in this system are small in agreement with literature reports and discussions.[18] Solvent interaction can give comparable effects.[15] The *p*-fluorophenyl ring could interact directly with the tricyanovinyl derivative (as a result of the $-\mathrm{R}$ effect of *p*-fluorine substituent) and could decrease electronic effects resulting from intermolecular interaction of the *p*-tricyanovinyl group with the π base. However, the K values are not significantly lower for the *p*-fluorophenyl, indicating that the *p*-fluoro does not significantly change the extent of complexing and also supporting the view that ionization in the π complex is negligible.

Acknowledgments. We wish to acknowledge with thanks the special assistance received from Miss Ellen Wallace for the ultraviolet measurements and Mr. Louis Walther for the nmr measurements.

Singlet and Triplet Nitrenes. II. Carbethoxynitrene Generated from Ethyl Azidoformate

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Abstract: Carbethoxynitrene, made by thermolysis and photolysis of ethyl azidoformate, was added to *cis*- and *trans*-4-methylpent-2-ene, and the dependence of the stereospecificity on olefin concentration was measured. The thermolysis experiments can be quantitatively explained by a scheme used previously to correlate the data of analogous experiments with carbethoxynitrene made by α elimination. This scheme assumes that all the nitrene is generated in the singlet state, and that addition of the singlet to olefin competes with intersystem crossing to triplet nitrene. The former adds stereospecifically, the latter nonstereospecifically. The photolysis data are quantitatively in accord with a scheme in which one-third of the nitrene is produced in the tripletst ate, while two-thirds is generated in the singlet form. The singlet nitrene can be trapped selectively by cyclohexane.

In a recent paper,[3] we have examined the addition of carbethoxynitrene,[4] made by α elimination,[5] to *cis*- and *trans*-4-methylpent-2-ene. We concluded the α-elimination reaction of N-(*p*-nitrobenzenesulfonyloxy)urethan ($\mathrm{Ar{-}SO_2O{-}NH{-}COOEt}$) gives exclusively the singlet form of carbethoxynitrene. This then decays to the triplet state at a rate of about $^1/_{30}$ of that of the addition of the singlet to *cis*-4-methylpent-2-ene. Skell's rules for the stereospecificity of the addition of singlet and triplet electron-deficient species to C=C double bonds[6] were found to be applicable to our nitrene. The dependence of stereospecificity of addition on olefin concentration was found to be quantitatively in accord with the kinetic scheme in Figure 1. Triplet carbethoxynitrene could be selectively trapped by α-methylstyrene.

In the present paper, we extend our work to the thermolysis and photolysis of ethyl azidoformate. As indicated by the selectivities in C–H insertion reactions, α elimination from $\mathrm{ArSO_2O{-}NH{-}COOEt}$ and photolysis and thermolysis of ethyl azidoformate give one and the same carbethoxynitrene.[5,7–10] However, the stereospecificity of addition to the double bond of 4-methylpent-2-enes was markedly lower in azide photolysis than in α-elimination experiments.[11] The purpose of the present paper is to resolve this discrepancy.

Results and Discussion

Thermolysis of Ethyl Azidoformate. Ethyl azidoformate was dissolved in mixtures of *cis*-4-methylpent-2-ene and dichloromethane, and thermolyzed in sealed tubes at 100° for 24 hr. The mixture of *cis*- and *trans*-N-carbethoxy-2-isopropyl-3-methylaziridines was analyzed by calibrated gas chromatography as described previously.[3] Figure 2 gives the fraction of *trans*-aziridine as a function of olefin concentration. The curve closely resembles that obtained with carbethoxynitrene produced by α elimination.

Table I contains the data on which Figure 2 is based. These data were treated in the same manner as in our earlier paper,[3] in order to see whether they are in accord with the kinetic scheme of Figure 1, shown for the specific system we used in Figure 3. As before,[3] [T] stands for the fraction of aziridine-forming reaction that goes through the triplet path ($k_1 \rightarrow k_2 \rightarrow k_4$ in Figure 3), [S] is

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[3] J. S. McConaghy and W. Lwowski, *J. Am. Chem. Soc.*, **89**, 2357 (1967).

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[11] W. Lwowski and J. S. McConaghy, *J. Am. Chem. Soc.*, **87**, 5490 (1965).

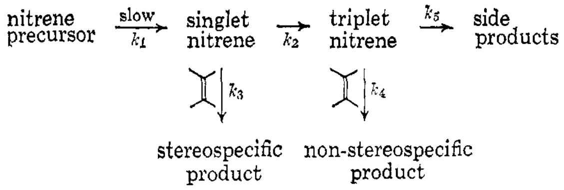


Figure 1.

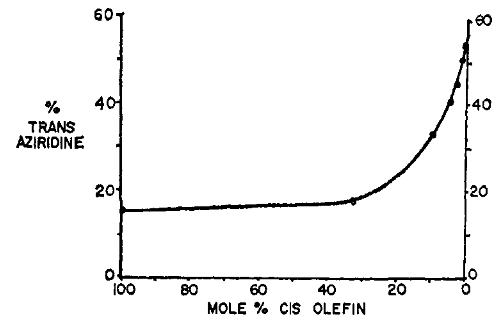


Figure 2. Thermolysis of ethyl azidoformate in *cis*-4-methylpent-2-ene solutions in dichloromethane. Fraction of *trans*-aziridine formed.

