

## REACTIONS OF ALKOXYCARBONYLNITRENES WITH TERTIARY AMINES

## Part I. Reaction of Methoxycarbonylnitrene with Triethylamine\*

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**Abstract.** Reaction of methoxycarbonylnitrene with triethylamine leads to some interesting products via a short-lived betain intermediate. Formation of these products is discussed in the light of IR, NMR and mass spectral evidence.

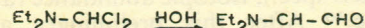
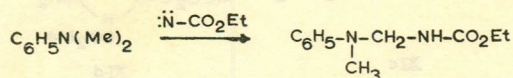
Nitrenes are known to react with various substrates.<sup>1-3</sup> Being electron deficient, they are very reactive, and become an easy prey for all electron-rich substrates. One class of such compounds is amines.

Thus, reaction of ethoxycarbonylnitrene (I) with aliphatic and aromatic amines leads to the insertion into the NH bond of the amine giving hydrazoformates as the major products.<sup>4</sup>

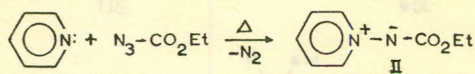
With *t*-amines one finds that the field has not been explored in much detail. Hafner<sup>5</sup> has reported a product of insertion into CH bond of methyl group of

of insertion into the primary (1°) and secondary (2°) CH bonds, small amounts of ethyl-*N,N*-diethylglycine is also formed, most probably via the formation of ylid(IV), through loss of ethylene.<sup>7</sup>

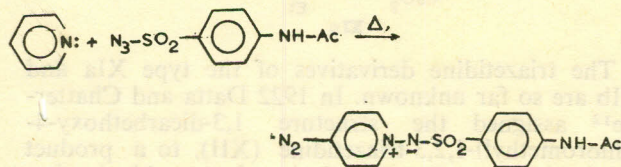
Diethylformamide is formed to the extent of 15.2% by the reaction of dichlorocarbene<sup>8</sup> with triethylamine in a reaction scheme similar to the one proposed above, via a zwitterionic intermediate and loss of ethylene.



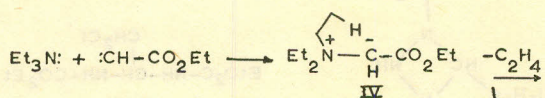
dimethylaniline by I. With pyridine, formation of *N,N*-betain (II), occurs in 67% yield. Thermal decomposition of *p*-acetamidobenzenesulphonyl azide



in pyridine also leads to the formation of a betain (III).



The counterparts of the alkoxy carbonylnitrenes, i.e. the alkoxy carbonylcarbenes react with *t*-amines, and a ylid or zwitterionic intermediate is postulated to be initially formed, leading to a variety of products other than those of insertion. Thus with triethylamine and ethoxycarbonylcarbene,<sup>7</sup> in addition to the products



In view of the above, the nonreactivity of triethylamine towards alkoxy carbonylnitrenes remained puzzling to us, particularly when the former is used to generate the latter from *N-p*-nitrobenzenesulphonylurethan.<sup>1,3,4</sup> One would expect the formation of nitrogen ylid similar to II and III, and following the analogy of IV, at least in the form of a short-lived intermediate, since the  $\text{p}K_b$  of triethylamine is 3.1 in comparison to about 9.0 for pyridine. Also, the negative charge on the nitrogen atom can be stabilized by the Coulombic interaction with the adjacent ammonium nitrogen, as well as by the delocalization over the adjacent carbonyl function. It has been the main clue to the identification and characterization of various 'strange' products of the reaction of methoxycarbonylnitrene(VI) and triethylamine during our investigation of the reaction of the former with isocyanates.<sup>2</sup>

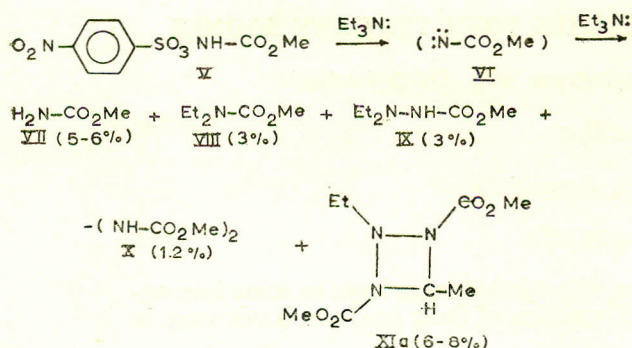
## Results

When a solution of methyl-*N*-(*p*-nitrobenzenesulphonyloxy)carbamate(V) in methylene chloride or diethyl ether is treated with two mole equivalents of triethylamine at 0-5°C, five products are isolated. The product distribution has been summarized in scheme 1<sup>a</sup>.

