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## Reaction of Carboethoxynitrene with Allenes<sup>1</sup>

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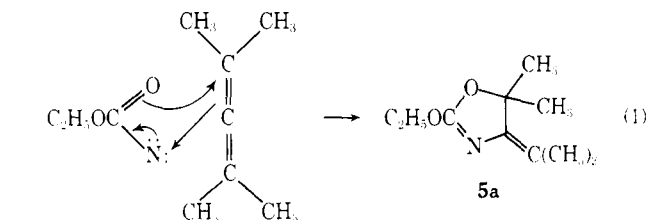
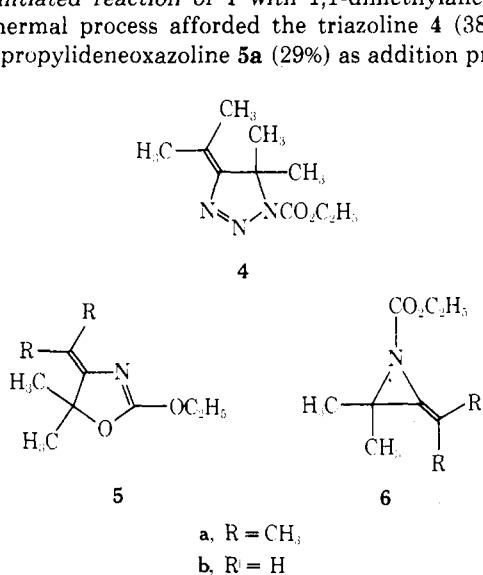
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Carboethoxynitrene, from base-catalyzed  $\alpha$  elimination of *N*-(*p*-nitrobenzenesulfonyl)urethane (9), reacts with allene and 1,1-dimethylallene to produce 1,2-cycloaddition products. Tetramethylallene fails to produce an adduct with the nitrene. The results appear to be most consistent with a cycloaddition mechanism in which the initial step is reaction of triplet nitrene with a terminal carbon atom of the allenic moiety. The thermal isomerization of 2-isopropylidene-*N*-carboethoxyaziridine (14) to 2-ethoxy-5,5-dimethyl-4-methylene-2-oxazoline (5b) is described.

The reaction of various types of carbenes or carbenoids with allenes has been investigated and proceeds in an unexceptional fashion to yield methylenecyclopropanes regardless of whether the divalent carbon species is in a singlet or triplet spin state.<sup>2,3</sup> In view of the recent interest in the chemistry of nitrenes,<sup>5</sup> isoelectronic analogs of carbenes, it is somewhat surprising that the corresponding reaction of this species with allenes has received only cursory examination. Thus, the sole reported investigation of this type of reaction is that of Bleiholder and Shechter in which they studied the thermally induced reaction of ethyl azidoformate (1) with tetramethylallene (2) and the photochemically initiated reaction of 1 with 1,1-dimethylallene (3).<sup>6</sup> The thermal process afforded the triazoline 4 (38%) and the isopropylideneoxazoline 5a (29%) as addition products;

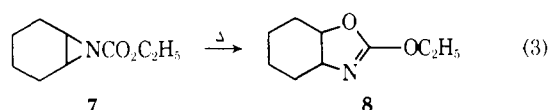
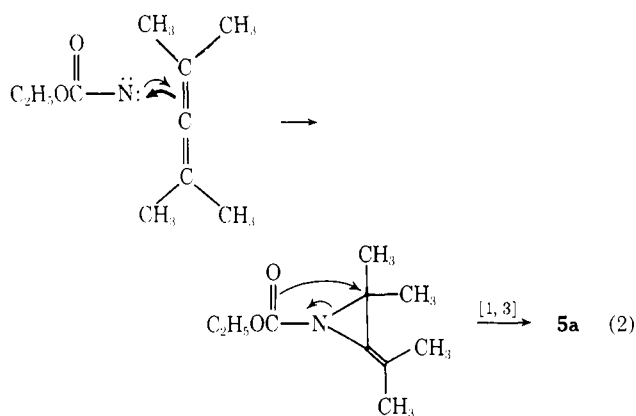
the photochemical reaction produced the methyleneoxazoline 5b (47%) as the only reported product. The *N*-carboethoxyaziridines, 6, products that might have been anticipated if allenes were to behave toward nitrenes as do carbenes, were not observed in either experiment.

