Singlet and Triplet Nitrenes. I. Carbethoxynitrene Generated by α Elimination

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Abstract: Carbethoxynitrene was generated by α elimination and the stereospecificity of its addition to *cis*- and *trans*-4-methylpentene-2 was investigated. The addition is the less stereospecific the lower the olefin concentration. The data fit quantitatively a scheme in which all the nitrene is generated in the singlet state, and then decays to triplet in competition with addition to the olefin. Both singlet and triplet add, the former stereospecifically, the latter completely nonstereospecifically. Triplet carbethoxynitrene can be trapped by α-methylstyrene, with which it reacts at least 85 times faster than with *cis*-4-methylpentene-2. Decay of the singlet nitrene to triplet is about one-thirtieth as fast as addition to the *cis* olefin. The structure of an α-methylstyrene dimer is revised.

Nitrenes[3] have long been discussed as intermediates in organic chemistry,[4,5] and the subject has been reviewed.[6-8] For a species $R{-}\dot{N}{:}$, singlet and triplet states are possible. The singlet with two paired sets of free electrons on the nitrogen, or the triplet with one pair and two electrons of parallel spins, might *a priori* be the ground state of a given nitrene. However, a nitrene need not be generated in its ground state, and it might well react before it reaches the ground state. Thus, beyond ascertaining the nature of the ground state, one has to determine the electronic state of the nitrene in a given chemical reaction before one can give a detailed mechanism for it.

Electron spin resonance studies have shown that the triplet is the ground state for a number of nitrenes,[9-12] including carbethoxynitrene.[13] The ultraviolet spectra of aromatic triplet nitrenes have also been reported.[14] Much less information is available for the electronic state of nitrenes at the moment of their chemical reaction. Attempts have been made to correlate chemical behavior with electronic multiplicity—radical character has been ascribed to the triplet species—but such correlations are not unequivocal.

In an attempt to determine the electronic state of carbethoxynitrene at the moment of reaction, we have investigated the stereochemistry of the nitrene's addition to *cis*- and *trans*-4-methylpentene-2. This is an extension into the nitrene field of a method developed by Skell[15] for carbenes. This method, although it caused much controversy,[16] works very well with carbenes. Skell proposed that addition of singlet species to an olefin should produce the three-membered ring adduct in one single step, thus in a stereospecific fashion. A triplet species, however, should first form an open-chain triplet diradical. This is supposed to establish conformational equilibrium, by rotation around the former double bond, much faster than close to the three-membered ring. Skell assumed that the delay in ring closure is due to the necessity of inversion of one of the spins of the triplet diradical. An alternative explanation by Hoffmann[17] does not alter the stereochemical consequences. Written for a nitrene, Skell's scheme is shown in Figure 1.

In the following, we want to show that Skell's scheme explains our data not only qualitatively, but quantitatively as well. Strictly speaking, what we observe is a "stereospecifically adding carbethoxynitrene" and a "nonstereospecifically adding carbethoxynitrene." Our final conclusion is that these can be identified with the singlet and triplet species, respectively. To make the discussion less awkward, we shall call them singlet and triplet from the beginning.

After completion of the work described here, Scheiner[18] presented data which independently support the validity of Skell's scheme, applied to aziridine formation. Scheiner obtained diradical intermediates, of the type shown in Figure 1, not by addition of a nitrene to an olefin, but by direct and by sensitized photodecomposition of triazolines. Direct photolysis gave aziridines stereospecifically, perhaps *via* a singlet diradical, perhaps by a concerted process. Photosensitized decomposition gave aziridines nonstereospecifically, presumably *via* triplet diradical intermediates.

Results and Discussion

Carbethoxynitrene, EtO–CO–N, was generated by

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[3] The name "nitrene" for species R–N is most often used, but is still controversial. The objection that systematic nomenclature reserves the ending -ene for unsaturated compounds can perhaps be met by dropping the last "e," and calling the species "nitren." This would be analogous to the change of "urethane" to "urethan," for the same reason.

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[5] J. Stieglitz, *Am. Chem. J.*, **18**, 751 (1896).

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[7] L. Horner, *ibid.*, **75**, 707 (1963).

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[10] G. Smolinsky, L. C. Snyder, and E. Wasserman, *Rev. Mod. Phys.*, **35**, 576 (1963).

[11] E. Wasserman, G. Smolinsky, and W. A. Yager, *J. Am. Chem. Soc.*, **86**, 3166 (1964).

[12] R. M. Moriarty, M. Rahman, and G. J. King, *ibid.*, **88**, 842 (1966).

[13] E. Wasserman, private communication.

[14] A. Reiser and V. Frazer, *Nature*, **208**, 682 (1965); A. Reiser, H. Wagner, and G. Bowes, *Tetrahedron Letters*, 2635 (1966).

[15] P. S. Skell and R. C. Woodworth, *J. Am. Chem. Soc.*, **78**, 4496 (1956); R. C. Woodworth and P. S. Skell, *ibid.*, **81**, 3383 (1959).

[16] *Cf.* P. P. Gaspar and G. S. Hammond in "Carbene Chemistry," W. Kirmse, Ed., Academic Press Inc., New York, N. Y., 1964, p 259 ff.

[17] R. Hoffmann, *Trans. N. Y. Acad. Sci.*, [2] **28**, 75 (1966).

[18] P. Scheiner, *J. Am. Chem. Soc.*, **88**, 4759 (1966).

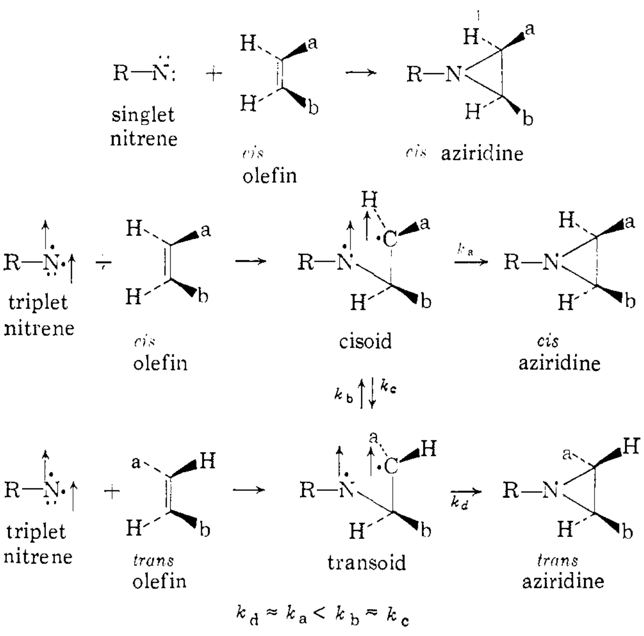


Figure 1.