The identification of products VII-X is confirmed by the identity of IR spectra with the authentic materials prepared by unambiguous routes and VPC retention time. The structure of product XIa was assigned on the basis of elemental analysis, IR, NMR and mass spectral evidence.

\*Part of the dissertation submitted by S.M.A. Hai to New Mexico State University, U.S.A., in partial fulfilment of the requirement for Ph.D.



Scheme 1<sup>a</sup>

The products were separated, purified and collected by VPC. Ordinarily oxygen was not excluded from the system. The yields of the products were, however, unaffected within the experimental error, when the reaction was done under an atmosphere of nitrogen. Use of diethyl ether as solvent instead of methylene chloride had no effect on the product distribution.

Generally after collection of pure samples of the various products by VPC (in addition to the other spectral and analytical data) structure elucidation was greatly facilitated by the derivation of molecular formula from elemental analysis, molecular weight (mass spec.), isotopic abundance ratio and the nitrogen rule.<sup>10</sup> After this preliminary assignment, it was confirmed by independent synthesis of the desired compound.

Formation of dialkylazodicarboxylates in the nitrene reactions is known, and there are also reports<sup>9</sup> and we have also observed during the present investigation that among other things they react with triethylamine. Therefore, methyl carbamate (VII) and dimethyl hydrazodiformate (X) were not so unexpected products, as they are usually found in a large number of nitrene reactions.

In a test run of the reaction of methyl azodicarboxylate and triethylamine, no triazetidine derivative (XIa) is detected. This indicates that the latter is an independent product of the reaction of triethylamine and methoxycarbonylnitrene, and is not formed as a result of secondary reaction of X and triethylamine, which could be surmised in view of the fact that X is known<sup>9</sup> to be formed in the reaction of methylazodicarboxylate (XVIII), and triethylamine.

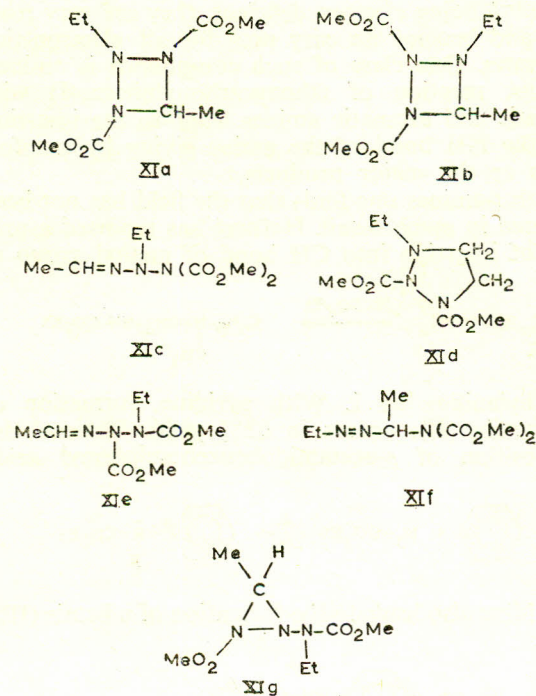
The triazetidine derivative (XIa) is the fourth fraction in the VPC separation of the crude mixture. It is formed in 6-8% yield. Its IR spectrum (in  $\text{CCl}_4$ ) showed no NH absorption, but alkyl CH stretching (2950, 2938 and a band of medium intensity at 2858  $\text{cm}^{-1}$  which was assigned to CH of  $\text{OMe}^{11}$ ). There is a strong carbonyl band at 1725  $\text{cm}^{-1}$ . No absorption band is observed between 1725 and 1438  $\text{cm}^{-1}$ , thereby excluding  $\text{C}=\text{N}$ ,  $\text{C}=\text{C}$ , and  $\text{N}=\text{N}^{22,26}$  bonds. A strong band at 1282  $\text{cm}^{-1}$  shows the presence of  $\text{C}-\text{O}$  linkage. In the NMR spectrum (in  $\text{CCl}_4$ ) we observe a triplet at 8.87,  $\tau$  3H; a doublet at 8.40,  $\tau$  3H; a quartet at 6.87,  $\tau$  2H; a singlet at 6.30,  $\tau$  6H; and a quartet at 4.51,  $\tau$  1H. Using the double resonance technique, the doublet

<sup>a</sup>The yields have been measured by VPC.

