

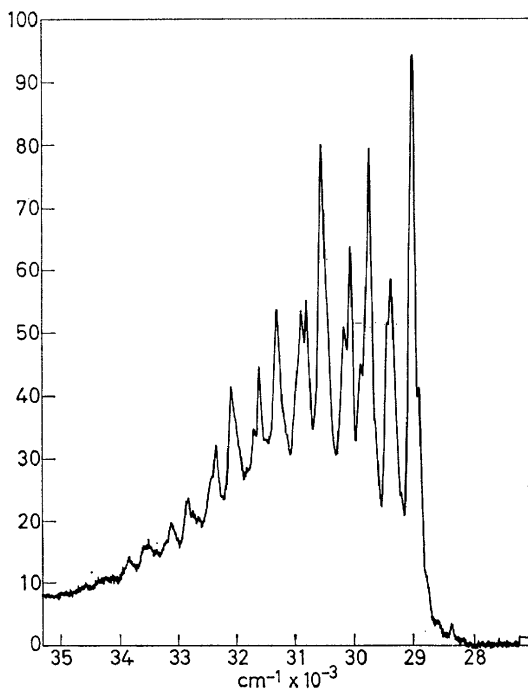
# PHOTOLYSIS OF THE DIAZIRINES

H. M. FREY

*Chemistry Department, University of Southampton, U.K.*

## INTRODUCTION

The first preparations of cyclic diazo compounds (diazirines) were described independently by Paulsen<sup>1</sup> and Schmitz and Ohme<sup>2</sup> only four years ago. It is remarkable that the synthesis of these compounds has been so long delayed since in many ways they are more readily obtained (and in higher yields) than the corresponding diazo compounds. Indeed already diazirines are known in the pure state where the corresponding diazo compounds have not been prepared or are available only in solution<sup>3</sup>. Chemically, diazirines are remarkably unreactive, resembling nitrogen rather than diazo compounds (they might perhaps be considered as homonitrogens!); they do however share the instability to heat and u.v. light of diazocompounds. There have been several reports of the explosive nature of



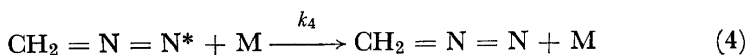
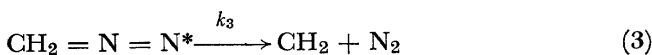
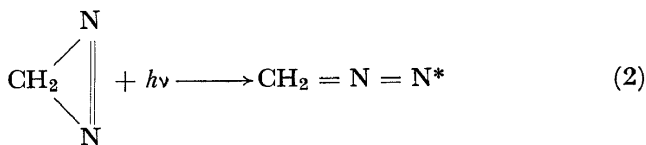
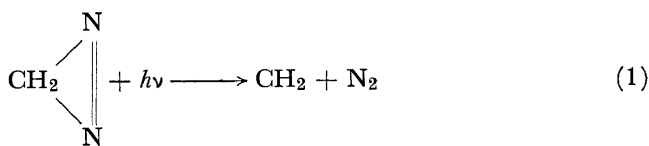
*Figure 1.* Absorption spectrum of 3-methyldiazirine (7 mm pressure)  
x axis : Frequency × 10<sup>-3</sup> cm<sup>-1</sup>  
y axis : Absorption (%)

some diazirines, though it seems likely that in the pure state and in the absence of catalytic surfaces they are reasonably safe at room temperature. We shall be principally concerned in this paper with the photochemical decomposition of some diazirines in the gas phase. Where, however, work on the liquid phase photolysis or the gas phase pyrolysis is helpful in elucidating the kinetic features of the main topic, it will be included.

The ultraviolet absorption spectra of the diazirines consists of a band extending from 300 to 370  $\mu$ . There is a small variation in these values from one diazirine to another but this is considerably less than in the corresponding diazo compounds. The band shows vibrational fine structure in all the diazirines so far investigated in the gas phase. *Figure 1* shows the absorption spectrum of 3-methyldiazirine.