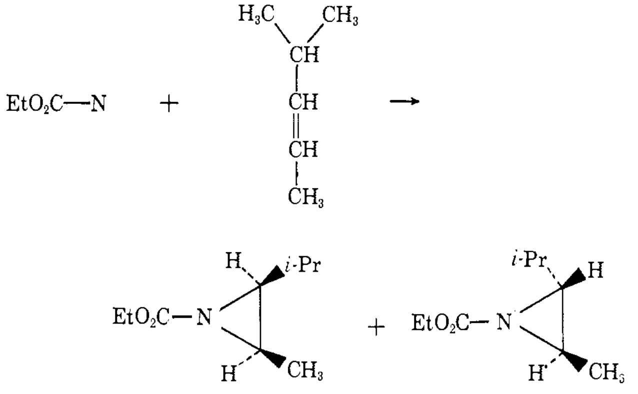
photolysis[19] and thermolysis[19,20] of ethyl azidoformate and by base-induced, α-elimination of arylsulfonate ion from N-(*p*-nitrobenzenesulfonyloxy) urethan.[21,22] Especially the latter reaction is expected to give initially the singlet carbethoxynitrene, since nonconservation of electron spin seems unlikely in a room-temperature ionic reaction.

$$\underset{\text{I}}{p\text{-}O_2NC_6H_4SO_2ONHCOOEt} + Et_3N: \rightleftharpoons \underset{\text{II}}{ArSO_2\bar{N}COOEt} + Et_3{}^+NH \xrightarrow{\text{slow}} ArSO_3^- + Et_3{}^+N + \underset{\text{III}}{N\text{—}COOEt}$$

Owing to the insolubility of the nitrene precursor I, the α-elimination method cannot be used in pure hydrocarbons, and a solvent, usually dichloromethane, was employed. Dichloromethane is quite inert toward the nitrene, as shown by the observation[23] that a 35% yield of aziridine was obtained from carbethoxynitrene in a 0.2 mole % solution of cyclohexene in dichloromethane. *cis*- and *trans*-4-methylpentene-2 were employed as the olefins, mostly because they are liquids and are commercially available. As communicated earlier,[24] the degree of stereospecificity of the aziridine formation is strongly dependent on the olefin concentration. Even in pure olefin, the addition is not fully stereospecific. While our work was in progress, Hafner reported[25] that the photolysis of methyl azidoformate in *cis*-and *trans*-2-butene gave 87% *cis*-plus 13% *trans*-aziridines in the former case, and 8% *cis* and 92% *trans* in the latter. During the progress of our work, studies of the dependence of stereospecificity of addition on substrate concentration have been carried out on fluorenylidene,[26] dicyanocarbene,[27] and cyanonitrene.[28]

The imperfect stereospecificity cannot be attributed to secondary reactions. The stability of the starting olefins and the products under the reaction conditions was established both by independent experiments and by taking samples during early and late stages of individual runs, and comparing the ratios of *cis* and *trans* products. Both olefins and the products were stable under the conditions employed.

Making carbethoxynitrene by α elimination in dichloromethane solutions of *cis*- and *trans*-4-methylpentene-2 gave, as the main products, mixtures of *cis*- and *trans*-1-carbethoxy-2-isopropyl-3-methylaziridine.



cis IV

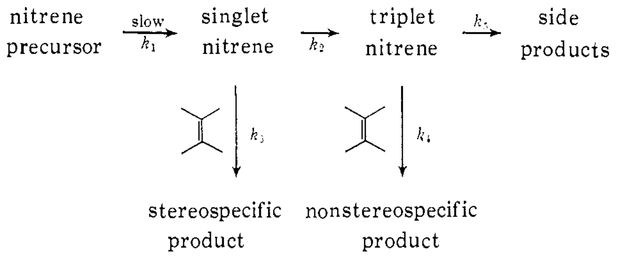
trans V

Table I gives yields and compositions of the aziridine mixtures obtained at olefin concentrations between 33 and 1.5 mole %. It is clear that the data of Table I are in qualitative agreement with Scheme I.

Table I. Addition of Carbethoxynitrene to *cis*- and *trans*-4-Methylpentene-2, α-Elimination Route, Dichloromethane Solutions

	From *cis* olefin, %		From *trans* olefin, %
Mole % olefin	Yield of aziridines	Fraction of *trans* product	Fraction of *cis* product
33	57	7.8	2.6
10	50	17.5	
5		26	8.0
3.3	38	34	
2.5		37.5	
1.5	24	43	12.3

Scheme I



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

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(24) W. Lwowski and J. S. McConaghy, Jr., *ibid.*, **87**, 5490 (1965).

(25) K. Hafner, W. Kaiser, and R. Puttner, *Tetrhaedron Letters*, 3953 (1964).

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(28) A. G. Anastassiou, *ibid.*, **88**, 2322 (1966).

If the proposed Scheme I holds true, the fraction of nonstereospecific reaction should depend only on the average time that elapses from the formation of a carbethoxynitrene molecule to its consumption. The singlet nitrene should produce only one geometric isomer of the aziridine from each (*cis* or *trans*) olefin; the nonstereospecific triplet reaction should produce the two geometric isomers from either olefin. The fraction of triplet reaction can be calculated from our experimental data if one assumes that the nonstereospecificity is total, *i.e.*, that the composition of the aziridine mixture produced by the triplet depends solely on the position of the equilibrium of the two conformers of the open-chain diradical intermediate of Figure 1, and not on the nature (*cis* or *trans*) of the starting olefin used. In the following discussion, we will show that, on the basis of the above assumption, and on Scheme I, our experimental data can indeed be correlated.

In any given experiment, a fraction of the nitrene is present as the triplet, and will produce (nonstereospecifically) a fraction of the total aziridines obtained. This fraction (different for each substrate concentration) is called X. The aziridine produced by the triplet nitrene is a mixture of *trans* and *cis* isomers; the ratio *trans*:*cis* should be constant (see preceding paragraph) and the fraction of *trans*-aziridine in this mixture is called Y. The values of X for each experiment and the value of Y are to be determined from the experimental data: the fractions of *trans*-aziridine in the aziridine mixture from *cis* olefin, called A (and depending on olefin concentration), and the fractions of *cis*-aziridine in the aziridine mixtures produced from *trans* olefin (also depending on olefin concentration) which we will call B. A and B will always be smaller than X, because some of the nonstereospecific reaction will produce the same aziridine isomer that is produced stereospecifically by the singlet nitrene. With Y being constant, we have

$$A = XY \qquad (1)$$

(experiments starting with the *cis* olefin)

and

$$B = X(1 - Y) \qquad (2)$$

(experiments starting with *trans* olefin, the fraction of *cis*-aziridine in the "nonstereospecific mixture" being $1 - Y$)