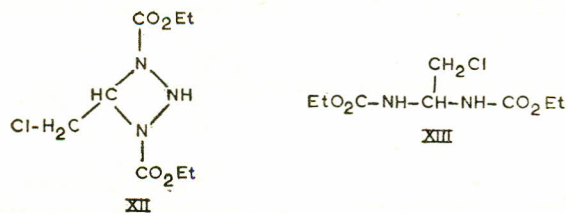
at 8.47  $\tau$  can be decoupled to a singlet by irradiating the 4.51  $\tau$  quartet with a secondary field ( $H_1 = 4.0$  mG). This shows a hydrogen atom on a tertiary carbon adjacent to a methyl group. The NMR spectrum also indicates the presence of two OMe and one  $-\text{NET}$  group. The mass spectrum of a concentrated methanol solution, or the neat compound shows the molecular weight as 217. From the elemental analysis, and  $P+1/P$  and  $P+2/P$  ratios in mass spectrum, the molecular formula was determined to be  $\text{C}_8\text{H}_{15}\text{N}_3\text{O}_4$ .

## Discussion

On the basis of the results mentioned above we have considered the following seven structures for compound XI:



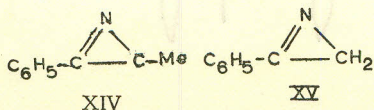
The triazetidine derivatives of the type XIa and XIb are so far unknown. In 1922 Datta and Chatterjee<sup>12</sup> assigned the structure 1,3-dicarboxy-4-(chloromethyl)-1,2,3-triazetidine (XII), to a product obtained from the hydrolysis of the chlorination product of urethane. Reinvestigation of this product by Kerber and Porter,<sup>13</sup> however, revealed that this compound has an open chain structure (XIII), based on elemental analysis, IR, NMR and mass spectral evidence.



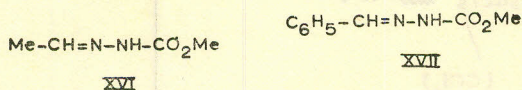
One could write reasonable pathways to arrive at the various structures for compound XI. Some of the



structures, however, can easily be left out of discussion on account of the spectral evidence alone. Thus XIc and XIe seem unlikely because they have a C=N bond, and we do not observe any IR absorption band for this function (in fact no absorption band between 1725–1438  $\text{cm}^{-1}$  is present). The 1725  $\text{cm}^{-1}$  band would be too high for a C=N bond, particularly for an open chain structure. The C=N stretching frequency in 2-phenyl substituted 1-azirines, compound XIV and XV appear at 1740  $\text{cm}^{-1}$  reflecting a highly strained ring system.<sup>14</sup>



The C=N stretching frequency of acetaldehyde<sup>15</sup> and benzaldehyde<sup>16</sup> carbomethoxyhydrazones prepared for comparison in our laboratory, appear at 1538 and 1555  $\text{cm}^{-1}$  respectively. In our view there is no apparent reason for C=N absorption of structure XIc and XIe to differ drastically from that of compounds XVI and XVII. One would also imagine that the observed position of the NMR signal for the methine hydrogen would be too high for structures



XIc and XIe. The methine hydrogens of XVI and XVII appear at 2.68 and 2.08  $\tau$  as a quartet and singlet respectively. Signals for the methine hydrogens of 2,4-dinitrophenylhydrazones of acetaldehyde, propionaldehyde and a few others appears between 2.42–2.50  $\tau$ .<sup>17</sup> From analogy, one would expect the methine hydrogens of XIc and XIe to appear between 2.5–3.0  $\tau$ .

Structure XIId also does not call for any discussion since it does not go along with the splitting pattern observed in the NMR spectrum.