It is not impossible that the spectrum consists of two overlapping bands. Thus the frequency differences between alternate peaks are close to 700 and 750  $\text{cm}^{-1}$ . There is some doubt whether the transition corresponding to this band (or these bands) is  $\pi^* \leftarrow n$  or  $\pi^* \leftarrow \pi$ . On the basis of small frequency shifts in various solvents, Lau<sup>4</sup> has argued that it is of the latter type. However, from the lack of any chemical reactivity of the lone pair electrons on the nitrogens (diazirines do not appear to form complexes of any kind, quite distinct for example from azo compounds), it seems clear that they are not to be treated as 'normal' lone pair electrons, and hence the accepted criterion for distinguishing between the two types of transition on the basis of solvent effects is unreliable. A solution of this problem will probably come when the exact nature of the bonding in these compounds is better understood. In the interim we believe the bulk of the evidence indicates a  $\pi^* \leftarrow n$  transition.

Photolysis of diazirine<sup>5, 6</sup> in the gas phase in the presence of nitrogen or various hydrocarbons shows that the compound decomposes with the formation of methylene (the methylene then reacting with the hydrocarbon or with the diazirine). There are two probable paths for the reaction:

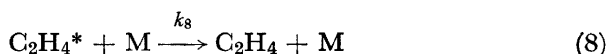
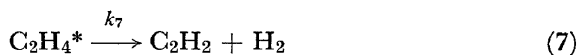
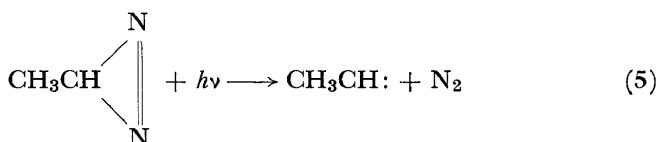


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The relative importance of reactions (1) and (2) is not yet known. By using light of 3200 Å, Amrich and Bell<sup>6</sup> were able to detect the formation of diazomethane. They set a lower limit on  $k_2/k_1$  of 0.1. Owing to the presence of scattered radiation of wavelength other than 3200 Å the yield of diazomethane goes through a maximum due to secondary photolysis. It is remarkable that the yield of diazomethane does not show a dependence on the pressure of added nitrogen, as is to be expected from the simple mechanism. Further, it is clear that initially the diazomethane must be formed in an electronically excited state, since the lifetime of a vibrationally excited ground state molecule would be far too short to allow collisional stabilization. More work on this system is clearly desirable before a detailed reaction mechanism can be discussed.

### 3-METHYLDIAZIRINE

This compound is quite stable as a gas and has been stored as a gas at 200 mm pressure at 0° for some months without appreciable decomposition. It has been reported<sup>7</sup> that an attempt to condense some of the vapour led to a violent detonation. We have in fact carried out this operation on numerous occasions without this result, but it is clear that caution should always be exercised when handling the low molecular weight diazirines. Photolysis of 3-methyldiazirine in the gas phase has been carried out using a medium pressure arc and a Pyrex reaction vessel. Under these conditions photolysis is due to the 3130, 3340 and 3660 Å lines in the mercury spectrum. The gaseous products are ethylene, acetylene, hydrogen and nitrogen. After numerous photolyses a very small amount of polymer is formed on the surface of the reaction vessel. The relative yields of ethylene to acetylene are pressure dependent. By analogy with the photolysis of diazoethane<sup>8</sup>, the following mechanism seems likely:



The complete absence of any C<sub>4</sub> olefins indicates that there is no reaction between the ethylidene (or the excited ethylene molecule) and the methyldiazirine. This contrasts markedly with the corresponding diazo system. The yields of acetylene as a function of pressure are shown in *Figure 2*. It will be seen that the yield of acetylene, at zero pressure (by extrapolation),

is 60.2 per cent. The suggested mechanism would lead to a value of 100 per cent. It thus appears that there is a reaction leading to the production

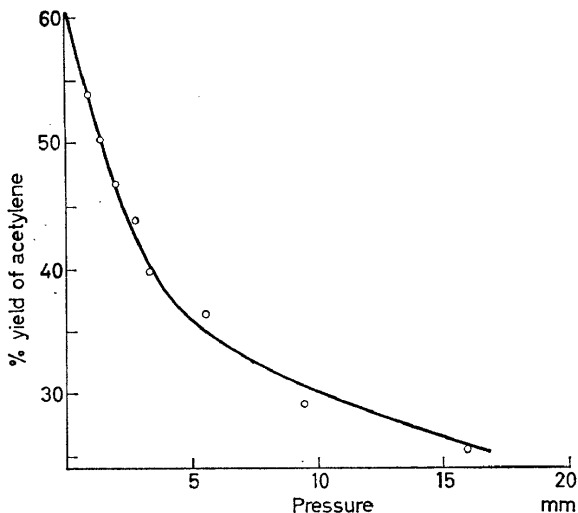
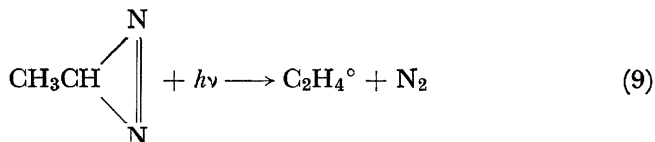