Adding eq 1 and 2 gives

$$A + B = X \qquad (3)$$

and substituting (3) into (1) gives

$$Y = A/(A + B) \qquad (4)$$

Since Y is supposed to be constant, $A/(A + B)$ and consequently A/B are also supposed to be constant. However, A is obtained from investigation of reactions of the *cis* olefin, and B from the *trans* olefin. To select proper values of (concentration-dependent) A and B to form a series of A/B values and to check for their concentration independence, it is not enough to compare A and B values obtained at the same concentrations of *cis* and *trans* olefins, respectively. One has to take into account the different reactivities of the two olefins toward the nitrenes. In our reaction Scheme I a competition is set up between k_2 and k_3[olefin]. When using olefins of different reactivity, the latter term contains different k_3 values, and it becomes necessary to know the ratio of $k_{3,trans}:k_{3,cis}$. This ratio was determined by direct competition, using a mixture of 10 mole % *cis*, 20 mole % *trans*-4-methylpentene-2, and 70 mole % dichloromethane. The ratio of reactivities at these particular olefin concentrations was found to be *trans*:*cis* = 0.7. Since the singlet:triplet ratio of carbethoxynitrenes is supposed to change with olefin concentration, one might anticipate that the reactivity ratio would also depend on olefin concentration. Fortunately, there is little or no such dependence. The values for A and B were plotted *vs.* olefin concentration, and A at a given concentration was compared with the B at 1/0.7 of that concentration. The values for A/B so obtained vary from 3.7 to 4.15 for concentrations from 33 to 1.5 mole %, and no clear trend is observed. Thus, the ratios of reactivities of *cis* and *trans* olefins seem to be nearly the same for the reactions with singlet and triplet carbethoxynitrene. The average of these reactivity-corrected A/B values is 3.9; thus Y is found to be 0.80 and the fraction of transoid open-chain diradical intermediate in our case is 80%. X, the fraction of triplet reaction, then is calculated as $A/0.8$ or $X = 1.25A$. X equals 1.25 times the fraction of *trans*-aziridine in the aziridine mixture produced from *cis* olefin. It may be mentioned here that the average value for A/B obtained from experiments with photolytically generated nitrene (100 and 1.5 mole % olefin) is 3.87. The relation $X = 1.25A$ is sufficiently accurate for our further use, since a 10% error in the ratio A/B would lead only to a 3% error in the factor 1.25.

If we use Scheme I, neglect side reactions of the triplet (k_5), and call the aziridine from singlet nitrene S, the aziridine mixture from the triplet nitrene T, the singlet nitrene N, the triplet nitrene ^{3}N, and assume that nitrene production is the slow reaction step, then

$$d[T]/dt = k_4[^3N][\text{olefin}]$$

$$d[S]/dt = k_3[N][\text{olefin}]$$

$$(d[T]/dt)/(d[S]/dt) = k_4[^3N]/k_3[N]$$

and with $d[^3N]/dt = 0$

$$d[^3N]/dt = k_2[N] - k_4[^3N][\text{olefin}] = 0$$

$$[^3N]/[N] = k_2/k_4[\text{olefin}]$$

and

$$(d[T]/dt)/(d[S]/dt) = k_4k_2/k_3k_4[\text{olefin}] = k_2/k_3[\text{olefin}]$$

with the olefin concentration constant throughout the run

$$[T]/[S] = k_2/k_3[\text{olefin}]$$

Consequently, a plot of [T]/[S] *vs.* 1/[olefin] should give a straight line with the slope k_2/k_3. Table II gives the data used to construct Figure 2.

The curve in Figure 2 follows the predicted straight line only down to about 3 mole % olefin. In our computation, k_5 was neglected; that is, the assumption was made that all triplet nitrene produced is quantitatively converted to aziridines. At low olefin concentrations, this seems not nearly to be true, and the scheme has to be refined. It is not necessary to take into account side

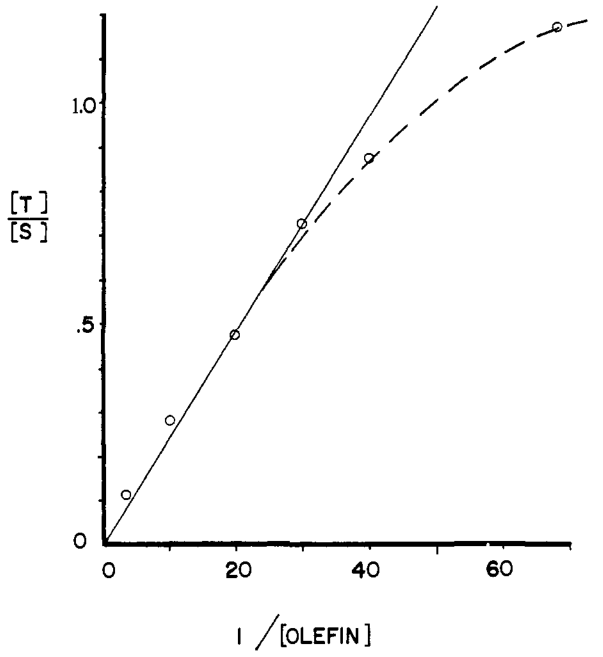


Figure 2.

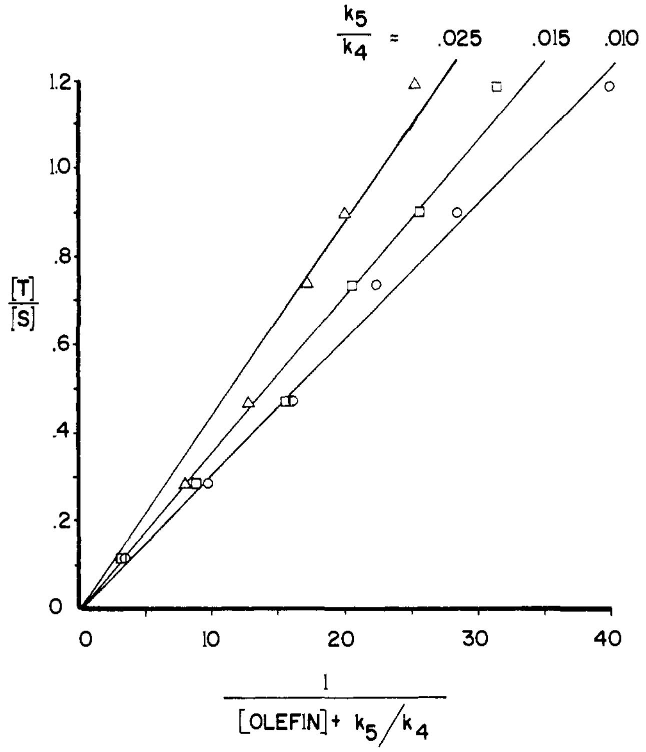


Figure 3.