In the case of compound XIg the methine hydrogens would be expected to appear at a higher field than the observed signal. The literature seems to be devoid of an example of absorption by a methine hydrogen in a diaziridine system, but considering the position of methylene signals in such a system, one can make a reasonable assumption. The methylene hydrogens of several substituted diaziridines<sup>18,19</sup> appear between 7.64–7.98  $\tau$  or higher. Also one would expect to observe in the mass spectrum a peak at  $m/e$  146 for the  $(\text{N}-\text{CO}_2\text{Me})_2^+$  ion, which is completely absent. IR and mass spectral evidence also excludes the structure XIIf, in which one would expect an IR band between 1510–1560  $\text{cm}^{-1}$  for N=N bond,<sup>22,26</sup> but it is also absent in the observed spectrum. Also one would expect to observe the ions  $^+\text{N}(\text{CO}_2\text{Me})_2$   $m/e$  132,  $\text{Me}-\text{CH}-\text{N}(\text{CO}_2\text{Me})_2$   $m/e$  160, and  $^+\text{N}-\text{CO}_2\text{Me}$   $m/e$  73 in its mass spectrum. We do not observe any of these ions in either 70 V or the 13 V spectra.

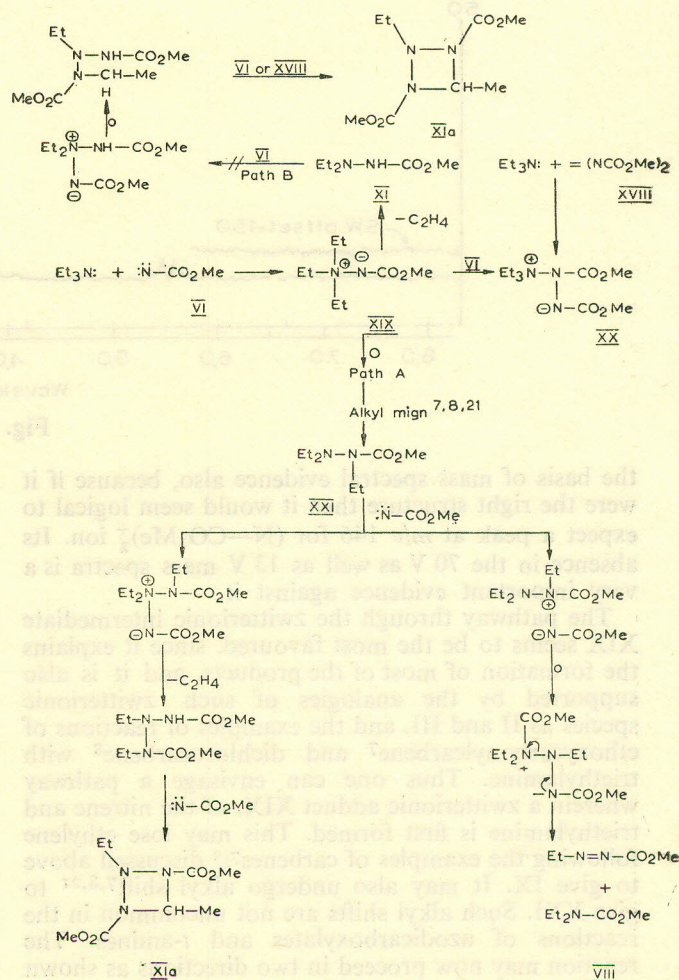
Now we are left with only two structures, i.e. XIa and XIb, and to choose from these is not an easy task.

The distinction between the two, however, becomes clear from the spectral data, (IR and NMR spectra are given in Fig. 1) and the discussion of the mechanism.

**Mechanism.** Of all the possibilities, two zwitterionic species XIX and XX (scheme 2) are considered as possible intermediates in the formation of various products. These may be simply derived by the coordination of triethylamine with methoxycarbonylnitrene (VI), and dimethylazodicarboxylate (XVIII), respectively. Intermediate (XX) may also be formed by addition of a nitrene to XIX and they are known to be formed in the reactions of *t*-amines with azodicarboxylates.