the fraction of aziridine formed through the stereospecific singlet path ($k_1 \rightarrow k_3$ in Figure 3). As established earlier,[3] the equilibrium mixture of **5** and **6** yields a mixture of *cis*- and *trans*-aziridines (**4** and **7**) in the ratio of 1:4. Hence, [T] can be obtained by multiplying the fraction of *trans*-aziridine (**7**) formed by 1.25, provided (*cf.* ref 3) that the reaction of triplet carbethoxynitrene with *cis*-4-methylpent-2-ene is totally nonstereospecific. As derived earlier,[3] the kinetic scheme of Figures 1 and 3 demands that a plot of [T]/[S] over 1/([olefin] + k_5/k_4) give a straight line of slope k_2/k_3. The earlier experiments,[3] in which the carbethoxynitrene was generated at 35°, gave values for k_2/k_3 of 0.036 and k_5/k_4 of 0.015. A plot of the [T]/[S] from Table I gives straight lines when one uses for k_5/k_4 0.03 to 0.04, as shown in Figure 4. The slope k_2/k_3 becomes 0.10 or 0.08, respectively. Since the temperature difference between the α-elimination reaction and the azide thermolysis is about 65°, these differences do not seem to be unreasonable. Furthermore, the leaving groups (*p*-nitrobenzenesulfonate ion *vs.* N_2), while they do not seem to greatly influence the C–H insertion reaction, might well exert different influences on the rate of singlet–triplet conversion while they are still in the vicinity of the incipient nitrene. It seems, then, that the reactions with olefin of carbethoxynitrene generated either by α elimination or by azide thermolysis are of the same nature.

Table I. Thermolysis of Ethyl Azidoformate in *cis*-4-Methylpent-2-ene Solutions in Dichloromethane at 100° for 24 hr

Olefin concn, mole %	Total aziridine, %	*trans*-Aziridine, %	[T]	[S]	[T]/[S]
100	67	14	0.175	0.825	0.21
33		18	0.225	0.775	0.29
10	78	33	0.410	0.590	0.70
5		41	0.515	0.485	1.06
3.3	60	46	0.575	0.425	1.35
1.5		51	0.64	0.36	1.78
1.0		54	0.675	0.325	2.08

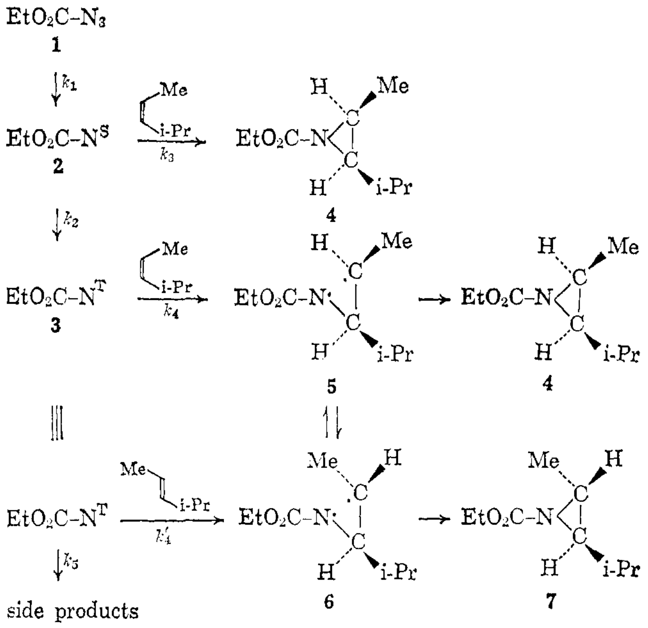


Figure 3. Reaction of carbethoxynitrene with *cis*-4-methylpent-2-ene according to the scheme in Figure 1.

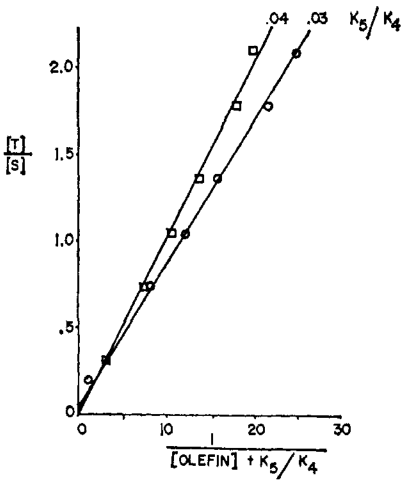


Figure 4. Thermolysis of ethyl azidoformate in *cis*-4-methylpent-2-ene solutions in dichloromethane. Plot according to the scheme in Figures 1 and 3.

The lines in Figure 4 go through the origin, indicating that all the carbethoxynitrene is generated in the singlet state (no nonstereospecific (triplet) reaction at infinite olefin concentration). The same was true in the α-elimination runs.

A thermolysis run employing concentrations of 3.3 mole % each of *cis*-4-methylpent-2-ene and α-methylstyrene gave a 15% yield of aziridine mixture, containing 95.6% *cis*- and 4.4% *trans*-aziridine. At the same olefin concentration, in the absence of α-methylstyrene, a 60% yield of aziridine mixture, containing 46% of the *trans* isomer, had been obtained. Obviously, the α-methylstyrene served as a triplet trap, as it did in the α-elimination experiments.[3] Calculation of the relative reactivities, done as before,[3] shows that the

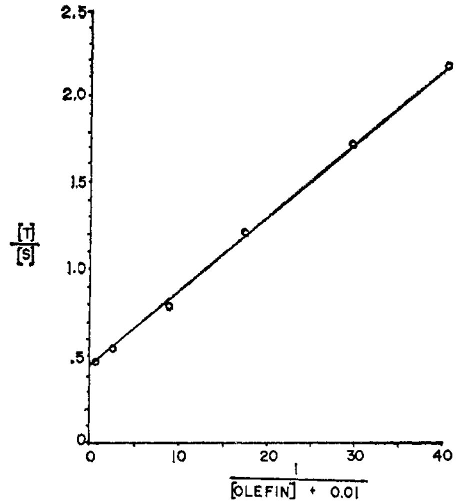
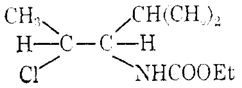


Figure 5.

triplet carbethoxynitrene reacts 50 times faster with α-methylstyrene than with *cis*-4-methylpent-2-ene, at 100°. In the earlier[3] experiments at 35°, a factor of 86 had been found.