Figure 2. Percentage yield of acetylene as a function of pressure  
 x axis : Pressure mm  
 y axis : % Acetylene

of ethylene which contains insufficient energy to undergo decomposition into acetylene and hydrogen. Accordingly the following reaction is added:



where  $\text{C}_2\text{H}_4^\circ$  indicates a molecule of ethylene with insufficient energy to decompose. Reaction (9) is responsible for approximately 40 per cent of the ethylene initially produced. The experimental data do not permit a differentiation to be made between whether reaction (9) occurs as a single step (with the nitrogen molecule formed in a vibrationally excited state) or *via* an excited molecule of methyl diazirine.

Reactions (5)–(9) yield the equation

$$\frac{\text{C}_2\text{H}_4 - \text{C}_2\text{H}_4^\circ}{\text{C}_2\text{H}_2} = \frac{k_8 M}{k_7} \quad (10)$$

If  $k_8 M$  is taken as directly proportional to the initial pressure (and there are experimental reasons for believing that this is a very good approximation), then a plot of the left hand side of equation (10) against the pressure should give a straight line. Such a plot is shown in *Figure 3*.

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At pressures below 10 mm, *i.e.* the pressure range covering the region where all the initially formed excited ethylene decomposes to the point where about half is collisionally stabilized, this relationship is obeyed. Above

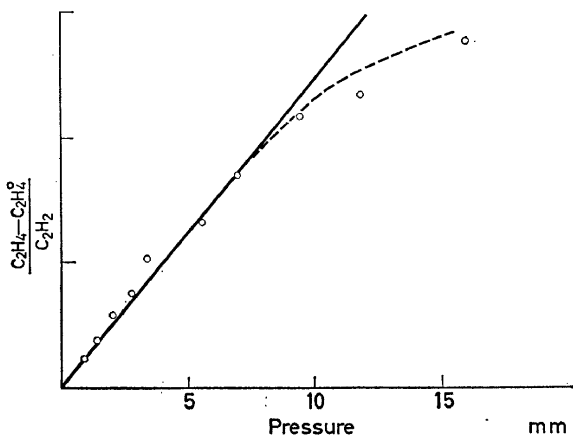
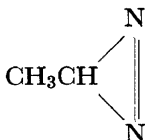


Figure 3. Plot of  $(\text{C}_2\text{H}_4 - \text{C}_2\text{H}_4^*)/\text{C}_2\text{H}_2$  as function of pressure  
*x* axis : Pressure mm  
*y* axis :  $(\text{C}_2\text{H}_4 - \text{C}_2\text{H}_4^*)/\text{C}_2\text{H}_2$

10 mm the plot shows marked curvature. This may be ascribed to a variation in the value of  $k_7$  which in turn probably indicates that the initially formed vibrationally excited molecules of ethylene contain a range of energies. If deactivation of  $\text{C}_2\text{H}_4^*$  by



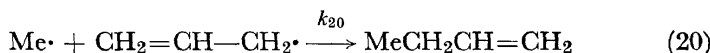
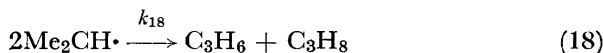
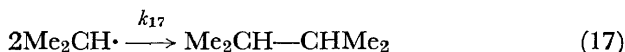
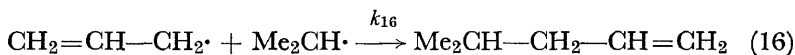
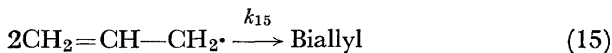
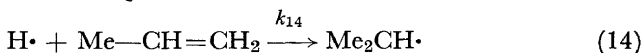
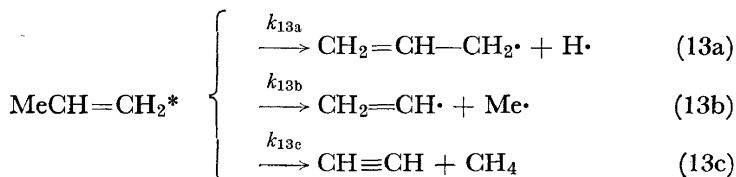
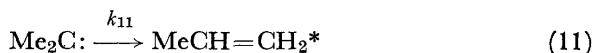
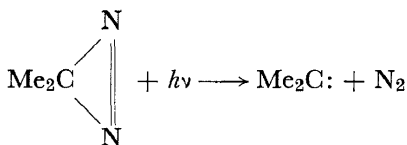
occurs on every collision then  $k_7 \approx 5.4 \times 10^7 \text{ sec}^{-1}$ .