One can think of a number of pathways leading to XIb via intermediate XX. But on the basis of above-mentioned results, and the fact that the reaction of triethylamine with dimethylazodicarboxylate does not give any triazetidine derivative in question, they do not warrant any discussion. Alternate routes initially involving products of insertion by the nitrene in the 2° CH bond of triethylamine, as the possible intermediate, leading to XIb are not considered either on the same grounds. This structure is discounted on

Scheme 2





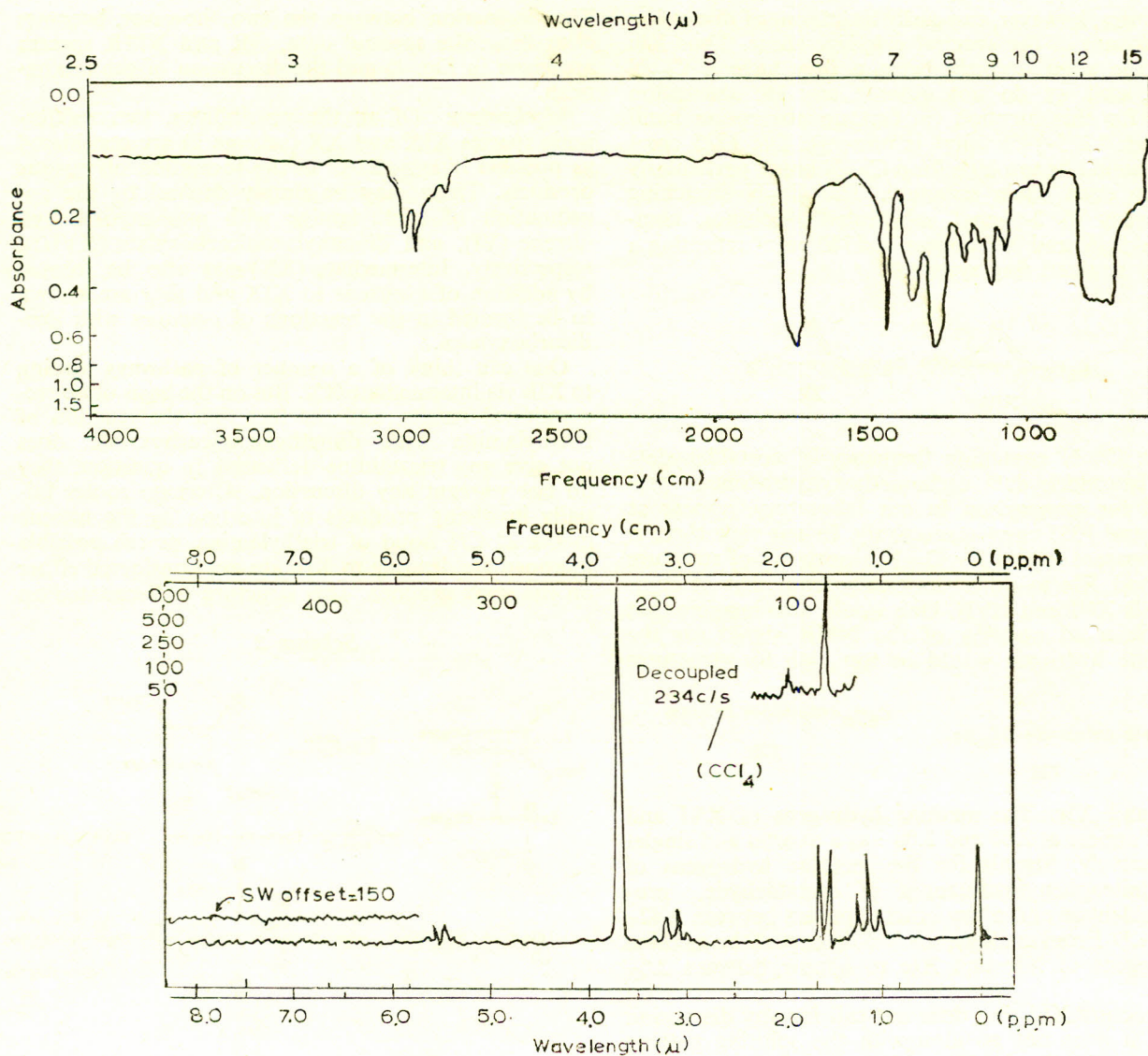


Fig. 1

the basis of mass spectral evidence also, because if it were the right structure then it would seem logical to expect a peak at  $m/e$  146 for  $(N-CO_2Me)_2^+$  ion. Its absence in the 70 V as well as 13 V mass spectra is a very important evidence against it.