Carbethoxynitrene by Photolysis. Photolysis of ethyl azidoformate, $EtOOC{-}N_3$, in *cis*-4-methylpent-2-ene at 38° gave a 70% yield of an aziridine mixture containing 26% *trans*- and 74% *cis*-aziridine. Photolysis thus is less stereospecific than thermolysis, and this is true at all olefin concentrations, as shown in Table II. The photolyses in dichloromethane solutions were not run to completion, because photolytic destruction of the aziridines occurs, especially after the azide has all disappeared. Prolonged photolysis led to the destruction of all aziridine, and the formation of **8** and **9**. The structure of **8** was assigned on the basis of its infrared, nmr, and mass spectra, that of **9** on the basis of its infrared and nmr spectra and its formation from the *trans*-aziridine **7** upon heating to 150°.



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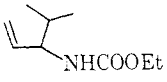

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Analysis of recovered olefin showed that under our experimental condition isomerization occurred to an extent of less than 3%, and the ratio of the amounts of aziridines **4** and **7** did not change throughout the run.

Treating the data of Table II in precisely the same manner as before[3] and as the thermolysis data above, the plot in Figure 5 is obtained. Using a k_5/k_4 (ratio of the rate constant of triplet side reactions to rate constant of triplet addition to olefin) of 0.01, gives a straight line. However, this line does not go through the origin but has an intercept at [T]/[S] of 0.44. In other words, at infinite olefin concentration, aziridine is formed by a nonstereospecific path to the extent of 0.44/1.44 or 30.5%.

Several possible explanations must be considered. (A) Azide thermolysis and azide photolysis could be entirely different reactions, which give the same products coincidentally. This explanation is unattractive, in view of the close similarity of the C–H insertion reactions produced by thermolysis and photolysis of the azide.[5,7,8,10] Also, the fact that a straight line is

Table II. Addition of Carbethoxynitrene from Azide Photolysis to *cis*- and *trans*-4-Methylpentene-2 in Dichloromethane

Olefin concn, mole %	From *cis* olefin		From *trans* olefin, *cis* prodt, %
	Aziridines, %	*trans* prodt, %	
100	70	26	6.4
33		28.5	
10	58	35	
5		43	
2.5		50	
1.5	55	54.5	14.7

produced in the plot of Figure 5 seems to indicate that a new process is simply added to the one obtained by azide thermolysis. (B) The result could be due to isomerization of starting olefin or products. This was excluded by control experiments. (C) A nonstereospecific aziridine formation which is not a nitrene reaction might be superimposed to the process obtained by azide thermolysis. In our case, that would have to be triazoline formation and subsequent, nonstereospecific triazoline decomposition to aziridine. The nonstereospecific, photosensitized decomposition of triazolines to aziridines has been observed,[12] and the presence of a suitable photosensitizer for the triazoline is possible in our system. However, triazoline is not formed by a dark reaction and would have to come from a photoreaction of the azide. Such a reaction would compete with the photodecomposition of the azide, and its rate would depend on olefin concentration, while the rate of azide decomposition would not. The hypothetical triazoline path would thus be important at high olefin concentrations, and unimportant at low ones. The dependence of stereospecificity on olefin concentration would, for explanation C, not give the curve of Figure 2. Rather, explanation C predicts a minimum of formation of *trans*-aziridine at intermediate olefin concentrations. This is not observed, dispensing with explanation C.

(D) We are left with the assumption that the azide photolysis produces initially one-third of the nitrene in the triplet state and two-thirds in the singlet state, and we will proceed to show that this is quantitatively in accord with the observed data. Under our reaction conditions, all incident light is absorbed, practically all of it by the azide. Since the reactions are not run to completion, this remains true throughout the run. Consequently, the rate of production of nitrenes remains constant. Since the olefin is used in large excess, its concentration also remains constant. The rate of formation of the nitrenes depends on the apparatus used (strength of the lamp, losses of light) but remains constant. Lumping the influence of the experimental conditions into a factor "L", and expressing the ratio of singlet and triplet formed by the ratio of two constants, s and t, we have

$$\text{azide} \xrightarrow{sL} {}^1\text{N}$$

$$\text{azide} \xrightarrow{tL} {}^3\text{N}$$

$${}^1\text{N} \xrightarrow{k_2} {}^3\text{N}$$

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(12) P. Scheiner, *J. Am. Chem. Soc.*, **88**, 4759 (1966).