Attempts to detect the formation of diazoethane by using monochromatic light of 3130 Å (which is not absorbed by diazoethane) were negative. Certainly not more than 5 per cent of the primary decomposition can occur by this path. Similarly, attempts to prove the intermediate formation of ethylidene by photolysing methyl diazirine in the presence of large excesses of ethylene, propylene and allene, and carefully looking for any addition products, were unsuccessful. Thus the postulated intermediacy of ethylidene rests largely on indirect analogies with other systems.

### 3,3-DIMETHYLDIAZIRINE

The photolysis of 3,3-dimethyldiazirine has been investigated in the gas phase, alone and in the presence of added nitrogen<sup>9</sup>. At pressures above about 200 mm, the reaction yields propylene and nitrogen in equimolar amounts with only trace amounts of other products. At pressures below

60 mm increasing amounts of other hydrocarbon products are formed. The primary step in the photolysis is thought to be the production of dimethylcarbene and nitrogen. The carbene rapidly rearranges to yield a "hot" molecule of propylene. The products formed at low pressures are explained in terms of the reactions of radicals formed by the decomposition of the excited propylene. Some of the suggested steps in the mechanism, which accounts for most of the major products observed, are:



The experimental results indicate that reactions between the various radicals produced and the dimethyldiazirine are relatively unimportant, a further indication of the chemical inertness of these compounds. Attempts to trap the dimethylcarbene by photolysis of the dimethyldiazirine in cyclohexene were not successful. If the carbene is an intermediate, then either reaction (11) must be very fast, or the addition of the carbene to a double bond must have an appreciable energy of activation, or both. No

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evidence was obtained for a photo-isomerization reaction leading to the formation of the normal diazo compound.

### 3-METHYL-3-ETHYLDIAZIRINE

Preliminary work on the gas phase pyrolysis and photolysis of this compound has been reported<sup>10</sup>. Thermal decomposition of the diazirine at 160° gives *cis*- and *trans*-butene-2, butene-1 and methylcyclopropane in essentially the same yields as obtained by the pyrolysis of the *p*-toluene sulphonylhydrazone of methylethylketone in an aprotic solvent in the presence of sodium methoxide. (See *Table 1*).

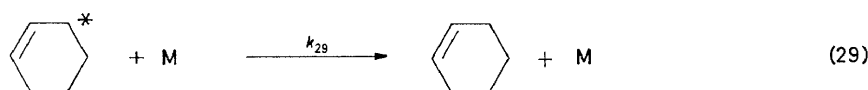
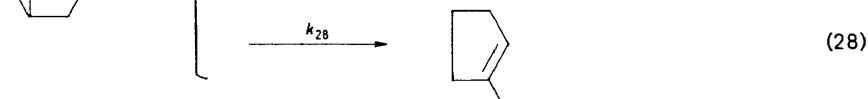
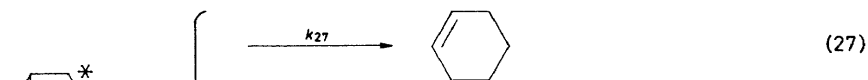
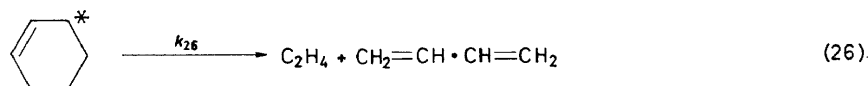
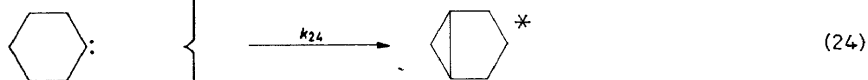
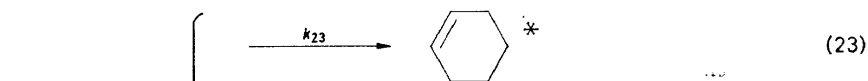
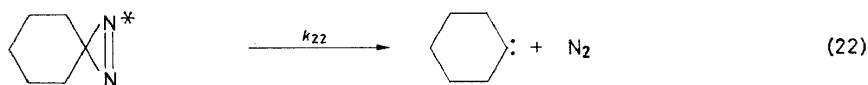
*Table 1.* Percentage yields of hydrocarbons from methylethylcarbene from different sources

