

field, Hammond⁴ has found that triplet methylene in solution (produced by photosensitation) did not insert into the C-H bonds of cyclohexene, but did add to the double bond. Singlet methylene, however, gave both insertion and addition products.

We have measured the ratios of addition to insertion products, formed from carbethoxynitrene and cyclohexene, and have carried out these reactions at much lower olefin concentrations than we did in our earlier work.^{1,2} The remarkable lack of reactivity of dichloromethane makes it possible to obtain good yields even at very low olefin concentrations. The products were identified and their yields measured as described earlier.^{1,2} Having observed earlier that primary C-H bonds are much less reactive than secondary and tertiary ones, we also ran experiments in neopentane as the solvent, but at high dilution the neopentane competes successfully with cyclohexene, and neopentylurethane was formed in about 7% yield.

The data collected in Table I show a change of reactivity of the reaction intermediate which parallels in all

Table I

Cyclohexene in CH ₂ Cl ₂ , mole %	Cyclohexyl-3- and 4-urethans, % ^a		
	Photolysis	α elimination	Abs. yield of I, %
100	16.7	14 ^b	52
17.5	12.5		
8.0	9.1		
7.8		11.1	60
5.2		10.5	50
4.5	7.1		53
3.4	6.5		
3.4		8.7	55
1.6		6.9	40
1.4	4.2		
1.1	3.6		
0.8		4.4	38
0.7	3.0		
0.2	1.7		35

Cyclohexene in neopentane, mole %	In neopentane solution		
	3- and 4-cyclohexyl urethans, abs. yield, %	Neopentyl-urethan, abs. yield, %	Aziridine I, abs. yield, %
10	3.9	7.5	53
1.7	0.7	5.1	56

^a Urethans plus aziridine I used as 100%. ^b In heterogeneous solution, from ref. 2.

respects the change in stereospecificity we found in the addition reaction of our intermediate with 4-methylpentene-2. Taken together, the observations indicate a change in the nature of the intermediate during the time that elapses when the intermediate is made to collide with many solvent molecules before reaching a molecule of substrate. At present, the most likely interpretation seems to be the change, with time, of an initially produced singlet nitrene to a more stable (ground-state) triplet.

(4) K. R. Kopecky, G. S. Hammond, and P. A. Leermakers, *J. Am. Chem. Soc.*, **83**, 2396 (1961).

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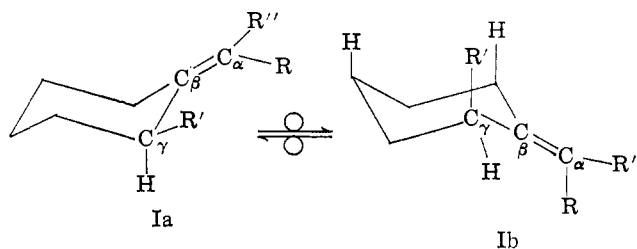
Steric Interference in Allylic and Pseudo-Allylic Systems. I. Two Stereochemical Theorems

Sir:

We wish to draw attention to two forms of steric hindrance that up to this time appear to have gone unrecognized as general phenomena. Both are associated with substituted allylic groups, or their equivalent, and both appear to operate in aliphatic and alicyclic systems. However we shall confine our remarks, for the present, to the latter type, and for purposes of simplicity shall consider only lightly substituted allylic groups associated with six-membered rings.

The first case can be exemplified by considering the conformers (Ia and Ib) of I which contain the

allylic system $\text{>C}_\gamma\text{-C}_\beta\text{=C}_\alpha\text{<}$. If one examines a model of Ia it is obvious that the dihedral angle between $\text{C}_\gamma\text{R}'$ and the double bond ($\text{>C}_\beta\text{=C}_\alpha\text{<}$) is essentially zero. Thus in the ideal case the spatial arrangement of the grouping $\text{R}'\text{-C}_\gamma\text{-C}_\beta\text{=C}_\alpha\text{-R}$ is planar. It can also be seen that even when R' and R are only moderate in size they will interfere with each other drastically, in fact more so than if they were 1,3-