$$\text{olefin} + {}^1\text{N} \xrightarrow{k_3} \text{S}$$

$$\text{olefin} + {}^3\text{N} \xrightarrow{k_4} \text{T}$$

$$ {}^3\text{N} \xrightarrow{k_5} \text{side products}$$

$$ {}^1\text{N} \xrightarrow{k_6} \text{side products}$$

Since the singlet nitrene is no longer the sole source of triplet nitrene, k_6 has to be included in our considerations. What is measured is [T]/[S]

$$\frac{[\text{T}]}{[\text{S}]} = \frac{k_4[{}^3\text{N}][\text{olefin}]}{k_3[{}^1\text{N}][\text{olefin}]}$$

$$\frac{[{}^3\text{N}]}{[{}^1\text{N}]} = \frac{k_3[\text{T}]}{k_4[\text{S}]} \tag{1}$$

using the steady-state approximations

$$\text{d}[{}^3\text{N}]/\text{d}t = tL + k_2[{}^1\text{N}] - k_4[{}^3\text{N}][\text{olefin}] - k_5[{}^3\text{N}] = 0 \tag{2}$$

and

$$\text{d}[{}^1\text{N}]/\text{d}t = sL - (k_2 + k_6)[{}^1\text{N}] - k_3[{}^1\text{N}][\text{olefin}] = 0 \tag{3}$$

and extracting from (3)

$$L = \frac{(k_2 + k_6 + k_3[\text{olefin}])[{}^1\text{N}]}{s}$$

we can substitute into (2) to obtain

$$t(k_2 + k_6 + k_3[\text{olefin}])[{}^1\text{N}] + k_2[{}^1\text{N}] = k_4[{}^3\text{N}][\text{olefin}] + k_5[{}^3\text{N}]$$

from which we find

$$\frac{[{}^3\text{N}]}{[{}^1\text{N}]} = \frac{t(k_2 + k_6 + k_3[\text{olefin}]) + sk_2}{s(k_4[\text{olefin}] + k_5)}$$

Substituting (1) and doing the arithmetic gives

$$\frac{[\text{T}]}{[\text{S}]} = \frac{t}{s} + \frac{tk_2 + tk_6 + sk_2 - (tk_3k_5/k_4)}{sk_3([\text{olefin}] + k_5/k_4)} \tag{4}$$

Equation 4 shows that our mechanistic scheme predicts a straight line for the plot of [T]/[S] against 1/([olefin] + k_5/k_4), and that the intercept of this line corresponds to t/s. Thus, our experimental results are indeed in accord with the proposed mechanism.

Trapping the triplet carbethoxynitrene with α-methylstyrene, as was done in the α-elimination and pyrolysis experiments, is unfortunately not possible in the photolytic runs. The light absorption of the α-methylstyrene prevents the decomposition of the azide. However, to derive eq 4, a steady-state assumption (3) had to be made for the singlet nitrene. Not all the triplet nitrene in the photolysis reactions is produced from the singlet, and removal of the singlet by side reactions will alter the ratio [T]/[S], which was not the case in the α-elimination[3] and pyrolysis experiments. We have shown[10b,13,14] thatt riplet carbethoxynitrene reacts only slowly or not at all with C–H bonds. This makes it possible to trap the singlet selectively.

Photolyses were run in cyclohexane rather than in dichloromethane solution. The cyclohexane was to remove part of the singlet nitrene, but leave untrapped the initially present triplet. Consequently, runs in cyclohexane should be less stereospecific than runs in dichloromethane at the same olefin concentration. Table III shows this to be true. In the α-elimination experiments,[3] all triplet is generated by intersystem crossing from singlet. Consequently, removal of singlet should not influence the degree of stereospecificity, and addition of cyclohexane should have no stereochemical effect in the α-elimination experiments. To test this prediction of our general scheme, α-elimination reactions were run with cyclohexane present. The results are shown in Table IV. Due to the insolubility of the nitrene precursor, dichloromethane had to be used as a solvent, and the solutions contained 67% of it, plus the stated concentration of *cis*-4-methylpent-2-ene and cyclohexane to 100%. Interference by side products increased the relative error to 10%.

Table III. Reaction of Carbethoxynitrene with *cis*-4-Methylpentene-2, Photolysis Route, Cyclohexane and Dichloromethane Solutions

	In cyclohexane solution			In dichloromethane	
Olefin concn, mole %	Cyclohexylurethan, % yield	Aziridines, % yield	Fraction *trans*, %	Aziridines, % yield	Fraction *trans*, %
10	35	46	49	58	35
5	33	33	54.5	57 (est)	43

Table IV. Reaction of Carbethoxynitrene with *cis*-4-Methylpentene-2, α-Elimination Route, Cyclohexane and Dichloromethane Solutions

	In cyclohexane–CH_2Cl_2 solution			In dichloromethane	
Olefin concn, mole %	Cyclohexylurethan, % yield	Aziridines, % yield	Fraction *trans*, %	Aziridines % yield	Fraction *trans*, %
5		15	30	43	26
3.3	28	12	39	38	34
1.5	26	5	47	24	43

The photolysis run at 10% olefin concentration (Table III) and the α elimination run at 3.3% olefin concentration (Table IV) have the same ratio of cyclohexane to olefin: 10. In the α-elimination run, 2.3 times as much cyclohexylurethan is formed than aziridines; much of the singlet inserts before going to triplet. In the photolysis run, the trapping effect of the cyclohexane is much lower; the ratio of cyclohexylurethan to aziridines is only 0.7. Nevertheless, the effect of this trapping on the stereochemistry of the photolysis experiment is strong: the fraction of *trans*-aziridine is raised to 49%, as compared with 34% in dichloromethane solution. The effect of cyclohexane in the α-elimination run is small, despite the fact that three times as much of the nitrene is removed. In the presence of cyclohexane, 39% of the aziridines is the *trans*

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[13] W. Lwowski and F. P. Woerner, *J. Am. Chem. Soc.*, 87, 5491 (1965).