Whereas photolysis of 4 was found to yield 5a (43%), thermolysis did not promote this transformation; thus 5a potentially represented a primary product of reaction of carboethoxynitrene with tetramethylallene. Two mechanistic pathways for formation of 5a appeared to be reasonable, *viz.*, 1,3-dipolar cycloaddition of the nitrene to tetramethylallene to generate 5a directly (eq 1) or 1,2 cycloaddition

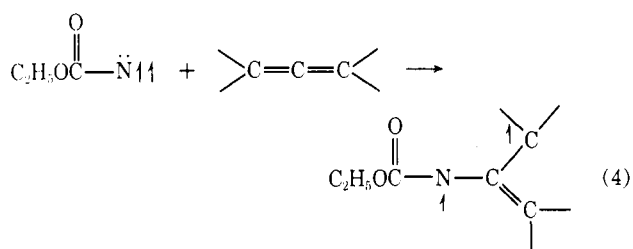


between the nitrene and the allene to produce 6a, which in turn underwent a [1,3]-sigmatropic isomerization to 5a (eq 2). Since the pathway involving 1,3-dipolar cycloaddition was without precedent in nitrene chemistry, Bleiholder and Shechter favored the second alternative (eq 2), a suitable analogy for the rearrangement of 6a being the reported thermal conversion of the aziridine 7 to the oxazoline 8 (eq 3).<sup>7</sup>

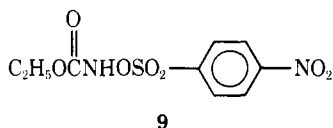
We have reinvestigated the reaction of carboethoxynitrene with allenes under conditions more conducive not only to isolation of alkylideneaziridines, should they be formed, but also to the extension of such studies to triplet



nitrenes. The latter aspect is of interest in that triplet carbethoxynitrene is radical-like in character and its addition to C-2 of the allenic moiety would potentially provide an entry into triplet heterotrimethylenemethanes (eq 4).<sup>8</sup>



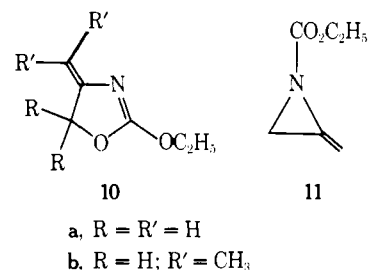
Thus we chose to generate carbethoxynitrene by treatment with base of *N*-(*p*-nitrobenzenesulfonyl)urethane (9), a



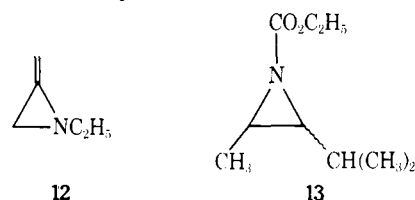
procedure known to yield singlet and/or triplet nitrenes depending on the reaction conditions employed.<sup>7,10</sup>

### Results

Triethylamine-catalyzed decomposition of 9 at room temperature in a 2.6 mol % solution of allene in dichloromethane afforded, upon careful work-up (see Experimental Section), a 6% yield of a colorless oil as the only isolable volatile product. The oil was isolated by vacuum transfer and polymerized with ease at 0°. It analyzed as C<sub>6</sub>H<sub>9</sub>NO<sub>2</sub> (high resolution mass spectroscopy), a molecular formula consistent with a 1:1 adduct of carbethoxynitrene and allene. The 100 MHz nuclear magnetic resonance (nmr) spectrum of the oil revealed broad singlet resonances at  $\delta$  2.73 (2 H, ring protons), 4.74 (1 H, vinyl proton), and 4.92 ppm (1 H, vinyl proton) in addition to absorptions at  $\delta$  1.32 [t (3 H)] and 4.16 ppm [q (2 H)] attributable to the ethoxy group. An intense absorption at 1730 cm<sup>-1</sup> indicated that the product retained the carbonyl function.<sup>11</sup> These spectral data exclude the oxazoline 10a as the structure of the reaction product; this substance, for example, would be expected to exhibit resonances in its nmr spectrum in the region of  $\delta$  4–4.5 ppm for its vinylic protons<sup>6</sup> and would not have absorptions in its ir spectrum in the range of 1730–1740 cm<sup>-1</sup>.

