

characteristic of a (π , π^*) triplet. Owing to the high degree of strain in the ethanol-NaOH glass, high polarizations could not be obtained. However, the polarization is always negative with respect to excitation throughout the region from 310 to 265 m μ , consistent with a $\pi \rightarrow \pi^*$ assignment for the longest wave length absorption band.

Unlike purine itself, the anion fluoresces at $\sim 298^\circ\text{K}$. in ethanol-NaOH solution (ν_{max} 27,400 cm^{-1}), in agreement with Borresen's observation.⁵ At 77°K., this fluorescence shifts 2000 cm^{-1} to the blue. The excitation spectrum, however, is identical at both temperatures. Such blue shifts of fluorescence in rigid media are attributed to emission from molecules in a strained environment.¹⁸

Emission of 9-n-Butyladenine in Hydrocarbon Media. The emission spectra of 9-n-butyladenine ($\sim 10^{-4}$ M) in hydrocarbon alone, and in solutions containing 1% triethylamine (N(Et)₃), 10% N(Et)₃, and 30% butanol (all at 77°K.) are given in Figure 4. In isopentane-methylcyclohexane (5:1), 9-n-butyladenine exhibits only a weak structureless fluorescence, $\nu_{\text{max}} = 28,600 \text{ cm}^{-1}$. This emission is intensified by approximately a factor of 4 through the addition of either 1% N(Et)₃ or 10% diethyl ether to the solution. In the hydrocarbon-10% N(Et)₃ solution, a strong phosphorescence appears (Figure 4d) which is similar to that occurring in EPA, but red shifted by 400 cm^{-1} . In butanol-isopentane (3:7), the fluorescence shifts to the blue by $\sim 1000 \text{ cm}^{-1}$, and again phosphorescence appears strongly (Figure 4e).

The salient feature of these emission spectra is the absence of phosphorescence in hydrocarbon solvent. One possible interpretation is that the hydrocarbon solvent and the low temperature favor the formation of self-associated, hydrogen-bonded complexes. Exciton interaction in the complex leads to electronic energy transfer with a consequent quenching of emission. This phenomenon has, in fact, been observed in the acridine carbazole complex.¹⁹ In the case of 9-n-butyladenine, phosphorescence is much more severely quenched than fluorescence. In strong hydrogen-bonding solvents, association of the solute with the solvent is favored, and phosphorescence from the non-associated species appears. To test this hypothesis, polarization measurements and low-temperature absorption studies are now being carried out on this and related molecules.

Acknowledgment. The authors acknowledge helpful conversations and the criticism of Professor Hiroaki Baba.

(19) M. A. El-Bayoumi and M. Kasha, *J. Chem. Phys.*, **34**, 2181 (1961).

(18) D. M. Hercules and L. B. Rogers, *J. Phys. Chem.*, **64**, 397 (1960).

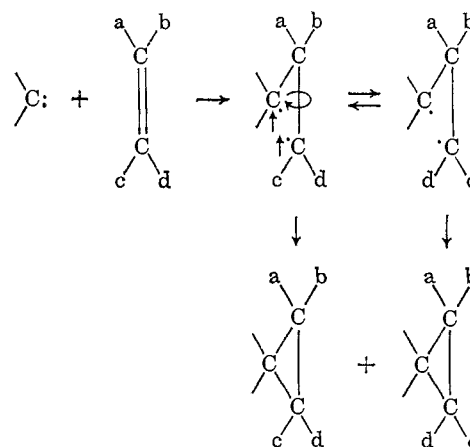
Communications to the Editor

Carbonylnitrene. Control of the Stereospecificity of an Addition to Olefins

Sir:

Investigation of the stereospecificity of carbene addition to olefins has been used frequently to gain information on the mechanism of the reaction, especially to determine whether the addition takes place in one or two steps. Since its introduction by Skell,¹ the reliability and the theoretical basis of the method have been widely discussed.² Stereospecific addition is generally interpreted as indicating the reaction of a singlet carbene, while nonstereospecific addition indicates the intervention of a triplet carbene, at least in condensed phase. In the latter case, a triplet diradical is supposed to be the intermediate, and rotation about the former double bond, preceding ring closure, causes nonstereospecificity.

We have investigated the addition of carbonylnitrene (produced both by photolysis of ethyl azidoformate³ and by α elimination from N-*p*-nitrobenzene-



sulfonyurethan⁴) to *cis*- and *trans*-4-methylpentene-2.⁵ While our work was in progress, Hafner⁶ reported the addition of carbomethoxynitrene to *cis*- and *trans*-

(4) W. Lwowski and T. J. Maricich, *ibid.*, **86**, 3164 (1964); **87**, 3630 (1965).

(5) The aziridines produced were identified by their infrared and n.m.r. spectra, their elemental analyses, and by comparison with authentic samples prepared by a modification of the method of Hassner [A. Hassner and C. Heathcock, *J. Org. Chem.*, **29**, 3640 (1964); **30**, 1748 (1965)].

(6) K. Hafner, W. Kaiser, and R. Puttner, *Tetrahedron Letters*, 3953 (1964).

(1) P. S. Skell and R. C. Woodworth, *J. Am. Chem. Soc.*, **78**, 4496 (1956).

(2) For a review see: P. P. Gaspar and G. S. Hammond in W. Kirmse, "Carbene Chemistry," Academic Press Inc., New York, N. Y., 1964, p. 258 ff.

(3) W. Lwowski and T. W. Mattingly, Jr., *Tetrahedron Letters*, 277 (1962); *J. Am. Chem. Soc.*, **87**, 1947 (1965).

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.

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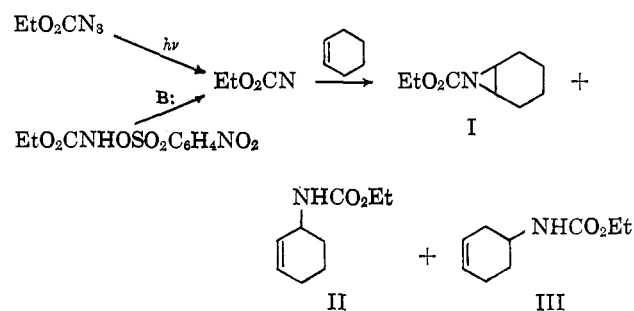
(10) W. Lwowski and F. P. Woerner, *ibid.*, **87**, 5491 (1965).

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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).