reactions of the singlet nitrene, since the steady-state assumption $d[N]/dt = 0$ was not needed in the calculations made above. However, the assumption $d[^3N]/dt = 0$ was made, and side reactions of the triplet nitrene have to be considered. Adding the reaction

$$^3N \xrightarrow{k_5} ?$$

is indeed all that is required to obtain a straight line in Figure 2. The reaction or reactions described by k_5 could be those of the triplet nitrene with solvent. Rearrangement or dissociation of the triplet nitrene, as well as return to the singlet state, could also be contained in k_5. With the new reaction, we have

Table II. Addition of Carbethoxynitrene to *cis*-4-Methylpentene-2, α-Elimination Route, Dichloromethane Solution, Reduced Data

$[\text{Olefin}]^{-1}$	A	[T]	[S]	[T]/[S]
3	0.078	0.098	0.90	0.11
10	0.175	0.22	0.78	0.28
20	0.26	0.325	0.675	0.48
30	0.34	0.425	0.575	0.74
40	0.375	0.47	0.53	0.89
67	0.43	0.54	0.46	1.18

$$d[^3N]/dt = k_2[N] - k_4[^3N][\text{olefin}] - k_5[^3N] = 0$$

In the same way as above, this yields

$$[T]/[S] = k_2/\{k_3([\text{olefin}] + k_5/k_4)\}$$

Thus, a plot of [T]/[S] *vs.* $1/([\text{olefin}] + k_5/k_4)$ should now give a straight line. To find k_5/k_4, the logarithms of all our [T]/[S] values were plotted against log $1/([\text{olefin}] + x)$ and various values tried. With $x = 0.01$ to 0.025, straight lines could be drawn that passed through the error boxes of all points. The best fit seems to be given by $k_5/k_4 = 0.015$. Figure 3 shows plots with k_5/k_4 taken as 0.01, 0.015, and 0.025. The slopes of the lines in Figure 3 correspond to k_2/k_3, the ratio of the (first-order) rate constant of singlet–triplet conversion and the (second-order) rate constant for the singlet addition to *cis*-4-methylpentene-2. If k_5/k_4 is taken to be 0.015 ± 0.005, the k_2/k_3 is equal to 0.036 ± 0.004. Thus it appears that the addition of the singlet nitrene is about 30 times as fast as the decay to triplet.

The quantitative compatibility of the observed data with a scheme based on singlet–triplet conversion competing with the addition of singlet to olefin is encouraging, but does not itself prove the validity of the scheme. To provide independent evidence, attempts were made to trap the triplet nitrene selectively.

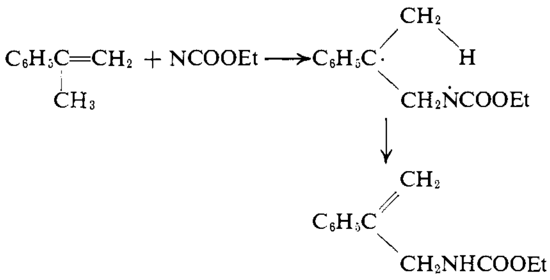
Trapping of Triplet Carbethoxynitrene. The reactions reported above were done in degassed solutions under nitrogen. Changing to solutions saturated with oxygen resulted in slightly more stereospecific addition (at 3.3 mole % olefin concentration), but the change was not large enough to be convincing. Since the first intermediate in the addition of the triplet nitrene to an olefin is supposed to be a diradical, we tried next an addend which would give a highly stabilized diradical, hoping that this stabilization might be reflected in the transition state enough to lead to very fast addition. Our choice was α-methylstyrene, which we did not expect to be particularly reactive toward the singlet nitrene. Indeed, addition of 3.3 mole % of β-methylstyrene to an otherwise unchanged run with 3.3 mole % *cis*-4-methylpentene-2 in dichloromethane gave a 16% yield of *cis*-1-carbethoxy-2-isopropyl-3-methylaziridine, and only a trace of the *trans* isomer. Without the α-methylstyrene, the reaction gave a 25% yield of the *cis*- and a 13% yield of the *trans*-aziridine. A similar experiment, using 1.5 mole % each of α-methylstyrene and *cis*-4-methylpentene-2, gave an aziridine mixture containing at the most 2.1% of the *trans* compound. Thus, the α-methylstyrene reduced the yield of the *cis* aziridine by a factor of 1.6, but the yield of *trans* product by a factor of greater than 30 (at 3.3 mole % concentration). The simplest explanation is that the triplet nitrene is removed because its reaction rate with α-methylstyrene is much greater than that of the singlet. If Scheme I is extended by the reaction

$$^3N + \alpha \xrightarrow{k_\alpha} \text{products}$$

where α stands for α-methylstyrene, then a treatment analogous to the one used above gives

$$[T]/[S] = k_2/\{k_3([\text{olefin}] + k_5/k_4) + k_\alpha[\alpha]/k_4\}$$

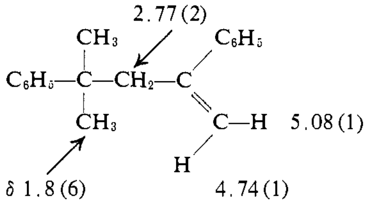
All values except $k_\alpha[\alpha]/k_4$ are known, and k_α/k_4 is calculated to be 86 (using $A = 0.021$ and $[T]/[S] = 0.027$). It appears that α-methylstyrene is 86 times more reactive toward triplet carbethoxynitrene than is *cis*-4-methylpentene-2. Since the 2.1% *trans*-aziridine in the product mixture is the maximum value, the rate factor for the α-methylstyrene might be greater. Our results agree very well with Skell's contention that the transition state in the triplet addition has much radical character. The nature of the product from α-methylstyrene and carbethoxynitrene supports this further. The aziridine corresponding to nitrene addition to the α-methylstyrene could not be found. The main product was a 1:1 adduct, 3-carbethoxyamino-2-phenylpentene-1 (VI). Its structure was established by its nmr and infrared spectra, elemental analysis, and independent synthesis. Presumably, VI is formed not by direct insertion into the methyl group, but *via* a diradical intermediate.



VI

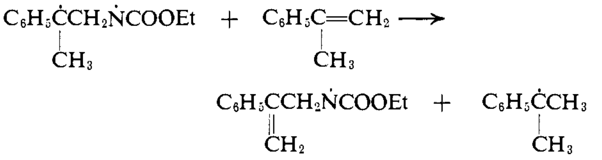
The possibility that VI is a decomposition product of the aziridine formed from α-methylstyrene was not rigorously excluded, but it was shown that VI is present in the reaction mixture before the gas chromatographic separation.