The pathway through the zwitterionic intermediate XIX seems to be the most favoured, since it explains the formation of most of the products, and it is also supported by the analogies of such zwitterionic species as II and III, and the examples of reactions of ethoxycarbonylcarbene<sup>7</sup> and dichlorocarbene<sup>8</sup> with triethylamine. Thus one can envisage a pathway wherein a zwitterionic adduct XIX, of the nitrene and triethylamine is first formed. This may lose ethylene following the examples of carbenes<sup>7,8</sup> discussed above to give IX. It may also undergo alkyl shift<sup>7,8,21</sup> to give XXI. Such alkyl shifts are not uncommon in the reactions of azodicarboxylates and *t*-amines. The reaction may now proceed in two directions as shown to give various products. The final dehydrogenation

and accompanied ring closure may be accomplished in a concerted fashion by the nitrene or the dimethylazodicarboxylate giving VII or X as the case may be, in addition to XIa.

We have also considered and discounted a pathway (path B, scheme 2) involving IX as the possible intermediate enroute to XIa, since the reaction of IX with methoxycarbonylnitrene generated by the reaction of potassium *t*-butoxide, lithium aluminium hydride or sodium hydride with methyl-*N*-(*p*-nitrobenzenesulphoxy)carbamate(V), under similar conditions does not give any of the triazetidine derivative in question.

### Experimental

All m.ps. were taken on a Fisher-Johns apparatus and are uncorrected. IR spectra were taken on a Perkin-Elmer grating IR spectrophotometer model 621. NMR spectra were recorded on a Varian A-60-A



spectrometer; measurements are expressed in p.p.m. ( $\tau$ ) down-field from tetramethylsilane (TMS) used as an internal standard. Mass spectra were taken on a Hitachi mass spectrometer model RMU-6E.

Vapour phase chromatography (VPC) was carried out isothermally on a Wilken aerograph model A-90-P3, having a thermal detector. Aluminium columns ( $\frac{3}{8}$ " I.D.) packed with 50/60 mesh Anakrom ABS solid support with various substrates were used. Quantitative VPC analyses were evaluated planimetrically, after calibration of the detector response by injecting weighed pure sample. Microanalyses were done by M.W.H. Labs., Garden City, Michigan.

*Preparation of Methyl-N-(p-nitrobenzenesulphonyloxy) carbamate(V).* It was prepared in 70% yield according to the reported method,<sup>4</sup> by the reaction of *p*-nitrobenzenesulphonyl chloride and *N*-hydroxycarbamate,<sup>23</sup> which in turn was prepared from hydroxylamine and methylchloroformate. M.p. 135°C, (lit.<sup>4</sup> 131–131.5°C). IR (KBr): NH, 3430w, 3285s, 3260s; CH, 2965m, 2870w; C=O, 1758s; other strong bands are 1545, 1532, 1470, 1390, 1354, 1278, 1194, 1088, 855, 770 and 745.

*Reaction of Methoxycarbonylnitrene with Et<sub>3</sub>N.* To a solution of 3.63 g (35.9 mmole) Et<sub>3</sub>N in 5 ml CH<sub>2</sub>Cl<sub>2</sub> in a 500-ml R.B. flask fitted with a condenser and mechanical stirrer, was added a solution of 4.5 g (16.3 mmole) of V in 200 ml CH<sub>2</sub>Cl<sub>2</sub> with stirring and cooling (0°C). Addition is completed in 45 min and the reaction mixture is further stirred for 2½ hr at room temperature. The precipitated triethylammonium salt (4.51 g) is filtered off. The volume of the filtrate is reduced to 2.0 ml and it is analysed by VPC on a 20% UCON Polar 50HB2000 (1 ft ×  $\frac{1}{4}$  in), and a 20% Silicone Gum Rubber SE-30 on 60/80 mesh Chromosorb W (5 ft ×  $\frac{1}{4}$  in) columns. VPC as described above separated all the components, in the order: VII (5.5%); VIII (2.3–3%); IX (2.6%); X (10–12%) and XIa (5–8%). Methyl carbamate VII, and dimethyl hydrazodiformate X were identified by comparison of their IR spectra, m.ps. and VPC retention times with those of the authentic materials.