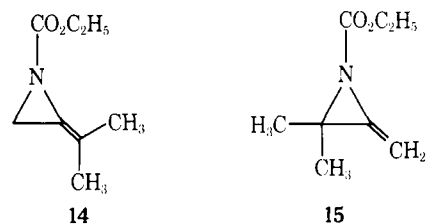


The data are, however, consistent with 2-methylene-*N*-carbethoxyaziridine (11). Although the resonance at  $\delta$  2.73 ppm that is assigned to the ring hydrogens may appear to be at unexpectedly low field, reference to model compounds supports the assignment. Thus the ring protons of the methylenearizidine 12 appear at about  $\delta$  2.0<sup>13</sup> and those of the *N*-carbethoxyaziridine 13 occur in the range of  $\delta$  1.7–2.6 ppm.<sup>10</sup> The addition to allene of carbethoxynitrene generated by  $\alpha$  elimination therefore occurs in the 1,2-cycloaddition mode common to the reaction of carbenes and allenes, albeit in low yields.



The generation as above of carbethoxynitrene in the presence of 1,1-dimethylallene and dichloromethane again afforded an unstable colorless oil, isolable by preparative thin layer chromatography (tlc) in yields of 3–8%. High resolution mass spectroscopy was consistent with formulation of the product as a 1:1 adduct of the nitrene and allene, and observation of a strong ir band at 1730 cm<sup>-1</sup> allowed exclusion of the oxazolines 5b and 10b as structural possibilities.

Two alkyldeneaziridines, 14 and 15, are possible adducts from this reaction, and the nmr spectrum of the isolated



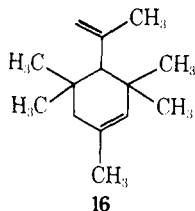
product allows differentiation between them as follows. The spectrum reveals an ethoxy moiety as a triplet at  $\delta$  1.30 and a quartet at 4.12 ppm, in addition to a two-proton singlet at 2.65 and two separate three-proton singlets at 1.75 and 1.80 ppm, respectively. The chemical shift of the lowest field singlet is that expected for the ring protons of an alkyldene-*N*-carbethoxyaziridine, cf. 11, whereas the two singlets at higher fields are consistent with the presence of allylic methyl groups. The spectral evidence thus confirms structure 14.

To test the premise that isomer 15 might have been formed during the reaction and subsequently either decomposed or underwent a rearrangement of the methylenecyclopropane type during work-up to produce the observed 14, an attempt was made to detect transient formation of 15 by nmr spectroscopy. Monitoring of the reaction was achieved by removal of aliquots over the course of 4 hr and analyzing them by nmr spectroscopy. Although formation of 14 could be detected within 60 min of initiation of the reaction, characteristic resonances for 15 which were expected to occur at about  $\delta$  5 and 1 ppm never appeared. Be-

cause it seems unlikely that 15 would be rapidly rearranging to 14 at room temperature and that 15 would be more labile toward decomposition than the unsubstituted methyleneaziridine 11, it is reasonable to conclude not only that 14 is a primary product of the reaction of carbethoxynitrene with 1,1-dimethylallene but also that 15 is not formed in the process.

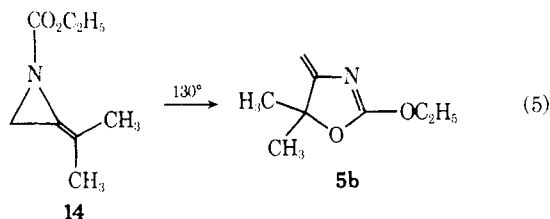
It was discovered that the urethane 9 which is the precursor of the nitrene contained trace amounts of acid (see below). To assess the possible effect the acid might have on the course of the reaction, 1,1-dimethylallene and carbethoxynitrene were allowed to react in the presence of 2,6-di-*tert*-butylpyridine, a proton scavenger. This modification had no effect on the course of the reaction, and 14 was isolable in 8% yield.