[14] J. Simson and W. Lwowski, unpublished.

isomer, compared with 34% in dichloromethane solution. The simplest explanation seems to be that of our general scheme. In the photolyses, much triplet is initially formed, and it cannot be removed by cyclohexane because it does not insert efficiently.

The cyclohexane experiments allow one to calculate the fraction of triplet initially produced in the photolysis. One can separate the term containing k_6 (for the side reactions of the singlet) in the equation given above, to obtain

$$\frac{[\mathrm{T}]}{[\mathrm{S}]} = \frac{t}{s} + \frac{tk_2 + sk_2 - (tk_5k_3/k_4)}{sk_3([\text{olefin}] + k_5/k_4)} + \frac{t}{s}\,\frac{k_6}{k_3([\text{olefin}] + k_5/k_4)}$$

In the absence of cyclohexane, k_6 is very near zero, so that the first two terms of the equation determine [T]/[S]. Thus, the first two terms are known from experiments without cyclohexane. Addition of cyclohexane is assumed to change only the last term, and measuring the change in [T]/[S] allows it to be evaluated. To find t/s, the desired ratio of formation of triplet and singlet nitrenes, we have to know $k_6/k_3([\text{olefin}] + k_5/k_4)$.

$$^1\mathrm{N} \xrightarrow{k_6} \mathrm{U}\ (\text{cyclohexylurethan})$$

$$^1\mathrm{N} + \text{olefin} \xrightarrow{k_3} \mathrm{S}$$

thus

$$\frac{[\mathrm{U}]}{[\mathrm{S}]} = \frac{k_6}{k_3([\text{olefin}])}$$

[U] can be measured, [S] can be calculated from the yield of aziridines and the composition of the aziridine mixture, the olefin concentration is known, and k_5/k_4 is known. Using the data from the photolysis in the presence of 10 mole % olefin, t/s is found to be 0.44, the same value as found by measuring the intercept in Figure 5. Using the data from the run with 5 mole % olefin, t/s is found to be 0.35, still close to the other values found above.

Having found experimental support for the photolysis scheme in which one-third of the carbethoxynitrene is directly produced in the triplet state, we wondered what the effect of changing the temperature might be. Photolyses were run as before, in dichloromethane–olefin mixtures, but at 12° rather than at 38°. The reactions were slightly more stereospecific. The k_5/k_4 required to get a straight line was 0.007, not an unexpected value since k_5/k_4 seems to vary directly with temperature (it was 0.01 at 38° and 0.03 at 100°). The intercept was [T]/[S] = 0.35, corresponding to 26% triplet carbethoxynitrene formed directly.

The mechanism of the direct formation of triplet nitrene in the photolysis experiments is not yet clear. One could assume intersystem crossing of singlet excited azide to triplet azide, followed by loss of nitrogen from the latter, to give triplet nitrene (with spin conservation). To test this hypothesis, we tried to produce triplet excited azide by photosensitization. Earlier experiments,[4] using acetophenone, had been carried out in cyclohexene solution, but with negative results. In cyclohexene, urethan ($\mathrm{EtOOC{-}NH_2}$) was produced in 74% yield, and no substantial amounts of insertion or addition products had been found. Similarly, acetophenone sensitized decomposition of ethyl azidoformate in the presence of *cis*-4-methylpent-2-ene gave only traces of the two aziridines and large amounts of urethan. The olefin was isomerized to a 1:1 mixture of the *cis* and *trans* isomers (and probably would have been isomerized to an equilibrium mixture upon further irradiation). Possible explanation for these results are as follows. (A) The triplet azide is formed but does not give triplet nitrene (which would add to the olefin). Rather the triplet azide dehydrogenates the solvent, then loses nitrogen, to give an urethanyl radical. The latter would effect a further H· abstraction, to give urethan. If explanation A should prove true, the triplet azide could not be involved in the formation of triplet nitrene. (B) No triplet azide is formed in the sensitized reactions. A Schönberg–Schenck type sensitizer–azide complex might be formed and effect the dehydrogenation. To check this hypothesis, it is desirable to compare the reactions using a variety of different sensitizers. Unfortunately, the choice of the latter is limited. Acetophenone has just enough triplet energy to induce decomposition of ethyl azidoformate; benzophenone is ineffective. Benzene has a higher triplet energy and is structurally rather different from acetophenone, and thus seems to be an attractive choice. However, it reacts readily with the nitrene to form N-carbethoxyazepine. The problem will have to be studied further.

One could speculate that photolysis produces singlet azide or nitrene in a highly vibrationally excited state, and that either species goes to triplet nitrene very rapidly. However, nothing definite can be said before further investigations are completed.

Solvent Effects. The observed singlet–triplet change of carbethoxynitrene could be a purely intramolecular process, or it could depend on weak orbital overlap with other atoms (such as the chlorines in dichloromethane). Such a heavy atom effect has been reported by Anastassiou[15] with cyanonitrene. We have run some of the photolyses in neopentane instead of dichloromethane. The low reactivity of primary, as compared with secondary, C–H bonds[5] (about a factor of 10) makes neopentane a useful solvent. The results are shown in Table V. No heavy atom effect is discernible. In neopentane solution, where all the nitrene can come in contact with is the hydrogens on the neopentane molecule, the reactions are a little less stereospecific than in dichloromethane, where overlap with chlorines is possible. If anything, dichloromethane seems to

Table V. Photolysis of Ethyl Azidoformate in Mixtures of Neopentane and the 4-Methylpent-2-enes[a]

	—Products using *cis* olefin—			Using *trans* olefin
Olefin, mole %	Yield of neopentylurethan, %	Yield of aziridines, %	% *trans*-aziridine[b]	% *cis*-aziridine[b]
33	1.4	77	33 (28.5)	. . .
1.5	6	58	60 (54.5)	16.5 (14.7)

[a] For comparison, the results obtained in dichloromethane solution are given in parentheses. [b] In total aziridines.