diaxially related in a cyclohexane ring. Barring a facile rearrangement of the double bond, relief of this strain can be attained most easily by conformational inversion to Ib. In the latter conformer the strain present is that due to the interaction of R' with two axial hydrogen atoms plus that due to the interaction of R with the C_γ -equatorial hydrogen atom. The difference in strain energies between Ia and Ib will determine the conformational composition of I. Thus if $\text{R} = \text{R}' = \text{CH}_3$, to a first approximation the strain energy difference between Ia and Ib would be $\approx [1(1,3\text{-diaxial CH}_3/\text{CH}_3\text{ interaction}) - 3(1,3\text{-diaxial CH}_3/\text{H interaction})] \approx [3.7 - (3 \times 0.9)] = 1.0$ kcal./mole, and I must therefore exist to the extent of 85% in conformation Ib¹. This deduction that, in the ground state, I might exist largely as the conformer with the ring substituent axial has important implications not only for conformational and isomerizational equilibria but also for reactions

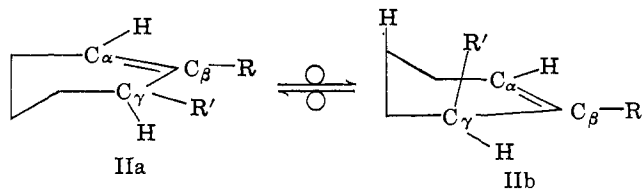
(1) We regard this as a minimum percentage for Ib, in this particular case, since the $\text{C}_\alpha\text{-CH}_3/\text{C}_\gamma\text{-CH}_3$ energy of interaction in Ia is undoubtedly much greater than the 3.7 kcal./mole which we have assigned to it.

potentially involving the formation of an exocyclic bond.

This type of interaction arising from substituents on the 1 and 3 positions of an allylic system we have termed $A^{(1,3)}$ strain. The effect, however, is not confined to purely carbon systems for if we replace $C_\alpha RR''$ by oxygen, the interaction becomes that of a nonbonded pair of electrons on oxygen with R' , and it reduces itself in principle to the much vaunted "2-alkyl ketone effect."² We must then classify the latter as a pseudo-allylic system³ exhibiting $A^{(1,3)}$ strain.

A large number of other important examples of this type of strain will be discussed in a subsequent full paper, but a most important application of the principle is described in the succeeding communication.

The second type of steric hindrance can be demonstrated if we inspect the allylic system in conformer IIa of II. By direct measurement on a model the dihedral angle⁴ $R'C_\gamma-C_\beta R$ is approximately 35° . Thus, in the idealized case, the introduction of a $\Delta^{1,6}$ -double bond into a 1,2-disubstituted cyclohexane causes a decrease of 25° in the dihedral angle between the substituents and a resulting increase in the steric or Pitzer strain between them.



If the substituents are moderately large, relief of strain may be attained by conformational inversion to IIb in which case the dihedral angle⁴ between $C_\gamma R'$ and $C_\beta R$ becomes 85° . Strain in IIb arises only from one 1,3-diaxial interaction of R' with a hydrogen atom plus the hindrance associated with R and the C_γ -quasiequatorial hydrogen atom. Here even in the simple case where $R = R' = CH_3$ it is difficult to calculate the significant nonbonded energies associated with these conformers, and no attempt will be made to do so here. However it is fairly obvious that with substituents (R and R') of reasonable size *once again it is that conformer (IIb) with the ring substituent (quasi-) axially oriented that will constitute the greater proportion of II in the ground state.* This type of strain arising from a 1,2-disubstituted allylic system we have designated $A^{(1,2)}$ strain.

The conclusions deduced from this empirical approach are essentially the same as those reached by Garbisch⁵ in his examination of a series of 1-phenyl-6-substituted cyclohexenes. Using n.m.r. spectroscopy he was able to prove that the group at the 6 position, if bulky, took up an axial orientation. This was valid

(2) B. Rickborn, *J. Am. Chem. Soc.*, **84**, 2414 (1962); W. D. Cotterill and M. J. T. Robinson, *Tetrahedron*, **20**, 765, 777 (1964).