Initial attempts to extend the investigation to the reaction of carbethoxynitrene with tetramethylallene resulted in isolation in high yield of a colorless oil analyzing as  $C_{14}H_{24}$  (high resolution mass spectroscopy). The nmr spectrum of this oil agrees with that reported by Poutsma for the dimer obtained by treatment of tetramethylallene with acids and to which structure 16 has been assigned.<sup>14</sup> The source of the acid catalyst in our experiment proved to be contaminants in the urethane 9.



Repetition of the reaction of the nitrene with tetramethylallene under conditions such that acid-catalyzed dimerization of the allene was completely suppressed by the addition of 2,6-di-*tert*-butylpyridine failed to afford any of the expected alkylideneaziridine in the dichloromethane-soluble portion of the reaction mixture. As adjudged by nmr analysis, only unchanged allene and the pyridine were present.

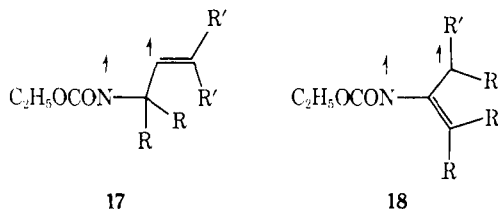
Thermolysis at 130° of a dilute degassed solution of 14 in carbon tetrachloride for 0.7 hr caused essentially complete disappearance of starting material and produced a substance having nmr resonances at  $\delta$  1.37 [t (3 H)], 1.42 [s (6 H)], 3.95 [s (1 H)], 4.32 [q (2 H)], and 4.50 ppm [s (1 H)]. This is the same nmr spectrum obtained by Bleiholder and Shechter for the adduct formed by photolysis of ethyl azidoformate in the presence of 1,1-dimethylallene and for which they assigned the structure of 2-ethoxy-5,5-dimethyl-4-methylene-2-oxazoline (5b) (eq 5).<sup>6</sup>



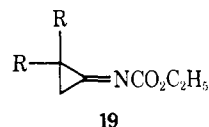
### Discussion

The characterization of 2-methylene-*N*-carbethoxyaziridine (11) as the adduct between carbethoxynitrene and allene itself demonstrates for the first time that nitrenes can undergo net 1,2-cycloaddition reactions with allenes. Mechanism of the reaction is unclear, however. Even though the conditions chosen for generation of carbethoxynitrene in the presence of the allenes were such as to favor formation of triplet nitrene,<sup>10</sup> in hopes that products re-

sulting from attack at C-2 of the allenic moiety might be discerned, the presence of the singlet species cannot be eliminated. The formation of 11, therefore, could be rationalized mechanistically as the result either of a concerted addition of a singlet nitrene to allene or of a stepwise addition of triplet nitrene to produce diradicals 17a or 18a followed by spin relaxation and collapse to product.



- a, R = R' = H  
b, R = H; R' = CH<sub>3</sub>

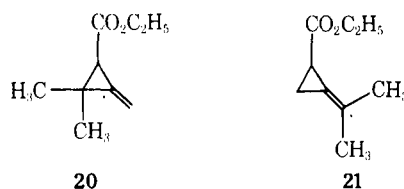


- a, R = H  
b, R = CH<sub>3</sub>

Two products, the methyleneaziridine (11) and the imine 19a, are possible from diradical 18a, but resonances attributable to 19a could not be detected in the volatile fraction obtained by vacuum line techniques. Because 19a would be anticipated to be extremely susceptible to nucleophilic attack, its absence can in no way be taken as evidence against the possible intermediacy of 18a in the reaction. Moreover, the low yield of product coupled with the paucity of detailed information regarding the relative rates of reaction of singlet and triplet nitrenes with  $\pi$  systems discourages attempts to designate the species responsible for product 11.<sup>15</sup>

Extension of the reaction of carbethoxynitrene to 1,1-dimethylallene was attempted because this system provided a different type of test of the possibility that triplet nitrenes might add initially at C-2 of an allenic function. The diradical 18b resulting from such a process could ultimately form both of the methyleneaziridines 14 and 15 as well as the imine 19b. Once again the low yields of the adduct 14 thwart the drawing of definitive conclusions regarding reaction mechanism, but the results do merit the development of some tentative proposals.