The Unsaturated Dimer of α-Methylstyrene. Vpc analysis of the product mixture from α-methylstyrene and carbethoxynitrene (produced by α elimination) revealed a further major product, which was found in the presence as well as in the absence of *cis*-4-methylpentene-2 in the reaction mixtue. The new product proved to be identical with the "liquid dimer" or "unsaturated dimer" of α-methylstyrene. This dimer had been characterized by Bergmann[29] and later by Hukki,[30] and had been assigned the structure of 2,4-diphenyl-4-methylpentene-2 on the basis of ozonization studies.[29] Hukki observed 2,4-ditoyl-4-methylpentene-1 among the products of the (analogous) acid-induced dimerization of α,*p*-dimethylstyrene, and proposed that the corresponding terminal olefin also might be present in the product from acid-induced dimerization of α-methylstyrene, and that Bergmann might have overlooked it. We prepared the α-methylstyrene dimer by Hukki's method, and found it to have vpc retention time, infrared, and nmr spectra identical with the product from the reaction of our nitrene with α-methylstyrene in dichloromethane. The vpc analysis shows that little or no isomeric olefin is present, and the nmr spectrum shows two nonequivalent vinyl protons. This, and the rest of the spectral data, establish the structure of the liquid, unsaturated α-methylstyrene dimer as 2,4-diphenyl-4-methylpentene-1.

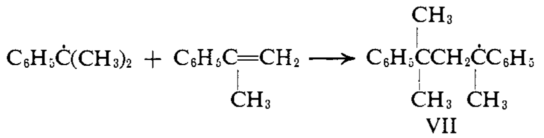


A broad multiplet representing the ten aromatic protons is centered around δ 7.1.

As shown by a control experiment, the strongest acid present in our system, triethylammonium ion, does not convert α-methylstyrene to the dimer. In our case, it is probably formed by a radical chain mechanism, such as

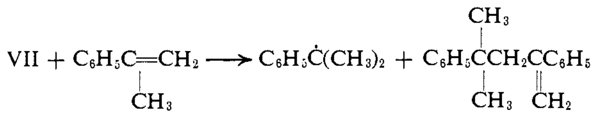


$$\underset{\substack{|\\ CH_3}}{C_6H_5\dot{C}}CH_2\dot{N}COOEt + \underset{\substack{|\\ CH_3}}{C_6H_5C}{=}CH_2 \longrightarrow \underset{\substack{\|\\ CH_2}}{C_6H_5C}CH_2\dot{N}COOEt + \underset{\substack{|\\ CH_3}}{C_6H_5\dot{C}CH_3} \quad (5)$$



$$C_6H_5\dot{C}(CH_3)_2 + \underset{\substack{|\\ CH_3}}{C_6H_5C}{=}CH_2 \longrightarrow C_6H_5\overset{\substack{CH_3\\ |}}{\underset{\substack{|\\ CH_3}}{C}}CH_2\underset{\substack{|\\ CH_3}}{\dot{C}}C_6H_5 \quad (6)$$

VII



$$\text{VII} + \underset{\substack{|\\ CH_3}}{C_6H_5C}{=}CH_2 \longrightarrow C_6H_5\dot{C}(CH_3)_2 + C_6H_5\overset{\substack{CH_3\\ |}}{\underset{\substack{|\\ CH_3}}{C}}CH_2\underset{\substack{\|\\ CH_2}}{C}C_6H_5 \quad (7)$$

Side Reactions of Carbethoxynitrene. In the preceding discussion, only aziridines were considered as products from nitrene and the 4-methylpentene-2. The experience gathered with other olefins[19,22] leads one to expect other products as well: all the possible insertion products, especially the allylic ones. A crude estimation, based on the data from cyclohexene experiments, shows that only the insertion product into the tertiary C–H bond at C-4 is expected to be formed in a quantity greater than 1% of the quantity of the aziridines. However, the 4-carbethoxyamino-4-methylpentene-2 might be formed in a quantity as much as 12% of that of the aziridines. While C–H insertion seems to be a property of the singlet only,[23] and thus should not influence the stereospecificity (see above), it was at first surprising that no tertiary allylic insertion product could be found. Inspection of models, however, shows that the tertiary allylic hydrogen in *cis*-4-methylpentene-2 is very shielded by three methyl groups, and attack on the C-4–H bond would be very difficult sterically. In the *trans* olefin, the steric hinderance of such an attack is also severe.

While C–H insertion seems to make a negligible contribution, a more serious interference could be caused

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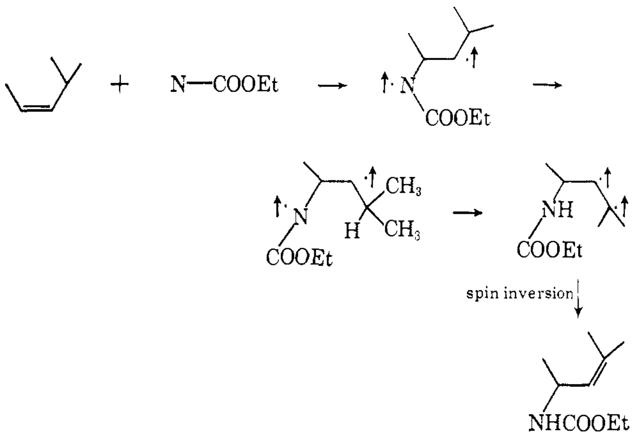
(29) E. Bergmann, H. Taubadel, and H. Weiss, *Ber.*, **64B**, 1493 (1931).
(30) J. Hukki, *Acta Chem. Scand.*, 3, 279 (1949).

by reactions of the triplet nitrene with olefin other than aziridine formation. Especially formation of 4-carbethoxyamino-2-methylpentene-2 (VIII) was anticipated.



VIII

Compound VIII was synthesized and a reaction mixture that contained a high proportion of triplet products (from a run with 1.5 mole % olefin concentration) was analyzed for VIII. A trace of a product with vpc retention time identical with that of VIII was found, but its quantity was too small to attempt identification by infrared spectrum. The peak area corresponded to its being formed in a yield no greater than 2.4% of the aziridine yield, or no greater than 4.5% of the yield of the part of the aziridines formed from the triplet nitrene. Consequently this side reaction does not seriously affect our conclusions.

Conclusion

The results discussed above show that the α-elimination route produces carbethoxynitrene that adds fully stereospecifically to the methylpentenes (extrapolation to infinite olefin concentration), but changes to a nitrene that adds nonstereospecifically. Since the mode of generation makes it very likely that the singlet nitrene is produced, and since the ground state has been proved to be the triplet,[13] we think it reasonable to identify the two species with the singlet and the triplet states. Our results with α-methylstyrene support the contention that the intermediate produced in the nonstereospecific process is a diradical.

