

butene-2 to be partially stereospecific. Hafner concludes that the nitrene "reacts preferentially in the singlet state." Our findings agree with those of Hafner, but in addition we find that the degree of stereospecificity⁷ of the addition of carbethoxynitrene to the 4-methyl-2-pentenes decreases drastically with decreasing olefin concentration. Table I shows this for solutions of the olefins in dichloromethane and in neopentane.⁸

Table I. Stereospecificity of the Addition of Carbethoxynitrene to *cis*- and *trans*-4-Methyl-2-pentene

Olefin, mole %	Solvent	Compn. of aziridine mixtures ^a		Aziridine yield, abs.
		<i>trans</i> , from <i>cis</i> olefin	<i>cis</i> , from <i>trans</i> olefin	
A. Carbethoxynitrene by Photolysis of EtOOC-N ₃				
100		25.6	6.6	70
33	CH ₂ Cl ₂	28.0		
10	CH ₂ Cl ₂	34.4		58
5	CH ₂ Cl ₂	42.8		
1.5	CH ₂ Cl ₂	54.4	14.9	55
1.5	Neopentane	59.7	16.7	58
1.5	Neopentane	54.0 ^b	14.8 ^b	58
B. Carbethoxynitrene by α Elimination				
33	CH ₂ Cl ₂	7.6	2.9	57
1.5	CH ₂ Cl ₂	41.7	12.5	25

^a *cis* + *trans* = 100%. ^b Corrected for the formation of neopentylurethan by adding the neopentylurethan yield to the stereospecific addition product yield.

An attractive explanation for our results is that in our solutions both singlet and triplet nitrenes add to the olefinic double bond, the singlet stereospecifically and the triplet nonstereospecifically. There are reasons to believe that carbethoxynitrene is generated in the singlet state^{8,9}: the triplet nitrene could arise from intersystem crossing of singlet nitrene when it is forced to exist for a prolonged span of time before encountering an olefin molecule in a reactive collision. Thus, a higher degree of stereospecificity is obtained in reactions in pure olefin than in dilute (1.5 mole %) solutions, where the probability of collision with an olefin molecule is reduced by a factor of 65.

An alternative explanation might be advanced: perhaps the singlet nitrene is trapped preferentially by the solvent, thus giving a higher proportion of triplet in solution and leading to more nonstereospecific addition. If this were an important process in the dichloromethane solution, the yield of aziridines should drop drastically, which is not observed. However, in neopentane the capture of singlet does occur: neopentylurethan is formed and the stereospecificity of the addition reaction is lower than in dichloromethane solution of equal concentration. If we assume (1) that only singlet is trapped and (2) that the singlet addition is entirely stereospecific, then correction for the trapping effect can be made and, indeed, the corrected value for

(7) We are employing the nomenclature proposed by H. E. Zimmerman, L. Singer, and B. S. Thygarajan, *J. Am. Chem. Soc.*, **81**, 108 (1959); see footnote 16.

(8) After completion of our work, Jones and Rettig reported a similar effect in the addition of fluorenylidene to olefins [M. Jones, Jr., and K. R. Rettig, *ibid.*, **87**, 4013 (1965)].

(9) D. W. Cornell, R. S. Berry, and W. Lwowski, *ibid.*, **87**, 3626 (1965).

the stereospecificity is the same as the one obtained in dichloromethane solution. Further evidence supporting assumption 1 is found in the accompanying communication.¹⁰

When the carbethoxynitrene is generated by α elimination, the degree of stereospecificity obtained is higher than with azide photolysis as the nitrene source. One possible cause is intersystem crossing of excited azide, followed by loss of nitrogen to give triplet nitrene directly. Another possibility is selective capture of triplet nitrene by the triethylammonium *p*-nitrobenzenesulfonate present in the α elimination reaction mixture. Further work to elucidate this point is in progress.

Acknowledgments. We are grateful for support of this work by the National Science Foundation (Grants GP 649 and 3846) and for a predoctoral fellowship from the National Institutes of Health for J. McC.

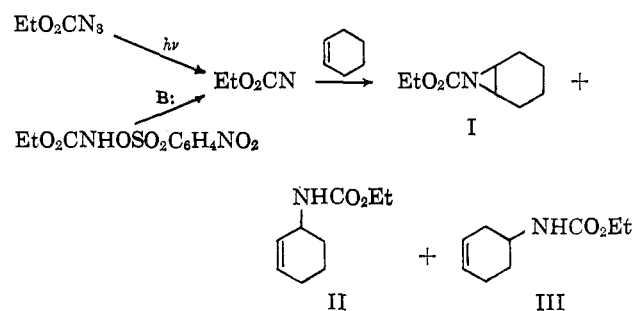
(10) W. Lwowski and F. P. Woerner, *ibid.*, **87**, 5491 (1965).

Walter Lwowski, John S. McConaghy, Jr.
Sterling Chemistry Laboratory, Yale University
New Haven, Connecticut 06520
Received September 23, 1965

Carbethoxynitrene. Control of Chemical Reactivity

Sir:

Carbethoxynitrene, generated by photolysis of ethyl azidoformate¹ or by α elimination,² inserts into C-H bonds and adds to double bonds. With cyclohexene, the ratio of the yield of 7-carbethoxy-7-azabicyclo[4.1.0]heptane (I) to the sum of the yields of 3- and 4-cyclohexenylurethans (II and III) was found to be about 4.5, with small variations for different reaction temperatures and conditions.



In the accompanying communication³ we report that the degree of stereospecificity of the addition of carbethoxynitrene to a pair of olefins changes drastically with the olefin concentration. As an explanation, we advance the hypothesis that the nitrene is produced in the singlet state (which is assumed to add stereospecifically) but crosses over to the triplet (ground) state (assumed to add nonstereospecifically) when given time by lowering the olefin concentration. If this explanation is correct, one would also expect changes of chemical reactivity with changing substrate concentration. For example, the relative reactivities of the singlet and the triplet nitrenes should be different toward olefinic double bonds and toward C-H bonds. In the carbene

(1) W. Lwowski and T. W. Mattingly, Jr., *J. Am. Chem. Soc.*, **87**, 1947 (1965).

(2) W. Lwowski and T. J. Maricich, *ibid.*, **87**, 3630 (1965).

(3) W. Lwowski and J. McConaghy, Jr., *ibid.*, **87**, 549 (1965).

field, Hammond⁴ has found that triplet methylene in solution (produced by photosensitization) 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).

Acknowledgment. We are grateful for support of this research by Grant GM 08762 from the National Institutes of Health.

Walter Lwowski, Frank Peter Woerner
Sterling Chemistry Laboratory, Yale University
New Haven, Connecticut 06520
Received September 23, 1965

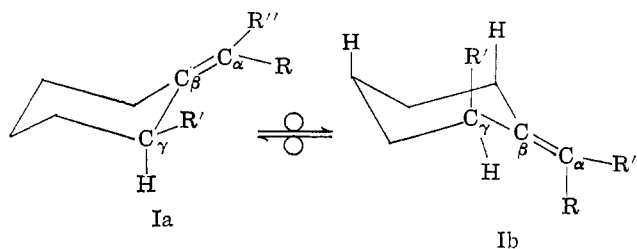
Steric Interference in Allylic and Pseudo-Allylic Systems. I. Two Stereochemical Theorems

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-



diagonally 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 $\approx [1(1,3\text{-di axial CH}_3/\text{CH}_3 \text{ interaction}) - 3(1,3\text{-di axial CH}_3/\text{H interaction})] \approx [3.7 - (3 \times 0.9)] = 1.0 \text{ kcal./mole}$, 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.