If formation of 14 is in fact a consequence of reaction of singlet nitrene with the allene, attack has occurred at the less nucleophilic of the two possible double bonds, a regioselectivity that is rarely observed for reactions of divalent carbon with  $\pi$  systems. For example, carbethoxy carbenoid, generated by copper-catalyzed decomposition of ethyl diazoacetate, adds to 1,1-dimethylallene to produce mainly 20 (96%) and little 21 (4%).<sup>16</sup> There is little reason to believe

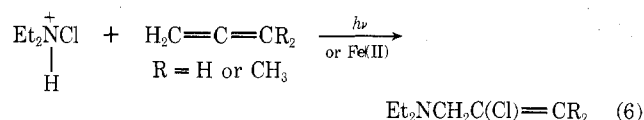


that the steric requirements for addition of carbethoxynitrene are greater than those of the corresponding copper carbenoid—in fact, just the reverse is more likely; so an alternative explanation for the exclusive formation of 14 seems desirable.

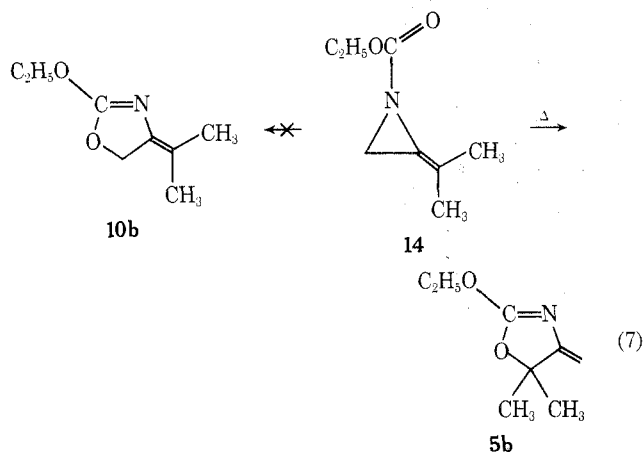
Such an explanation is found in the proposal that triplet

rather than singlet nitrene is the entity responsible for the cycloaddition product. If this be true, the absence in the reaction mixture of **15** can be taken as evidence that diradical **18b** is not being generated in significant quantities and that attack of the triplet nitrene has occurred preferentially at the sterically less encumbered terminal position of the allenic moiety to produce diradical **17b**, the precursor to **14**. Support for the hypothesis that steric factors are of importance in the reaction of carbethoxynitrene with allenes is derived from the observation that none of the 1,2-cycloaddition product **6a** is formed if tetramethylallene is used as a trap for the nitrene.

Thus our experimental results seem most compatible with the intervention of triplet diradicals of type **17** in the addition of triplet carbethoxynitrene with allenes.<sup>17</sup> It is to be noted that this orientation of attack has analogy in the report that diethylaminium radical adds exclusively to a terminal carbon atom of either allene or 1,1-dimethylallene (eq 6).<sup>18</sup>

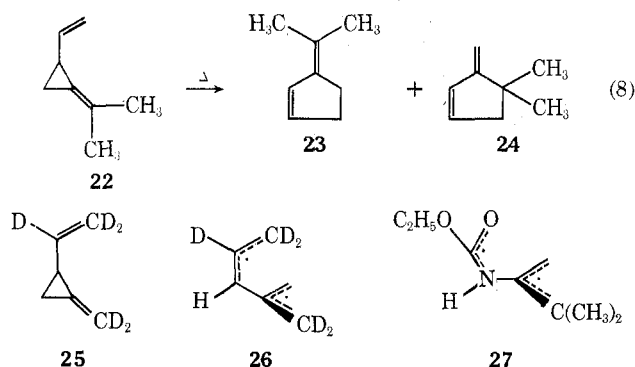


The thermolysis of 2-isopropylidene-*N*-carbethoxyaziridine (**14**) was of interest because of the proposal by Schechter and Bleiholder that alkylidene-*N*-carbethoxyaziridines may have been precursors to the oxazolines observed in their work.<sup>6</sup> The fact that **14** does rearrange to **5b** (eq 7) offers support of their hypothesis, but the absence of