(3) We define a pseudo-allylic system as one in which one of the atoms of the allyl group itself has been replaced by an element other than carbon (e.g., O, N, S, etc.).

(4) A vector analysis of cyclohexene has been carried out by E. J. Corey and R. A. Snee (*J. Am. Chem. Soc.*, **77**, 2505 (1955)), who calculated this angle to be 37° at a time when Dreiding models were not available. Thus this value, and their corresponding value for the dihedral angle $R'C_\gamma-C_\beta R$ (83°) in IIb, are in excellent agreement with the more empirical measurements made on the model.

(5) E. W. Garbisch, Jr., *J. Org. Chem.*, **27**, 4243, 4249 (1962).

only of course provided no other substituents on the ring blocked conformational inversion.

The value of the theorem becomes apparent only from its generality, for if we replace R by an oxygen or nitrogen atom then II is reduced to an enol or an enamine, respectively. We have recently shown that both solvated enolate anions⁶ and certain enamines⁷ of 2-substituted cyclohexanones exist largely with the ring substituent in the quasixial orientation. Thus it is clear that both the systems studied by Garbisch and those examined by us fall into the same category, that of being controlled by $A^{(1,2)}$ strain.

Further refinement and elaboration of these ideas will be presented later in a subsequent article but, without citing specific examples, it can be stated that many anomalous stereochemical observations recorded in the literature can be explained easily by application of the above principles.

(6) S. K. Malhotra and F. Johnson, *J. Am. Chem. Soc.*, **87**, 5513 (1965).

(7) F. Johnson and A. Whitehead, *Tetrahedron Letters*, 3825 (1964); S. K. Malhotra and F. Johnson, *Tetrahedron Letters*, 4027 (1965).

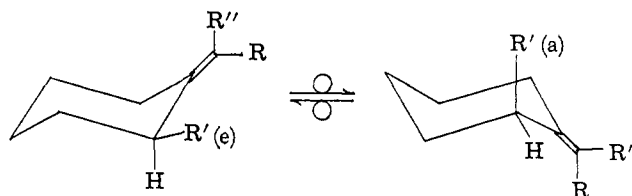
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Steric Interference in Allylic and Pseudo-Allylic Systems. II. Stereochemistry of Exocyclic Enolate Anion Protonation

Sir:

In the preceding communication¹ we have discussed strain which arises in substituted allylic systems that constitute part of a six-membered ring. Empirically it was deduced that molecules containing either an exocyclic or an endocyclic double bond would, with the appropriate substitution, have internal nonbonded interactions. These were classified as $A^{(1,3)}$ and $A^{(1,2)}$ strain, respectively.

In the exocyclic double bond case shown below, if R and R' are small, the equilibrium should lie to the left. If R and R' are medium or large in size it should lie to the right. Axiomatically, the extent of



conformation inversion from left to right in the ground state will depend on the free-energy difference between the conformers.

A logical vehicle on which to test these ideas appeared to be the systems discussed at length by Zimmerman and co-workers.² In 1955 it was reported that

(1) Part I: F. Johnson and S. K. Malhotra, *J. Am. Chem. Soc.*, **87**, 5492 (1965).

(2) (a) H. E. Zimmerman, *J. Org. Chem.*, **20**, 549 (1955); (b) H. E. Zimmerman, *J. Am. Chem. Soc.*, **78**, 1168 (1956); (c) H. E. Zimmerman, *ibid.*, **79**, 5554 (1957); (d) H. E. Zimmerman and T. E. Nevins, *ibid.*, **79**, 6559 (1957); (e) H. E. Zimmerman and T. W. Cutshall, *ibid.*, **80**, 2893 (1958); (f) H. E. Zimmerman and T. W. Cutshall, *ibid.*, **81**, 4305 (1959).