Experimental Section

General. Infrared spectra were obtained with a Perkin-Elmer Model 421 spectrometer. Unless specified otherwise, carbon tetrachloride was the solvent used for the infrared as well as the proton magnetic resonance spectra. Tetramethylsilane was used as an internal standard for the latter, and the chemical shifts are reported as δ values (ppm downfield from the TMS signal). Ultraviolet spectra were taken on a Cary Model 14 spectrometer, mass spectra on a Model 21-103 Consolidated Electrodynamics Corp. instrument.[31] Microanalyses are by Galbraith Laboratories. Melting points were taken on a Fisher-Jones block, and are uncorrected, as are the boiling points. Vapor phase chromatography was done with a Varian Aerograph Model A-90-P unit and helium was used as the carrier gas. The columns employed were: column A: 6 ft × 0.25 in. stainless steel; 20% GE-SF-96 silicone oil on 60–80 mesh Firebrick; column B: 15 ft × 0.25 in. aluminum; 5% cyanosilicone XF 1150 on 45–60 mesh Chromosorb W; column C: 15 ft × 0.25 in. aluminum; 20% Carbowax 20M on 45–60 mesh Chromosorb W; and column F: 11 ft × 0.25 in. stainless steel; 25% silver nitrate in glycerol on 60–80 mesh Chromosorb P.

Quantitative vpc analyses were carried out by making four injections per determination, tracing the peaks on unlined filing cards, cutting them out, and weighing. The error was taken to be twice the standard deviation found. Relative errors were less than 2% where the ratio of compared peak areas was less than 10:1. To obtain absolute yields, the peaks from aliquots of reaction mixtures were compared with peaks from the injections of known volumes of standard solutions of the product in question. Unless stated otherwise, all reactions were run under nitrogen, and the solvents were deoxygenated before use. *cis*- and *trans*-4-methylpentene-2 were Phillips "pure grade," 99+% pure. The olefins were distilled before use and gave a negative peroxide test. Each sample of olefin was first analyzed by gas chromatography on column F. If a measurable amount of the other isomer was found, it was corrected for, but such corrections never were larger than 1%. Triethylamine (Matheson Coleman and Bell) was distilled from barium oxide. Dichloromethane (Fisher Certified Reagent) was used without further purification.

Preparation of Authentic *cis*- and *trans*-1-Carbethoxy-2-isopropyl-3-methylaziridines (IV and V). The aziridines were prepared by a slight modification of Hassner's method.[32]

a. N-Carbethoxy-2-amino-3-iodo-4-methylpentanes. Iodine (25.4 g, 0.1 mole) was added in one portion to a stirred, cooled mixture of 20 g (0.133 mole) of freshly prepared, dry, silver cyanate, 8.4 g (0.1 mole) of *cis*- or *trans*-4-methylpentene-2, and 200 ml of anhydrous ether. After 2 hr of stirring in an ice–salt bath and 1 hr at room temperature, the filtered solution was concentrated to half its original volume, 200 ml of absolute ethanol was added, and the solution heated to reflux for 2 hr. Solvent was distilled to reduce the volume by half, and the solution was poured into 150 ml of water, containing a little sodium sulfite. The aqueous layer was washed once with ether, and the combined organic layers were washed five times with water. The combined aqueous extracts were once extracted with ether, and this ether extract was washed five times with water. The washed ether extract was combined with the other organic phase, washed once with saturated sodium chloride solution, and dried over sodium sulfate. Evaporating the ether left the products as yellow oils. The crude yield from the *cis* olefin was 23.3 g (78%), from the *trans* olefin 20.8 g (70%). Both iodo urethans show the ester carbonyl band at 1720 cm^{-1}; the NH band of the compound from *cis* olefin is at 3435, that from the *trans* olefin is at 3440 cm^{-1}. The nmr spectra of the products from *cis* and *trans* olefin are different in that the isopropyl CH_3 signals form two doublets at δ 1.01 and 1.07 in the product from *trans* olefin, while they are not separated (at δ 1.00) in the product from *cis* olefin. The other nmr signal positions are common to both products: CH_3 at C-1 at δ 1.12, ethoxy CH_3 at 1.12, isopropyl CH at 1.3–1.8, N–C–H at 3.3–3.7, I–C–H at 3.8–4.1, ethoxy CH_2 at 4.04, and N–H at 5.25. The products crystallized on standing in the refrigerator, but were usually used as oils without further purification.

b. 1-Carbethoxy-2-isopropyl-3-methylaziridines (VI and V). A solution of the appropriate N-carbethoxy-2-amino-3-iodo-4-methylpentane (15 g, 0.05 mole) in 15 ml of *t*-butyl alcohol was added in one portion to a rapidly stirred solution of 15 g (0.134 mole) of potassium *t*-butoxide (MSA Research Corp.) in 200 ml of *t*-butyl alcohol. After 10 min of stirring at room temperature, the mixture was poured into a solution of 15 g of ammonium chloride in 400 ml of water. The solution was extracted twice with 200-ml portions of ether, and the ether phase was washed with water and sodium chloride solution and dried. After removal of ether and *t*-butyl alcohol, the product was distilled over a short Vigreux column. The *cis*-aziridine had bp 63–66° (3 mm); the *trans* boiled at 67–70° (3 mm). The yields were 3.38 g (40%) for the *cis*, and 4.42 g (51%) for the *trans* isomer. Vpc analysis on column B showed the products not to be contaminated by the other isomers. Infrared and nmr spectra confirm the structures of IV and V. The signals from the methyl groups are split not only by the H on the adjacent carbon, but also due to the asymmetry on ring carbon 2 (J = 12 cps for the *cis*-, J = 4 cps for the *trans*-aziridine). Similar effects have been observed,[33] and it has been suggested that restricted rotation

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[31] We wish to thank Mr. David Friedland for his generous and competent help with the mass spectra.

[32] A. Hassner and C. Heathcock, *J. Org. Chem.*, **29**, 3640 (1964); **30**, 1748 (1965).

[33] A. T. Bottini, R. L. VanEtten, and A. J. Davidson, *J. Am. Chem. Soc.*, **87**, 755 (1965).

causes most of the effect,[34] but the spectrum of our *cis*-aziridine was not appreciably different at 150° and at room temperature. The nmr spectra showed correct integrals, and the chemical shifts were assigned as shown in Table III.