**10b** as a product raises some questions regarding the detailed mechanism of the isomerization.

There is a clear structural analogy between **14** and 2-vinyl-1-isopropylidene-cyclopropane (**22**), and the latter substrate is known thermally to rearrange to a mixture of 3-isopropylidene-cyclopentene (**23**) and 4,4-dimethyl-3-methylenecyclopent-1-ene (**24**, eq 8).<sup>19</sup> Studies of the fate



of the deuterium label upon isomerization of the labeled vinylmethylenecyclopropane **25** to the methylenecyclopentenes indicated that the diradical **26** was a crucial reaction intermediate.<sup>20</sup> Had the analogous species **27** been formed from **14**, then, in analogy to the results illustrated in eq 8, both **5b** and **10b** would have been expected as products. That only **5b** was observed suggests that the mechanism for thermal isomerization of **14** is best represented as a concerted [3,3]-sigmatropic process as opposed to a stepwise reaction involving **27**.<sup>21</sup> The basis for the difference in mechanistic pathways for **14** as compared to **22** and **25** most likely resides in the lack of conjugative stabilization afforded radicals by carbonyl groups, thereby making **27** unstable relative to the all-carbon analog.

### Experimental Section

Infrared (ir) spectra were obtained with a Beckman Model IR-5A or a Perkin Elmer Model 237-B spectrometer. Nmr spectra were recorded on either a Varian A-60, a Perkin-Elmer R-12, or a Varian HA-100 spectrometer. Unless specified otherwise, carbon tetrachloride was the solvent used for all ir as well as nmr spectra. Tetramethylsilane (TMS) was used as an internal standard for the nmr spectra, and all the chemical shifts are reported as  $\delta$  values in parts per million (ppm) downfield from the TMS signal.

High resolution mass spectra were obtained with a Du Pont (CEC) Model 21-110 mass spectrometer.

A Varian Aerograph A-90-P3 was used in all gas-liquid phase chromatography (glpc) analyses. With few exceptions, the flow rate of helium, the carrier gas, was  $\sim 60$  ml/min. The following columns were used: column A, 3 ft.  $\times$   $\frac{1}{8}$  in., 15% FFAP on 60/80 Chromosorb P (acid-washed); column B, 4 m  $\times$   $\frac{1}{4}$  in., 15% FFAP on 60/80 Chromosorb P (acid-washed); column C, 2 ft.  $\times$   $\frac{1}{4}$  in., 20% dinonyl phthalate on 60/80 Chromosorb P (acid-washed).

Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

Unless stated otherwise, all reactions involving the generation of nitrenes were run under nitrogen, and the resulting products were stored at  $-78^\circ$ . All solvents and substrates involved in this series of reactions were purified before use.

**2-Methylene-*N*-carbethoxyaziridine (11).** A 500-ml three-neck round-bottomed flask was equipped with a magnetic stirring bar, a dropping funnel, a Dry Ice-methanol condenser connected to a nitrogen source, and a gas inlet. While a continuous blanket of dry nitrogen was maintained in the system, the reaction flask was immersed in a Dry Ice-methanol bath and was charged with *N*-(*p*-nitrobenzenesulfonyl)urethane (**9**)<sup>12</sup> (4.4 g, 15 mmol) and 350 ml of purified anhydrous dichloromethane. A tenfold excess of allene (6.0 g, 150 mmol) was then condensed into the reaction flask to produce a solution containing 2.5 mol % of allene. The reaction flask was removed from the cooling bath, and a solution of triethylamine (1.7 g, 17 mmol) in dichloromethane (10–15 ml) was slowly added from the dropping funnel with good stirring. The reaction mixture was then stirred for 6.5 hr at room temperature, with a nitrogen atmosphere being maintained at all times. Pentane was added to precipitate salts, the organic solution was decanted, and then the solvents were removed with the aid of a rotary evaporator. Vacuum line transfer of the residue that resulted gave 0.25 g of a sample containing  $\sim 50\%$  dichloromethane and 50% a compound whose spectral characteristics were consistent with 2-methylene-*N*-carbethoxyaziridine (**11**) (see Results). On this basis, the actual yield of aziridine is 6%. Pure **11** was obtained by removal of residual solvent under vacuum: calculated mass for C<sub>6</sub>H<sub>9</sub>NO<sub>2</sub> 127.0633, found *m/e* 127.0638.