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(15) A. G. Anastassiou, *J. Am. Chem. Soc.*, **88**, 2322 (1966).

stabilize the singlet, perhaps through a polar effect. Dibromomethane was tried as solvent. The photolysis reaction gave only a black mixture, still containing much azide. The α-elimination route gave low aziridine yields and large quantities of diethyl hydrazoformate. The use of dibromomethane was not pursued further.

Experimental Section

Spectral data and analyses were obtained as previously described.[3] Analyses for the composition of the product mixtures and the purity of the starting olefins and the vpc columns used have been reported,[3] as well as the syntheses of materials for comparison.[3]

Photolyses were conducted in a Rayonet photochemical reactor, consisting of 16 tubular ultraviolet lamps around the inner surface of a polished cylinder, along the axis of which the irradiation vessel is suspended. The vessel, of fused silica, can be cooled by a coldfinger. Direct photolyses were carried out with low-pressure mercury lamps, 84% of whose emission (of 12,800 μw/cm^2) is of the wavelength of 2537 A. For the photosensitized reactions, fluorescent lamps with maximum emission at 3500 A and thick-walled Pyrex vessels were used.

Thermolysis of Ethyl Azidoformate in *cis*-4-Methylpent-2-ene. Solutions of 0.1 g (0.0009 mole) of ethyl azidoformate[4] in 2 ml of *cis*-4-methylpent-2-ene were heated in sealed tubes in a boiling water bath. After the reaction, the contents were analyzed on columns A and B as described before.[3] Analysis of the solvent showed that isomerization had occurred to less than 1%. The results are summarized in Table VI.

Table VI

Reaction time, hr	Yield of **4** + **7**, %	**7** in (**4** + **7**), %
8	30	13.7
24	67	14
49	60	14.1

Thermolysis of Ethyl Azidoformate in Olefin–Dichloromethane Solutions. Dichloromethane solutions of *cis*-4-methylpent-2-ene (in more than 15-fold excess) and ethyl azidoformate were thermolyzed as above, for 24 hr (for the results, see Table I and Figure 2).

Thermolysis in the Presence of α-Methylstyrene. A solution of 0.0484 g (0.00042 mole) of ethyl azidoformate, 0.71 ml of *cis*-4-methylpent-2-ene, and 0.73 ml of α-methylstyrene (3.3 mole % each) in 10 ml of dichloromethane was heated in a sealed tube to 100° for 24 hr. The contents were analyzed as before. A total yield of 15% of aziridines was found, consisting of 4.4% *trans* and 95.6% *cis* isomer.

Photolysis of Ethyl Azidoformate in *cis*- and *trans*-4-Methylpent-2-ene. A solution of 1.0 g (0.0087 mole) of ethyl azidoformate in 20 ml of *cis*-4-methylpent-2-ene was irradiated until nitrogen evolution ceased (13.5 hr). Analysis on columns A and B showed a total aziridine yield of 70%, the mixture containing 26% of the *trans* isomer. Analysis of the excess olefin on column F showed that isomerization was less than 1%. A similar irradiation of the *trans* olefin gave a mixture of aziridines containing 6.4% of the *cis*-aziridine. An irradiation in *cis* olefin was carried only to 13% conversion, the aziridine mixture produced contained 24.5% of the *trans* isomer. Another experiment employing a five times greater azide concentration (0.5 g in 2 ml of olefin) gave, from the *cis* olefin, an aziridine mixture containing 26% *trans* isomer. Thus, within experimental error, the changes in conditions do not influence the degree of stereospecificity.

Photolysis of Ethyl Azidoformate in Olefin–Dichloromethane Solutions. A. Prolonged Irradiation. A solution of 0.50 g (0.0044 mole) of ethyl azidoformate in 200 ml of a 1.5 mole % solution of *cis*-4-methylpent-2-ene in dichloromethane was irradiated for 16.5 hr. Analysis on columns A, B, and C showed only a small yield of aziridines **4** and **7**, three other components in at least the quantities of the combined aziridines, and six minor components. Most abundant of the former three was **8** (see below).

B. Short Irradiation. Solutions of about 0.1 g (0.0009 mole), in 20 ml solvent, consisting of *cis*- or *trans*-4-methylpent-2-ene in dichloromethane, were irradiated for 1.5 hr. The temperature of the solution, during irradiation, was close to the boiling point of dichloromethane (38°). Analyses were done as before, and it was shown that the olefin isomerization was less than 3%. The results are shown in Table II.

Low-temperature irradiations were carried out by pumping a cooling fluid through a cold finger in the irradiation vessel, with otherwise unchanged conditions. The results are listed in Table VII.