	<i>Butene-1</i>	<i>trans-Butene-2</i>	<i>cis-Butene-2</i>	<i>Methyl cyclopropane</i>
From toluenesulphonyl hydrazone	5	67	28	0.5
Pyrolysis of methylethyldiazirine	3.6	66.5	29.5	0.4
Photolysis of methylethyldiazirine	23.4	38.6	35.6	2.4

There is strong evidence that the decomposition of tosylhydrazones in aprotic media proceed *via* the intermediate formation of a carbene. It is therefore reasonable to assume, in view of the similarity of the results shown in *Table 1*, that the pyrolysis of methylethyldiazirine involves methylethyl carbene. The photolysis of methylethyldiazirine also yields the same hydrocarbons but with much increased amounts of the thermodynamically less stable isomers. These results have been rationalized in terms of the formation of a vibrationally excited carbene in the photochemical reaction. The suggestion that carbenes can be produced as "hot" radicals has been made previously<sup>11</sup> and has received considerable experimental support<sup>12</sup>.

### 3,3-PENTAMETHYLENE DIAZIRINE

The photolysis of pentamethylene diazirine in the gas phase<sup>13</sup> at pressures above 20 mm yields cyclohexene and nitrogen as the major products. Minor products are bicyclo[3,1,0]hexane and methylene cyclopentane. The relative yields of cyclohexene, bicyclohexane and methylene cyclopentane are 97.0:2.5:0.4. Once again the primary process can be considered as the formation of a carbene, followed by rapid intramolecular reactions to yield the various hydrocarbons. At pressures below 10 mm some of the cyclohexene has sufficient energy to decompose into butadiene and ethylene. At pressures below about 3 mm very small quantities of 1-methylcyclopentene have been detected. This compound is probably formed by the unimolecular decomposition of the "excited" bicyclohexane<sup>14</sup>. The mechanism postulated<sup>13</sup> to explain these observations is shown below:



The suggested mechanism leads to the the equation

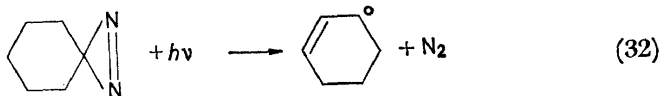
$$\frac{[\text{cyclohexene}]}{[\text{butadiene}]} = \frac{k_{29}\text{M}}{k_{26}} \quad (31)$$

if the small contribution to the concentration of cyclohexene formed *via* reaction (29) is neglected. A plot of the left hand side of equation (31) against the pressure shows very considerable curvature. This has been



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ascribed to the production of molecules of cyclohexene with a wide range of energy contents. However if the percentage yield of cyclohexene is plotted against the total pressure and extrapolated to zero pressure the intercept is not zero, as is to be expected from the suggested mechanism. While the actual value at  $P = 0$  cannot be determined with high accuracy the value obtained of approximately 52 per cent should not be in error by more than  $\pm 3$  per cent. It would therefore appear that there is a reaction leading directly to the formation of molecular cyclohexene with energy insufficient to undergo decomposition, *i.e.*



though this reaction may equally well occur *via* an excited molecule of the diazirine. In this respect the primary steps are analogous to those occurring in the photolysis of 3-methyldiazirine. If reaction (32) is included, then equation (31) becomes

$$\frac{[\text{cyclohexene} - \text{cyclohexene}^\circ]}{[\text{butadiene}]} = \frac{k_{25}M}{k_{26}} \quad (33)$$

where cyclohexene<sup>°</sup> is the yield of cyclohexene formed according to reaction path (32). A plot of the left hand side of equation (33) against the initial pressure shows far less curvature than when equation (31) is used. In the region where more than 50 per cent of the cyclohexene formed *via* reaction (23) decomposes the plot is linear, indicating the essentially monoenergetic nature of the excited molecules. The curvature at high pressures indicates some energy spread, which is of the same order as that found in excited molecules produced by the photolysis<sup>15</sup> of 2,3-diazobicyclo[2,2,1] hept-2-ene.

