.42; H, 6.62; N, 4.84. Found: C, 66.77; H, 6.49, N, 4.92.

1-Phenyl-2-bis(carbomethoxy)methylenpyrrolidine (7). Triethyloxonium fluoroborate (24.5 g; 0.13 mol) was added to 20 g (0.125 mol) of 1-phenylpyrrolidone in 25 ml of methylene chloride. The mixture was heated in a water bath at 45° for 1 hr, the upper layer was separated, and to the lower layer was added 16.5 g (0.125 mol) of dimethyl malonate. The reaction mixture was kept 48 hr at room temperature and chloroform and water were added. The organic layer was separated, dried ($MgSO_4$), concentrated, and the residue distilled at 188° (0.04 mm) to give 1.5 g (4%), crystallized from ethyl acetate–hexane, mp 104–106.5°; uv max (isooctane 297 (ϵ 12,500), 240 mμ (ϵ 8000); ir ($CHCl_3$) 1683 cm^{-1} (ester C=O). *Anal.* Calcd for $C_{15}H_{17}NO_4$: C, 65.44; H, 6.22; N, 5.09. Found: C, 65.33; H, 6.03; N, 5.33.

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[22] H. Bredereck, F. Effenberger, and G. Simchen, *Angew. Chem.*, 73, 493 (1961).

[23] Prepared according to the procedure for the corresponding diethyl ester; A. Michael and G. H. Carlson, *J. Amer. Chem. Soc.*, 57, 165 (1935).

[24] H. Bredereck and K. Bredereck, *Chem. Ber.*, 94, 2278 (1961).

Internal Rotation in Olefins. II. Thermodynamic and Kinetic Investigation by Nuclear Magnetic Resonance

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Abstract: Low energy barriers for rotation about carbon–carbon double bonds were discovered in various substituted 1-carbomethoxyacrylonitriles. Rotational rates were found to be within the nmr time scale, and activation energies were determined by variable temperature studies. Thermodynamic as well as kinetic properties of the exchanging diastereomers were investigated by the varying of structural parameters.

While the investigation of the diester compounds, presented in the preceding publication,[2] has yielded kinetic information regarding the isomerization process about the C=C bond, thermodynamic as well as kinetic data were obtained in the present study. The structure of the presently investigated compounds (Table I) may be arrived at by a single structural modification in the compounds of the preceding publication,[2] namely, the substitution of one carbomethoxy group by a nitrile. Again, two kinds of kinetic processes which occur within one molecule were discovered. The observed nmr phenomena could be unambiguously identified with the rotational process about the carbon–carbon double bond and about the nitrogen-to-sp^2 carbon bond (nitrogen rotation). In most of the compounds which are listed in Table I the rates of these processes are within the nmr time scale.

Consideration of the above-mentioned two types of rotational processes in the compounds of the present investigation leads to an equilibrium system depicted in Figure 1. Since all double-bond substituents are structurally different, the maximum number of diastereomeric species possible in the above equilibrium is four.

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[1] H. Shanan-Atidi, M.S. Thesis, Tel-Aviv University, Tel-Aviv, Israel, 1968.

[2] Y. Shvo and H. Shanan-Atidi, *J. Amer. Chem. Soc.*, 91, 6683 (1969).