Table VII

cis olefin, mole %	Temp, °C	Irradiation time, hr	% *trans*-aziridine in total aziridines
100	11	4	19
100	12	2	19
33	12	1.5	24.5
33	5	1.5	25.5
10	12	1	33
10	5	1.5	32.5
3.3	12	1.5	43.5
3.3	5	1	42.5
1.5	12	1.5	53

Photosensitized Decomposition of Ethyl Azidoformate in *cis*-4-Methylpent-2-ene. A solution of 1.1 g (0.0095 mole) of ethyl azidoformate, and 2.3 g (0.019 mole) of acetophenone in 20 ml of *cis*-4-methylpent-2-ene was irradiated in a 3-mm-walled Pyrex vessel with lamps (RPR-3500) which emit 90% of their light between 3200 and 4100 A. After 210 hr, 75% of the theoretical amount of nitrogen had been evolved. Analysis on column F showed that the olefin had been changed to a 1:1 mixture of the *cis* and *trans* isomers. Very little aziridine was found, but urethan was present in large amounts and was identified by comparison of its infrared spectrum and vpc retention time with those of an authentic sample.

Photolysis of Ethyl Azidoformate in Olefin–Cyclohexane. A solution of 0.205 g (0.0018 mole) of ethyl azidoformate and 2.3 ml of *cis*-4-methylpent-2-ene in 17.7 ml of cyclohexane (10 mole % olefin) was photolyzed for 3.5 hr. Isomerization of the olefin occurred to less than 1%. The yield of cyclohexylurethan was determined on column A, at 175°. Analysis of the other components (at 112°) was done as usual. Photolysis for 2 hr of a solution of 0.114 g (0.001 mole) of ethyl azidoformate, 1.5 ml of *cis*-4-, ethylpent-2-ene, and 18.7 ml of cyclohexane provided the values for 5 mole % olefin concentrations, as shown in Table III.

Carbethoxynitrene by α Elimination in Cyclohexane–Dichloromethane–Olefin Solutions. The nitrene precursor, N-(*p*-nitrobenzene)sulfonoxyurethan, was decomposed as described earlier[3] in the dichloromethane–cyclohexane–olefin mixtures listed in Table IV. The cyclohexylurethan yield was measured on column A at 170°, **4** and **7** as usual. Infrared analysis showed **4**, as collected from the gas chromatograph, to be only about 90% pure. The values were corrected for this impurity, but the probable error associated with them is larger than in the other experiments, particularly so in the run with 1.5 mole % olefin.

Thermolysis of *trans*-N-Carbethoxy-2-isopropyl-3-methylaziridine (7). Two 50-μl samples of **7** were sealed in glass tubes. One was heated to 150° for 24 hr, the other to 225° for 3.5 hr. Analysis of the latter on column B showed that nearly all of the aziridine had disappeared; analysis of the sample heated to 150° showed a 1:1 mixture of **7** and the new compound. From its infrared and nmr spectra, the new compound was assigned the structure **9**; infrared spectrum: NH at 3460 cm^{-1} (sharp) and 3365 (broad), carbonyl at 1715, olefinic C–H at 3090, C=C at 1645 cm^{-1}; nmr spectrum (in δ values): 0.90 (isopropyl-CH$_3$, doublet, 6.0 H), 1.22 (ethoxy-CH$_3$, triplet, 3.4 H), 1.4–1.8 (isopropyl-CH, multiplet, 1.5 H), 4.04 (ethoxy-CH$_2$, quartet), 3.8–4.2 (N–C–H, multiplet, together with CH$_2$, 3.0 H), and 4.8–5.8 (olefinic CH and NH, multiplet, 3.6–4.5 H).

Irradiation of *cis*-N-Carbethoxy-2-isopropyl-3-methylaziridine (4) in Dichloromethane. A solution of 0.1 ml of **4** in 2 ml of dichloromethane was irradiated for 13 hr. Only a trace of **4** remained, some **9** had been formed, as identified by its infrared spectrum, and a new compound was the main product. Its infrared, nmr, and mass spectra indicate that it has the structure **8**, 3-(2-chloro-4-

methylpentyl)urethan; infrared spectrum: N-H at 3450 cm^{-1} (sharp) and 3350 (broad), carbonyl at 1715 cm^{-1}; nmr spectrum: (in δ values): 0.99 (isopropyl-CH$_3$, doublet, 6.0 H), 1.22 (ethoxy-CH$_3$, triplet, 3.1 H), 1.50 (CH$_3$ at C-1, doublet, 3.1 H), 1.5–2.1 (isopropyl-CH, multiplet, 1.7 H), 4.47 (N–C–H, triplet, 1.0 H), 4.08 (ethoxy-CH$_2$, quartet), 4.0–4.5 (Cl–C–H, multiplet, CH$_2$ + CH, 3.2 H), and 5.17 (N–H, doublet, 1.0 H).

The mass spectrum showed a parent peak at *m/e* 207 (as expected) and a base peak at 164, corresponding to the loss of CH(CH$_3$)$_2$, leaving the ion CH$_3$-CHCl-C$^+$H-NHCOOEt. Calcd for C$_6$H$_{11}$ClNO$_2$ (ratio of M + 2 to M): 32.4. Found: 31.8. Also, a major peak at 144, corresponding to the loss of H$_3$C–CHCl, was shown, leaving the ion (H$_3$C)$_2$CH–C$^+$H–NHCOOEt. Calcd for C$_7$H$_{14}$NO$_2$ (ratio of M + 1 to M): 8.2. Found: 8.3.

Neopentylurethan was prepared from neopentylamine (0.35 g, 0.040 mole), ethyl chloroformate (0.04 mole), and triethylamine (0.04 mole) in 15 ml of anhydrous ether with cooling. Analysis on column B showed neopentylurethan to be the only ether-soluble product. The neopentylamine had been prepared by reduction of pivalamide with lithium aluminum hydride; infrared spectrum: N–H at 3470 cm^{-1} (sharp) and 3370 (broad), carbonyl at 1720 cm^{-1}; nmr spectrum (in δ values): 0.90 (*t*-butyl-CH$_3$, singlet, 9.0 H), 1.20 (ethoxy-CH$_3$, triplet, 3.3 H), 2.93 (methylene-CH$_2$, doublet, 2.0 H), 4.08 (ethoxy-CH$_2$, quartet, 2.0 H), and 5.3–6.0 (N-H, broad, 1.0 H).