Table III

Group	*cis*, δ	*trans*, δ
Isopropyl CH_3	0.94, 1.13	0.95, 1.02
Ring CH_3	1.21	1.21
Ethoxy CH_3	1.22	1.22
Isopropyl C–H	1.3–1.7	1.3–1.6
Ring protons	1.7–2.6	1.7–2.4
Ethoxy CH_2	4.04	4.04

The carbonyl frequencies of both isomers were at 1720 cm^{-1}

	Anal., % C	 H	 N
Calcd for $C_9H_{17}NO_2$	63.13	10.01	8.18
Found *cis*	62.72	10.18	8.20
trans	63.18	10.13	8.47

Base-Induced Decomposition of N-(*p*-Nitrobenzenesulfonyl)urethan (I) in Solutions of 4-Methylpentene-2 and Dichloromethane. To a rapidly stirred solution of 0.252 g (0.00087 mole) of I in 30 ml of the appropriate dichloromethane–olefin mixture was added dropwise over 8 min 0.10 g (0.0010 mole) of triethylamine in 10 ml of the same dichloromethane–olefin mixture. The temperature was maintained between 35 and 40°. After 3 hr, the volume was reduced to about 5 ml, and 50 ml of ether was added to precipitate the triethylammonium *p*-nitrobenzenesulfonate, which was usually obtained in 80–90% yield. The solvent was removed from the filtrate, and the residue analyzed by vpc. Urethan, IV, and V, were identified by their retention times and their infrared spectra, IV and V also by their nmr spectra. No single column was found to separate all the products. Column A separated urethan and diethyl hydrazodiformate from the aziridines IV and V; column B separated the aziridines from each other, but not V from diethyl hydrazodiformate; column C separated all components but a decomposition product (possibly from the aziridines) appeared together with IV. The standard procedure used was to separate the aziridines from the other components on column A (120°), collect them, and analyze them on column B (112°) to determine their ratio. A synthetic mixture of IV and V was analyzed on column B directly, and after first passing it through column A, the fraction of IV was found to be 44.8 and 45.1%, respectively, showing that passage over column A did not affect the ratio of IV:V. Aziridine mixtures containing negligible quantities of urethan were analyzed both directly on column B and after passage over column A. The results confirmed the reliability of the method. Analysis of recovered olefin on column F (at 40°) showed that less than 1% had isomerized. To determine a possible influence of the ratio of nitrene precursor to olefin, the experiment using 1.5 mole % olefin concentration was repeated, using not 40 but 400 ml of the dichloromethane–olefin mixtures. The results are shown in Table IV.

Table IV. Reactions of I, Base, and Olefin in Dichloromethane Solutions

Mole % olefin	Yields from *cis* olefin, % Aziri-dines	 Urethan	 Diethyl hydrazo-diformate	From *cis* olefin, % V in IV + V	From *trans* olefin, % IV in IV + V
33	57	1.5		7.8	2.6
10	50	5	6–7	17.5	
5				26	8.0
3.3	38	3		34	
2.5				37.5	
1.5	24	4–8	42	43	12.3
		In 400-ml Solution			
1.5	43	1.5	5.7	45.5	
In 400-ml Solution and with Fivefold Excess of Triethylamine					
1.5	35			43	

Competition of *cis*- and *trans*-4-Methylpentene-2 for the Nitrene. Decomposition of I as above in solvent consisting of 10 mole % of *cis* and 20 mole % of *trans* olefin, and 70 mole % of dichloromethane, and work-up as above, gave IV and V in the ratio 1:1.73. The relative reactivity was calculated assuming that the nitrene would react with the *cis* olefin with the same stereospecificity as in a solution containing 10 mole % *cis* olefin, 90 mole % dichloromethane [V:(IV + V) = 0.175], and with the *trans* olefin as if in a solution of 20 mole % *trans* olefin and 80 mole % dichloromethane [IV:(IV + V) = 0.04]. Under these assumptions, the reactivity of the *trans* olefin is calculated to 0.70 times that of the *cis* olefin.

Preparation of 3-Carbethoxamino-2-phenyl-propene-1. a. Bromination of α-methylstyrene[35] gave a mixture of about 75% 3-bromo-2-phenylpropene-1 and 25% 1-bromo-2-phenylpropene-1 in 52% yield. This mixture, a powerful lachrymator, was used in the next step.

b. To prepare 3-N-phthalimido-2-phenylpropene-1, 5.07 g (0.0257 mole) of the bromophenylpropene mixture was treated with 4.7 g (0.0254 mole) of potassium phthalimide in 20 ml of dimethylformamide at 40°, then 55° for 2 hr. Diluting with chloroform, washing with water and sodium hydroxide solution, drying, and concentrating *in vacuo* gave crystals. Recrystallization from cyclohexane gave product (3.94 g, 58% yield), mp 123–124°.

c. To prepare 3-amino-2-phenylpropene-1, 3.4 g (0.013 mole) of the phthalimido compound was heated to reflux for 1 hr in 30 ml of methanol containing 1.2 ml (0.02 mole) of 85% hydrazine hydrate. After addition of 20 ml of water, just enough hydrochloric acid was added to make the solution acidic. After filtration, the solution was concentrated, 15 ml of 6 *N* sodium hydroxide solution was added, and the mixture extracted four times with 30-ml portions of ether. From the dried ether extract, 1.03 g (60% yield) of 3-amino-2-phenylpropene-1 was isolated by distillation, bp 95–98° (17 mm). Tiffeneau reported bp 90–92° (14 mm).[36]

d. **3-Carbethoxamino-2-phenyl-propene-1.** A solution of 0.85 g (0.0064 mole) of the amine and 0.65 g (0.0064 mole) of triethylamine in 15 ml of ether was treated in an ice bath with 0.70 g (0.0064 mole) of ethyl chloroformate. Filtration and removal of the ether gave a product, bp 123–125° (2 mm), a pale yellow solid, mp 39.5–41.5°, yield 0.82 g (63%). The infrared spectrum showed N–H at 3457 (sharp) and 3360 (broad); olefinic and aromatic C–H at 3090, 3060, and 3030; carbonyl at 1720; C=C at 1628; aromatic ring at 1600 (weak) and 1500 cm^{-1}. The nmr spectrum showed the ethoxy CH_3 at δ 1.22 (t), ethoxy CH_2 at 4.04 (q), CH_2 at 4.15 (d), olefinic C–H's at 5.20 and 5.34, N–H at 5.3–5.8, and the aromatic CH's at 7.34.

Anal. Calcd for $C_{12}H_{15}NO_2$: C, 70.22; H, 7.37; N, 6.83. Found: C, 70.27; H, 7.44; N, 7.01.

The α-methylstyrene dimer, 2,4-diphenyl-4-methylpentene-1, was prepared after Hukki.[30] Its infrared spectrum showed olefinic and aromatic C–H's at 3087, 3060, 3025; C=C at 1623; aromatic ring at 1600 and 1490 cm^{-1}. The nmr spectrum showed the methyl signal at δ 1.18 (s, 6.0); CH_2 at 2.77 (s, 2.1); olefinic C–H at 4.74 (broad, 1.0) and 5.08 (broad, 0.95); aromatic CH centered around 7.1 (multiplet, area 9.5).

Reaction of Carbethoxynitrene with α-Methylstyrene. A solution of 0.254 g (0.00088 mole) of I in a mixture of 35 ml of dichloromethane and 2.5 ml of α-methylstyrene (3.5 mole % in α-methylstyrene) was decomposed and worked up as described above. Vpc analysis on column A (210°) gave two major peaks, identified as 3-carbethoxamino-2-phenylpropene-1 and 2,4-diphenyl-4-methylpentene-1, respectively, by comparison of their vpc retention times and infrared and nmr spectra with those of the authentic compounds.

