

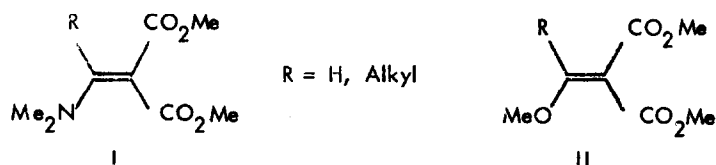
## STERIC ACCELERATION OF ROTATION AROUND CARBON-CARBON DOUBLE BOND.

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The detection and measurement of exceptionally low energy barriers for rotation about carbon-carbon double bonds in delocalized  $\pi$  systems have been reported in recent communications (1-3). Both the symmetry of the systems which have been studied (interconversion of identical species), and the method of investigation (nmr), allowed the determination of the energy barriers ( $< 12-22$  kcal/mole) associated with the rotational process.

In the previous communication (1) we have presented nmr and activation data for the degenerate isomerization of vinyl amines of type I. The present work reveals that vinyl ethers of the general structure II, also possess unusually low energy barriers for rotation about the carbon-carbon double bond, and the kinetic process may be studied by nmr, provided specific structural features are present in the



molecule. While in all the vinyl amines (I) the two signals of the carbomethoxy groups coalesce within the temp range available in nmr spectroscopy, those in the vinyl ether II ( $R = H$ ) persist at  $200^\circ C$  as an equal intensity doublet. This result seems, at first sight, to exclude the possibility of studying the kinetics of isomerization of vinyl ethers by nmr spectroscopy. However, from the investigation of both the kinetic and the equilibrium aspects of this process in the vinyl amines (4), it has been revealed that the energy barrier under consideration is extremely sensitive to the nature of the alkyl group R. Consequently, these experimental results, as well as theoretical considerations which will be presented, have been exploited in constructing vinyl ether systems which will isomerize at rates amenable to study by nmr spectroscopy.

The series of enol ethers listed in Table I have been prepared (5) and studied by nmr. The experimental results and activation parameters for rotation around C-C double-bond are presented in this

table. The reversible changes in the lines shape of the two diastereotopic (6) carbomethoxy groups have been determined as a function of temp. Two equal intensity signals have been observed at room temp which, in all cases, excluding compd (III), coalesce to a single broad line at the indicated temp ( $t_c$ ). Raising the temp above  $t_c$  results in narrowing of the signal. This behavior indicates that the two carbomethoxy groups are undergoing a kinetic process of exchange. Considering the magnitude of the  $\Delta G^\ddagger$  values and the fact that the two signals are of equal intensity, it is concluded that the exchange necessarily takes place by rotation of  $180^\circ$  around the C-C double-bond via maximum energy conformation IX.

TABLE I  
Nmr and Activation Data for  $R(\text{MeO})\text{C}=\text{C}(\text{CO}_2\text{Me})_2$ .

Compd	R.	$\Delta\nu$ (cps) <sup>a</sup>	$t_c$ (°C)	$\Delta G^\ddagger$ (kcal/mole) <sup>b</sup>	Solvent
III	H	3.10	> 206	$\sim 27.7^c$	Hexachlorobutadiene.
IV	CH <sub>3</sub>	3.30	191	25.7	"
V	C <sub>2</sub> H <sub>5</sub>	2.90	162	24.7	"
VI	i-C <sub>3</sub> H <sub>7</sub>	3.90	152	23.3	"
	i-C <sub>3</sub> H <sub>7</sub>	5.32	152	23.0	Bromobenzene
VII	t-C <sub>4</sub> H <sub>9</sub>	3.28	61	18.3 <sup>d</sup>	"

<sup>a</sup> Recorded at 100 Mc. <sup>b</sup> Calculated from Eyring activation function. <sup>c</sup> Calculated for  $t_c$  of 225°C, the estimation is based on the observation that at 206° the two lines were still 2 cps apart. <sup>d</sup> No separation of signals is attained in hexachlorobutadiene.

Inspection of the results in Table I reveals that a stepwise increase in the bulk of substitution (R), from H to t-butyl, causes a monotonous lowering of the free energy of activation for rotation; the total change being ca. 9.4 kcal/mole. The mode of intervention of the various factors which govern the observed behavior is best interpreted by analysing the geometries and the electronic effects in the ground and transition states. The energy difference between these two states should correspond to the experimental  $\Delta G^\ddagger$  values.

From thermochemical data it has been established that the ground state of conjugated olefins is stabilized, (7,8) probably by inductive and hyperconjugative mechanisms, by ca. 1 kcal/mole when H is substituted by an alkyl group. This stabilization is independent of the nature of the alkyl group (7,8). On the other hand, replacement of H by Me in II should destabilize the ground state energy level by an estimated 1 kcal/mole due to the introduction of cis steric interactions (9). Since these two energy contributions are of comparable magnitude but have opposite signs, the replacement of H by Me (comps

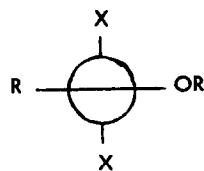
(III) & (IV) can not significantly raise the ground state energy of the molecule. Consequently, the energy changes in the ground state do not account for the observed decrease of ca. 2 kcal/mole in  $\Delta G^\ddagger$  in going from III to IV (Table I). It is therefore concluded that the above decrease is due mainly to lowering of the energy of the transition state. The geometry of the postulated transition state is depicted in projection formula IX. Since the two sets of substituents occupy orthogonal planes, no significant steric interactions are anticipated upon changing R from H to Me. However, since the transition state most probably involves separation of charges (positive charge being enhanced on the  $\beta$  carbon atom), the



VIII

R = H, Alkyl

X =  $\text{CO}_2\text{Me}$



IX

lowering of its energy may be attributed to the electron release capacity, upon demand, of the methyl group (hyperconjugation). The observed energy magnitude of this effect, ca. 2 kcal/mole, is within the limit of about 5 kcal/mole observed in lowering of transition states of alkylated substrates in electrophilic substitution reactions (11).

Further alkylation beyond Me produces considerable reduction of  $\Delta G^\ddagger$  values (IV - VII, Table I). The effect of this additional alkylation on the ground and transition states must now be considered. From reaction rate data it is apparent that neither the ground (7,8) nor the transition state (11,12) is sensitive to the nature of alkylation. The changes are in the range of only few tenths of a kilocalorie and can not therefore account for the observed decrease in  $\Delta G^\ddagger$  upon alkylation beyond Me, which is in the kilocalorie range. It must therefore be concluded that the observed changes in  $\Delta G^\ddagger$  (compds (IV) - (VII), Table I) are due mainly to the intervention of steric factors. From projection formulas of the ground state conformation (VIII) and transition state (IX), it is clear that steric interactions are by far more important in the ground than in the transition state. This should result in raising the energy level of the ground state to a larger extent than the transition state. The net result is a diminution of  $\Delta G^\ddagger$  which accounts for the observed acceleration in the rate of rotation upon the increase of the size of R (13).

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5. Chemical analysis and spectral properties of all compounds listed in Table I are consistent with their structure. Purity was checked by vpc.
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9. The appropriate model system for the evaluation of the magnitude of this interaction is the cis-trans methyl crotonate. To the best of our knowledge no enthalpy data are available for this or other pairs of isomers of  $\alpha\beta$  - unsaturated esters. The approximated value of 1 Kcal/mole is based on the  $\Delta H$  of hydrogenation for cis-trans methyl-isopropylethylene (10).
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13. It is probable that a positive entropy of activation term becomes important as the size of R is increased. This can be clarified upon detailed kinetic study.