In addition to the gaseous products, after numerous photolyses a relatively non-volatile oil was formed on the walls of the reaction vessel. The oil was found to contain nitrogen and is probably an azine.

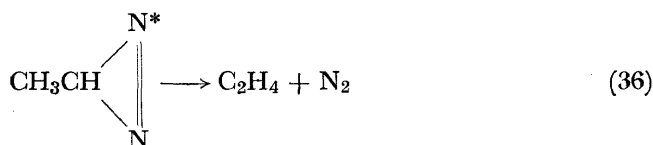
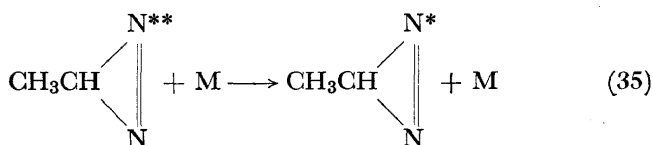
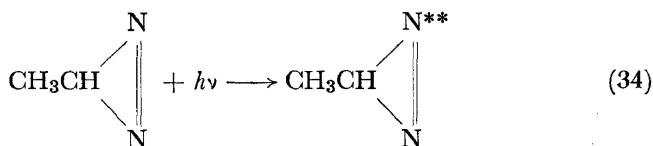
Photolyses of pentamethylene diazirine in the liquid phase<sup>16</sup> gave rise, in addition to cyclohexene, bicyclodexane and methylene cyclopentane, to between 15 and 20 per cent of dicyclohexylazine. Further, by infrared examination of the liquid mixture immediately following partial photolysis, the presence of diazocyclohexane was detected. Under these conditions the diazo compound has a lifetime of only a few minutes. It is probable that the azine results directly from a bimolecular reaction between two molecules of the diazo compound. Thus in the liquid phase the photo-isomerization reaction may account for as much as 40 per cent of the primary process. The relative importance of the photo-isomerization reaction in the gas phase is uncertain but it is probable that an appreciable fraction of the primary process follows this path.

The photolysis of the diazirines so far investigated in the gas phase appears to involve at least three primary steps. The photo-isomerization reaction to the corresponding diazo compound has been directly observed in the case of the photolysis of diazirine itself and this probably occurs, though

with varying importance, in most substituted diazirines. Whether the diazo compound is formed directly from an electronically excited diazirine or a vibrationally excited ground state molecule is as yet unknown. Further, whether or not the diazo compound is initially formed in an electronically excited state is also unknown, though consideration of the probable lifetime of a vibrationally excited ground state molecule makes this likely.

All the evidence for the reaction path proceeding *via* the formation of a carbene is indirect, since all attempts to trap this intermediate have been unsuccessful except in the case of the photolysis of diazirine itself. The failure to detect any addition products of the intermediate carbene cannot be taken as strong evidence for their non-formation, since the addition reaction is a bimolecular process and would be in competition with the various unimolecular processes leading to the formation of hydrocarbons. If the energies of activation for the two processes are similar, the unimolecular process will always be several powers of ten faster. In addition, if the carbene is formed initially with excess vibrational energy this will favour the unimolecular rearrangement. Perhaps the strongest evidence for the intermediate formation of a carbene is the identification of bicyclo[3,1,0]-hexane from the photolysis of pentamethylenediazirine and of 1,1-dimethylcyclopropane in the photolysis<sup>17</sup> of 3-t-butyl diazirine.

The formation of hydrocarbons in the photolysis of some diazirines whose yield is not pressure dependent suggests a third primary process. This may occur directly as suggested by reaction (9) where the nitrogen would have to contain the bulk of the excess energy of the reaction. Alternatively the reaction may occur by a two-step mechanism:



This postulates two excited states for the methyldiazirine, the higher energy state produced initially (reaction 34) giving rise to ethylidene, and the lower energy state, produced by deactivation (reaction 35) leading to ethylene directly. Of course a mechanism involving two excited states of ethylidene would be kinetically indistinguishable from this scheme. More work on these systems is required before these mechanisms can be accepted.

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