To determine whether the 3-carbethoxamino-2-phenylpropene-1 was formed during the vpc analysis from some other original reaction product, the original reaction mixture was analyzed by thin layer chromatography, using five solvent systems (cyclohexane: dichloromethane:ethyl acetate, 2:2:1; benzene–ether, 1:1; benzene–ether, 95:5; benzene; and dichloromethane). On silica gel (Merck), in all cases a spot was found that had run as far as a spot of the authentic compound.

Reaction of Carbethoxynitrene with *cis*-4-Methylpentene and α-Methylstyrene in Dichloromethane. The same procedure as described above for solutions not containing α-methylstyrene was employed. The analysis procedure could be employed unchanged,

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(34) G. M. Whitesides, D. Holtz, and J. D. Roberts, *J. Am. Chem. Soc.*, **86**, 2628 (1964), and references therein.

(35) H. Pines, H. Alul, and M. Kolobielski, *J. Org. Chem.*, **22**, 1113 (1957).

(36) M. Tiffeneau and H. Cahnmann, *Bull. Soc. Chim. France*, [5] **2**, 1876 (1935).

since products formed from the α-methylstyrene did not overlap with the aziridines IV and V.

Preparation of 4-Carbethoxamino-2-methylpentene-2 (VIII). A solution of 1.5 g (0.005 mole) of the N-carbethoxy-2-amino-3-iodo-4-methylpentane (from *trans*-4-methylpentene-2) and 2.5 g (0.025 mole) of triethylamine in 50 ml of absolute ethanol was stirred at room temperature for 3 hr, poured into water, and extracted with ether. From the washed ether solution, a residue was obtained that yielded VIII by gas chromatography on column B (145°). It was identified by its infrared, nmr, and mass spectra. The infrared spectrum showed N-H at 3450 (sharp) and 3350 (broad), carbonyl at 1715 cm^{-1}. The nmr spectrum showed the ethoxy CH_3 at δ 1.22 (t), ethoxy CH_2 at 4.10 (q); CH_3 at 1.17 (d), CH_3 groups at C-2 1.72 and 1.74; N-C-H at 4.0–4.7 (m); olefinic C-H and N-H at 4.7–5.2 (m); all with the proper integrals. The parent peak in the mass spectrum was, as expected, at m/e 171; ratio $(M + 1)/M$ 10.4% (calcd for $C_9H_{17}NO_2$: 10.6%); base peak at m/e 156, corresponding to the loss of a methyl to give $EtOOC\text{-}NH\text{-}CH\text{-}CH{=}C(CH_3)_2$ for this latter peak, the ratio of $(M + 1)/M$ was found as 8.5% (calcd for $C_8H_{14}NO_2$: 9.3%).

Analysis for 4-Carbethoxamino-2-methylpentene-2 (VIII), A reaction mixture from a run with 1.5% olefin concentration (*cis*-olefin) was analyzed for VIII on column B. A trace of material with the retention time of VIII was noted; its peak area was 2.4% of that of the combined aziridines, IV + V.

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Disproportionation of Organic Polysulfides

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Abstract: The thermal decomposition of dimethyl tetrasulfide and trisulfide at 80° has been followed by the use of nmr spectroscopy. In the first case, dimethyl tri-, tetra-, penta-, and hexasulfides were found in the early stages of the decomposition. In the second case, decomposition was much slower and dimethyl di-, tri-, and tetrasulfides were initially present. Addition of a stable free radical to dimethyl tetrasulfide was found to inhibit the formation of tri- and higher polysulfides. A mechanism for the decomposition of dimethyl tetrasulfide is suggested.

The facile thermal decomposition of organic tetra- and trisulfides has been known for many years. For example, Twiss recorded that diethyl tetrasulfide gives diethyl trisulfide and free sulfur on distillation *in vacuo*;[1] Jones and Reid reported that the same tetrasulfide decomposes to diethyl disulfide and sulfur at 140–150°;[2] Bloomfield found that dicyclohexyl tetrasulfide gives a material of reduced sulfur content and dicyclohexyl hexasulfide when heated at 140–150°;[3] Fuson, *et al.*, found that bis(2-chloroethyl) trisulfide gives a mixture of bis(2-chloroethyl) disulfide, higher sulfides, and sulfur on heating at 145–160°;[4] and Guryanova, *et al.*, showed that when ditolyl trisulfide, in which the central sulfur atom is radioactive, is heated with diethyl trisulfide the latter becomes radioactive through exchange of the central sulfur atoms.[5] Recently we have illustrated the instability of the tetrasulfide linkage in a more quantitative manner with the finding that the dissociation energy of the tetrasulfide linkage in dimethyl tetrasulfide is only about 36 kcal/mole.[6]

Although the lability of the polysulfide linkage has been recognized, systematic studies of the thermal decomposition of organic polysulfides have been hindered by lack of suitable means of analysis. Because the products of decomposition are themselves thermally unstable, quantitative data based on classical methods of separation are not only difficult to obtain but are also suspect. Recently Grant and Van Wazer have reported that various dimethyl and di-*t*-butyl polysulfides can be distinguished by nmr spectroscopy.[7] Using an analogous procedure we have followed the thermal decomposition of dimethyl tetrasulfide and trisulfide at 80°. Investigations into the mechanism of decomposition were also carried out.

Experimental Section

Reagents. Dimethyl tetrasulfide was prepared as previously reported by us.[6] Dimethyl trisulfide was prepared by an analogous procedure using sulfur dichloride (Matheson Coleman and Bell) distilled immediately before use, bp 57–58°. The trisulfide had bp 56–57° (13 mm) (lit. 59° (12 mm),[8] 54–55° (11 mm),[9] 58–59° (15 mm)[10]); $n^{30}{}_D$ 1.5973 (lit.[10] 1.5972). The yield was 87%.

Anal. Calcd for $C_2H_6S_3$: C, 18.95; H, 4.78; S, 76.24. Found: C, 18.99; H, 4.75; S, 76.30.

β-(Phenyl nitrogen oxide)-β-methylpentan-δ-one oxime (hereafter called Banfield's free radical) was prepared by the method of Banfield and Tüdös.[11,12] Azobisisobutyronitrile (Du Pont) was used as received.

Procedure. The polysulfide under investigation (0.6 ml) and a small sealed capillary tube containing tetramethylsilane were placed in a precision-bore Pyrex nmr tube to which a standard taper joint had been attached. The tube was then degassed and sealed off under a slight pressure of nitrogen following the method previously

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(4) R. C. Fuson, C. C. Price, D. M. Burness, R. E. Foster, W. R. Hatchard, and R. D. Lipscomb, *J. Org. Chem.*, **11**, 487 (1946).

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(11) F. M. Banfield and J. Kenyon, *J. Chem. Soc.*, 1612 (1926).

(12) F. Tüdös and N. I. Smirnow, *Acta Chim. Acad. Sci. Hung.*, **15**, 389 (1958).