*N-N-Diethylmethylcarbamate(VIII).* A colourless liquid (b.p. 150–51°C/664 mm Hg) was the second fraction in the VPC separation; IR (CCl<sub>4</sub>): CH, 2973s, 2942m and 2873m; C=O, 1700s; NMR (CDCl<sub>3</sub>), 8.87  $\tau$  (T) 6H; 6.75  $\tau$  (Q) 4H; 6.34  $\tau$  (S) 3H; mass spectrum *P*, 131, *P*+1/*P*, 7.22% (calcd. 7.15%). Major fragmentation: *P*—CH<sub>3</sub>=116 (92%), *P*—CO<sub>2</sub>Me=72 (29%), *P*—72=59 (37%), and *P*—87(CO<sub>2</sub>, 100%). Compound VIII was independently synthesised by reaction of diethylamine with methyl chloroformate as follows: To a solution of 11.1 g (105 mmole) methyl chloroformate in 30 ml dry ether was added a solution of 17.4 g (237 mmole) diethylamine in 30 ml Et<sub>2</sub>O over a period of 15 min with stirring and cooling (0°C). The hydrochloride of the amine was filtered off, and Et<sub>2</sub>O was removed under reduced pressure on a rotary evaporator and VIII was distilled using a 3½ in Vigreux column, b.p. 150–51°C/664 mm Hg (lit.<sup>24</sup> b.p. 154–55°C), yield = 11.5 g (88.3%).

*2,2-Diethyl Methylcarbazate(IX).* A white solid was the third fraction in the VPC separation and purification of the crude reaction mixture: IR (KBr)

NH, 3440s, 3195s; CH, 2975s, 2938w and 2875m; C=O, 1725s. The following strong bands were displayed in the finger print region: 1530, 1464, 1246, 1112, 1052, 985 and 818 cm<sup>-1</sup> NMR (CDCl<sub>3</sub>): 8.9  $\tau$  (T) 6H, 7.27  $\tau$  (Q) 4H and 6.3  $\tau$  (S) 3H.

The IR and NMR were identical with the authentic material synthesized by reaction of Me<sub>2</sub>CO<sub>3</sub> with *N,N*-diethylhydrazine. The latter was synthesized after Vogel *et al.*<sup>25</sup> by nitrosation of diethylamine and subsequent reduction of the nitroso compound. Crystallisation from ether gave a white solid, m.p. 117–118°C. The same compound was also obtained by the reaction of methyl carbazate with EtI in the presence of pyridine.

*Compound XIa.* A colourless liquid was isolated by VPC as the fourth fraction as described above. IR and NMR spectrum is given in Fig. 1. It gave elemental analysis within  $\pm 0.3\%$  of the calculated value for C<sub>8</sub>H<sub>15</sub>N<sub>3</sub>O<sub>4</sub>. IR (CCl<sub>4</sub>), no absorption above 3000 cm<sup>-1</sup>; CH, 2940m, 2956s, 2858w; C=O, 1725s (sh at 1750 cm<sup>-1</sup>). The following strong bands were observed in the finger print region: 1438, 1364, 1282, 1112 cm<sup>-1</sup> NMR (CCl<sub>4</sub>): 8.87  $\tau$  (T) 3H, *J* 7.0 c/s; 8.40  $\tau$  (D) 3H, *J* 6.0 c/s; 6.87  $\tau$  (q) 2H, *J* 7.0 c/s; 6.30  $\tau$  (S) 6H, and 4.51  $\tau$  (Q) 1H, *J* 6.0 c/s. Irradiation of 4.51  $\tau$  quartet with a secondary field (*H*<sub>1</sub> = 4.0 mG) resulted in the decoupling of the 8.40  $\tau$  doublet to a singlet. This indicates the presence of Me—CH— grouping. Mass spectrum: *P*, 217; *P*+1/*P* = 9.00% (calcd. 9.18%), *P*+2/*P* = 1.21% (calcd. 1.19%). 70 eV spectrum:

<i>m/e</i>	Relative abundance (%)	<i>m/e</i>	Relative abundance (%)
219	0.23	61	3.70
218	1.85	60	12.57
217	19.31	59	100.00
188	4.23	58	39.68
159	1.11	57	20.71
158	11.45	56	23.01
117	2.38	45	11.90
116	4.23	44	16.13
115	0.92	42	53.96
103	2.77	41	6.61
102	17.59	32	6.08
101	1.71	30	21.69
87	3.17	29	77.77
86	2.64	28	48.80
85	4.62	18	33.33
84	2.66	15	74.60
75	2.38		
72	3.83		
71	3.96		
70	28.57		

*Reaction of Dimethyl Azodicarboxylate with Et<sub>3</sub>N.* To an ice-cooled solution of 3.0 g (20.5 mmole) of XVIII, in a 100-ml RB flask fitted with a condenser and a drying tube, was added an equimolar amount (2.85 ml) of Et<sub>3</sub>N. After addition, it was stirred for 3 hr. Colour change from orange to dark brown was observed. VPC on a 20% UCON Polar 20HB2000



on 50–60 mesh Anakrom ABS column (col. temp. 140°C, gas flow, 50 ml/min) showed some unreacted (XVIII) and dimethyl hydrazoformate. There was no compound (XIa) detected in this reaction.

*Reaction of Methoxycarbonylnitrene with 2,2-Diethyl Methylcarbazate (IX).* 1.46 gram (10 mmole) of IX, and 2.24 g (20 mmole) K *t*-butoxide was taken in a 250-ml two-neck RB flask. To this a solution of 5.52 g (20 mmole) nosylate (V), in CH<sub>2</sub>Cl<sub>2</sub> or Et<sub>2</sub>O was added dropwise with stirring under cooling (ice+water). After filtration the volume of the reaction mixture was reduced and analysed by VPC under identical conditions of the original reaction. Starting material (IX) was among the products, but no triazetidene derivative (XIa) was detected. The reaction was repeated with LiAlH<sub>4</sub> or NaH used as a base for  $\alpha$ -elimination. None of the two experiments yielded XIa.

*Preparation of Methoxycarbonyl Hydrazone of Acetaldehyde (XVI).* It was prepared by the reaction of methyl carbazate with acetaldehyde. The former was prepared by dropwise addition of a MeOH solution of 13.5 g (270 mmole) of hydrazine hydrate to an ice-cooled solution of 22.5 g (250 mmole) Me<sub>2</sub>CO<sub>3</sub> in 15 ml MeOH, in a 100 ml RB flask fitted with a condenser, drying tube and a magnetic stirrer. The reaction is exothermic. Removal of solvent gave a white solid. Recrystallisation from MeOH gave 15.7 g (69.7%) white needles, m.p. 69–70°C. IR (KBr): NH, 3344s; CH, 2976s, C=1724s. NMR (CDCl<sub>3</sub>): 6.27 $\tau$  (S).

In the second step to an ice-cooled solution of methylcarbazate was added a MeOH solution of an equimolar amount (1.69 ml) of MeCH=O in a 50-ml R.B. flask fitted with a condenser and drying tube. Removal of methanol, on a rotary evaporator under reduced pressure gave a white solid. Crystallisation from MeOH gave 3.58 g (92.5%) of XVI. IR (KBr): NH, 3236s; CH, 3067s, 2976s, 2874m and 2818w; C=O, 1709s; C=N, 1538s; other strong bands are: 1447, 1385, 1351, 1250, 1143, 1026, 917, 885, 808, 733. NMR (CDCl<sub>3</sub>): 8.02 (D) *J* 5.5c/s, 3H; 6.2 $\tau$  (S) 3H; 2.68  $\tau$  (Q) *J* 5.5 c/s 1H.

*Preparation of Methoxycarbonyl hydrazone of PhCH=O (XVII).* It was prepared in (53% yield) in the same way as described for XVI, m.p. 146°C. IR (KBr): NH, 3348s and 3226m; CH, 3058s, 3021 and 2985s; C=O, 1695s, C=N, 1555s; following strong bands were displayed in the finger print region: 1488, 1449, 1366, 1250, 1047, 956, 861, 769 and 698. NMR (CDCl<sub>3</sub>): 6.13 $\tau$  (S); 2.6 $\tau$  (M) 5H, and 2.08 $\tau$  (S) 1H.

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