The compound polymerized when kept under nitrogen and at  $0^\circ$ . When the product was stored at  $-78^\circ$  and under an inert atmosphere, polymerization was significantly inhibited. Nevertheless, microanalytical data for a sample kept at this temperature at all times were not completely satisfactory. The data are summarized as follows. *Anal.* Calcd for C<sub>6</sub>H<sub>9</sub>NO<sub>2</sub>: C, 56.60; H, 7.08; N, 11.00. Found: C, 55.76; H, 7.21; N, 10.69.

**2-Isopropylidene-*N*-carbethoxyaziridine (14).** A 500-ml round-bottom three-neck flask immersed in an ice-water bath was fitted with a dropping funnel and an ice-water-cooled condenser which was connected to the nitrogen source. A tenfold excess of 1,1-dimethylallene (10.2 g, 150 mmol) was added in one portion to a rapidly stirred solution of 4.4 g (15 mmol) of the urethane **9** which had been dissolved in  $\sim 350$  ml of dichloromethane. A solu-

tion of 1.7 g (17 mmol) of freshly purified triethylamine in 15 ml of anhydrous dichloromethane was then added dropwise over 1.5 hr to the rapidly stirred reaction mixture. After addition was complete, the ice-water bath was removed, and the reaction mixture was allowed to stir at room temperature for ~7 hr. After addition of pentane, the precipitated triethylammonium salts were removed from the reaction mixture by filtration. This salt was obtained in 87% yield. The solution was concentrated *in vacuo* to give a yellow liquid weighing 3.0 g.

Attempts at purification of crude product by vacuum transfer using pot temperatures up to 40° did not effect separation of the reaction mixture. Even at these low temperatures, significant decomposition was observed.

Gpc (columns A, B, C) using either carbon tetrachloride solutions or neat samples of the product mixture were also ineffective in product purification. Column temperatures between 50 and 160° were tried. For the most part, the products polymerized on the columns. At 160° (column A) a product was collected which was initially clear but decomposed immediately to a light brown liquid.

Thin layer chromatography (tlc) on silica gel H using a 5:5:1 mixture of benzene-hexane-methanol for development proved effective in the isolation of pure product. Two product bands were observed under uv light. Extraction with carbon tetrachloride of the band having the lower mobility followed by removal of solvent afforded a yellowish viscous liquid of a polymeric nature; similar treatment of the band of higher mobility provided 72 mg (~3% yield) of a compound assigned as the 2-isopropylidene-*N*-carbethoxyaziridine (14): the nmr and ir spectral data are consistent with 14 (see Results); calculated mass for C<sub>8</sub>H<sub>13</sub>O<sub>2</sub>N 155.0946, found *m/e* 155.0951.

To detect the possible transient formation of 15 during the course of the reaction, product formation was monitored by nmr spectroscopy at short reaction times. The reaction was carried out by a procedure analogous to that described above except that the three-neck reaction flask was fitted with a rubber septum to permit the removal of aliquots at appropriate intervals. Aliquots of 20 ml were removed after 30, 60, 120, 180 and 240 min. Detection of 14 by nmr was possible after 60 min. At this point, and in all subsequent aliquots, no resonances characteristic of 15 could be detected, however. Examination by nmr analysis of the crude product following completion of the reaction also failed to reveal measurable quantities of 15.

The reaction of 1,1-dimethylallene with carbethoxynitrene was repeated under conditions designed to inhibit any acid-catalyzed reactions that might be occurring as the result of the presence of traces of acid.<sup>14</sup> All glassware with which the reaction mixture or product mixture was to come in contact was rinsed with concentrated ammonium hydroxide and dried in an oven at 110°. In addition, 2,6-di-*tert*-butylpyridine was added as a proton scavenger to the solution of 9 in dichloromethane. The rest of the procedure remained unchanged. After concentration of the reaction mixture *in vacuo*, a crude product (2.20 g), which was ~50% di-*tert*-butylpyridine, was obtained. Again the spectrum of the crude product mixture contained no evidence for the presence of 15. Purification of the reaction mixture by tlc as described above afforded 14 (8% yield) as the second most mobile band; the pyridine was the most mobile under our conditions of development.