Anal. Calcd for C$_8$H$_{17}$NO$_2$: C, 60.34; H, 10.76; N, 8.80. Found: C, 60.41; H, 10.90; N, 8.85.

Photolysis of Ethyl Azidoformate in Neopentane. Ethyl azidoformate (0.5 g, 0.004 mole) was placed in a 20-ml silica tube, fitted with a fused silica insulating jacket, and a dewar-type condenser filled with ice–salt mixture. Neopentane (Matheson, 99+% pure) was condensed into the tube, to a volume of 10 ml. Boiling of the neopentane served to mix the components. The solution was irradiated for 3 hr, under reflux. The residue was analyzed on column B at 120°. The two major components were undecomposed ethyl azidoformate and neopentylurethan.

Photolysis of Ethyl Azidoformate in Olefin–Neopentane. Solutions of 0.1 g of ethyl azidoformate in 30–36 ml of the appropriate solutions of *cis*- or *trans*-4-methylpent-2-ene in neopentane were photolyzed for 3 hr, as above, and the reaction residues analyzed on columns A and B. The results are found in Table V.

Acknowledgment. We are greatly indebted to the National Science Foundation for support of this work by Grant GP 3846, and to the National Institutes of Health for a Predoctoral Fellowship to J. S. M.

Small Charged Rings. IX.[1] Expansion of the Azirine Ring[2]

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Abstract: The ring expansion of an azirine has been effected, proceeding through the azirinium salt, generated *in situ*, as a probable intermediate. The representative azirine, 3,3-dimethyl-2-phenyl-1-azirine, on treatment with acetone and perchloric acid (or fluoroboric acid), formed an oxazolinium salt, 4-phenyl-2,2,5,5-tetramethyl-3-oxazolinium perchlorate (or fluoroborate), identified by infrared, ultraviolet, and nmr spectra, and by hydrolysis to ammonium perchlorate and benzoyl dimethyl carbinol. Using deuterium-labeled acetone, it was possible to determine how this moiety took its place in the five-membered ring product: by a mechanistic pathway following 1,3-bond cleavage in the original azirine. The corresponding base, 4-phenyl-2,2,5,5-tetramethyl-3-oxazoline, was obtained from the perchlorate by treatment with alkali. 3,3-Dimethyl-2-phenyl-1-azirine and perchloric acid in ethyl methyl ketone furnished 2-ethyl-4-phenyl-2,5,5-trimethyl-3-oxazolinium perchlorate. The ring expansion of the same azirine with perchloric acid in acetonitrile yielded the hydrated form of 5-phenyl-2,4,4-trimethyl-4H-isoimidazolium perchlorate, namely, 4-hydroxy-4-phenyl-2,5,5-trimethyl-2-imidazolinium perchlorate, the structure of which was established by spectroscopy, by hydrolysis and hydrogenation products, and by chemical interconversions with 4-ethoxy-4-phenyl-2,5,5-trimethyl-2-imidazolinium perchlorate and 4-isopropoxy-4-phenyl-2,5,5-trimethyl-2-imidazolinium perchlorate, the latter also being made independently by ring enlargement of 3,3-dimethyl-2-isopropoxy-2-phenylaziridine in acetonitrile with perchloric acid generated *in situ*. By the use of ^{15}N-labeled acetonitrile in the case of the azirine and mass spectrometric analysis of the product it was possible to determine that the path of incorporation in the final product necessitated cleavage of the 1,3 bond in the azirine. By contrast, the perchloric acid catalyzed methanolysis of 3,3-dimethyl-2-phenyl-1-azirine resulted effectively in 1,2-bond cleavage. Additional ring expansion reactions were realized in the conversion of 3,3-dimethyl-2-methoxy-2-phenyloxirane to 4-methoxy-4-phenyl-2,5,5-trimethyl-2-oxazolinium perchlorate with acetonitrile and perchloric acid and of 3,3-dimethyl-2-isopropoxy-2-phenylaziridine to 5-isopropoxy-5-phenyl-2,2,4,4-tetramethyloxazolidinium perchlorate with acetone and acid.

The ring expansion of aziridinium salts with aldehydes,[3] ketones,[4] and nitriles[5,6] comprises a general family of reactions resulting in the conversion of positively charged three-membered rings to five-membered rings (③$^{+}$ + 2 → ⑤$^{+}$). We have extended our study on small-ring heterocycles by taking an azirine under consideration. The azirines, and the related possible azirinium salts, are of special interest because of their comparative relation to aziridinium salts, since the

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[1] (a) For the preceding article in this series, see N. J. Leonard, R. Y. Ning, and R. L. Booth, *J. Org. Chem.*, **30**, 4357 (1965). (b) The substance of this article has been presented at the 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965, Abstracts, p 19S, and at the 1st Annual Midwest American Chemical Society Meeting, Kansas City, Mo., Nov. 1965, Abstracts, p 40. (c) N. J. Leonard, *Record Chem. Progr.* (Kresger-Hooker Sci. Lib.), **26**, 211 (1965).

[2] This investigation was supported by a research grant (GP 2012) from the National Science Foundation, to whom we are pleased to acknowledge our thanks.

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