**Reaction of Carbethoxynitrene and Tetramethylallene.** All glassware was rinsed with ammonium hydroxide solution and dried in an oven at 110° prior to use and 2,6-di-*tert*-butylpyridine was added to the reaction mixture to suppress acid-catalyzed dimerization of tetramethylallene.<sup>14</sup>

Small-scale reactions at ambient temperature and at 42° were performed maintaining the same molar ratios as in the previous experiments. *N*-(*p*-Nitrobenzenesulfonyl)urethane (9, 0.3 g, 1 mmol) was dissolved in a minimum amount of dichloromethane, 2,6-di-*tert*-butylpyridine (~5 drops) was added, and the solution was tested with litmus to assure neutrality. After 1.0 g (10 mmol) of tetramethylallene had been added to the reaction flask, addition

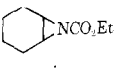
of triethylamine (0.12 g, 1.2 mmol) was commenced. After a reaction time of ~6 hr, the precipitated salts were removed as before, and the reaction mixture was concentrated *in vacuo*. The nmr spectrum of the recovered material indicated the presence of only di-*tert*-butylpyridine and tetramethylallene. No evidence of any product formation was found.

**Thermolysis of 2-Isopropylidene-*N*-carbethoxyaziridine (14).** A 20 (v/v) % solution of a pure sample of 14 in carbon tetrachloride was placed in a thick-walled nmr tube, the solution was degassed, and the tube was sealed. This solution was then heated at 130°. Monitoring (R-12) of the solution showed that essentially all of the aziridine had rearranged to 2-ethoxy-5,5-dimethyl-4-methylene-2-oxazoline (5b) and small amounts of decomposition products within 40 min. The 100-MHz spectrum of this sample was consistent with oxazoline 5b (see Results).

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**Registry No.**—5b, 53336-56-4; 9, 2955-74-0; 11, 53336-57-5; 14, 53336-58-6; carbethoxynitrene, 2655-26-7; allene, 463-49-0; 1,1-dimethylallene, 598-25-4; tetramethylallene, 1000-87-9.

## References and Notes

- This work taken in part from the M.A. Thesis of E.M.B., UT—Austin, 1972.
  - M. Jones, Jr., *et al.*, *J. Amer. Chem. Soc.*, **94**, 7469 (1972), and references therein cited.
  - The reaction with allenes of carbenes in the latter spin state is of particular interest because attack at C-2 of the allene moiety would produce triplet trimethylenemethanes.<sup>4</sup>
  - For a review on trimethylenemethanes, see P. Dowd, *Accounts Chem. Res.*, **5**, 247 (1972), and references therein cited.
  - (a) W. Lwowski, "Nitrenes," Interscience, New York, N.Y., 1970; (b) T. L. Gilchrist and C. W. Rees, "Carbenes, Nitrenes, and Arynes," Thomas Nelson and Sons, London, 1969.
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  - Although the location of attack of a free radical on an allene is a function both of the nature of the attacking radical and of the substituents on the substrate allene,<sup>9a</sup> some analogy for the possible attack of triplet nitrene at C-2 is available from the reported exclusive attack of ethylthyl radical on this position of 1,1-dimethylallene.<sup>9b</sup>
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  - Cf.* the strong absorption noted for 1 at 1720 cm<sup>-1</sup> assigned to the carbonyl function.<sup>12</sup>
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  - It is to be noted that performance of the reaction under conditions favorable to the singlet reaction, *viz.*, 33 mol % allene in dichloromethane, also affords 11 as the only isolable ether-soluble product (C. Fletcher, unpublished results).
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  - Jones, *et al.*, have reached the analogous conclusion with regard to the reaction of triplet carbenes and allene.<sup>2</sup>
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  - J. C. Gilbert and D. P. Higley, *Tetrahedron Lett.*, 2075 (1973).
  - The possibility that the reaction involves a prior isomerization of 14 to *N*-carbethoxy-3,3-dimethyl-2-methyleneaziridine (15) followed by a [1,3]-sigmatropic rearrangement cannot rigorously be excluded but seems less likely on steric grounds.