

THE THERMAL DECOMPOSITION OF  
2-METHOXY-2,5,5-TRIMETHYL- $\Delta^3$ -OXADIAZOLINE

by



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Thermal decomposition of a  $\Delta^3$ -oxadiazoline

To my family

### ABSTRACT

2-Methoxy-2,5,5-trimethyl- $\Delta^3$ -1,3,4-oxadiazoline was synthesized and decomposed neat, in the presence of carbon tetrachloride and in the presence of deuterated benzene. Because of the production of propene when  $C_6D_6$  was the solvent and chlorinated products when  $CCl_4$  was the solvent, a carbene mechanism is proposed. The evidence in support of this mechanism is strengthened by the trapping of the carbene intermediates with 1,1-diphenylethylene and the reaction of independently generated dimethylcarbene with  $CCl_4$ .

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## INTRODUCTION

A study of oxadiazolines revealed that in some cases they thermolyze through carbene intermediates. Therefore, the introduction will deal with some carbene chemistry with the addition of some background on oxadiazoline chemistry.

### I: Carbenes

#### A: Introduction

Carbenes are neutral, bivalent carbon intermediates in which a carbon atom has two covalent bonds, and two non-bonding orbitals containing two electrons. If the two electrons are spin-paired the carbene is a singlet; if the spins are parallel the carbene is a triplet.<sup>1</sup> A triplet carbene often reacts as a diradical.<sup>2</sup>

Singlet carbenes are electron deficient like carbonium ions, while possessing a non bonding pair like that of carbanions. Electrophilic or nucleophilic character of singlet carbenes depends on the ability of adjacent groups to withdraw electrons from or supply electrons to the carbene carbon.<sup>2</sup>

Carbenes with  $\text{NR}_2$ , SR or OR substituents behave like nucleophiles, in contrast to the electrophilic behaviour of many divalent carbon intermediates.<sup>2</sup>

This part will deal with the formation and the nucleophilic or electrophilic reactivity of carbenes.

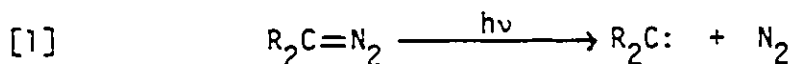
#### B: Generation of Carbenes

Carbenes can be generated from diazoalkanes, ketenes,

diazirines, and by other routes.

a) From diazoalkanes

Pyrolysis or photolysis of diazoalkanes generates carbenes.<sup>2</sup> The first suggestions that the decomposition of diazomethane might involve methylene,  $\text{:CH}_2$ , as an intermediate, were made by Nef at the end of the last century. The photolysis of diazo compounds, both in the gas phase and in solution, initiates a methylene transfer.<sup>3</sup>

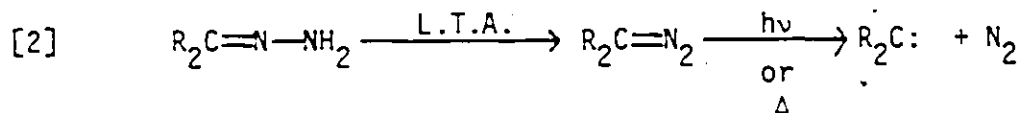


Carbenes generated by this method are highly energetic and their reactions may be indiscriminate.

Diazoalkanes can be generated from hydrazones, toluene-p-sulfonyl hydrazones,  $\Delta^3$ -1,3,4-oxadiazolines, and other compounds.

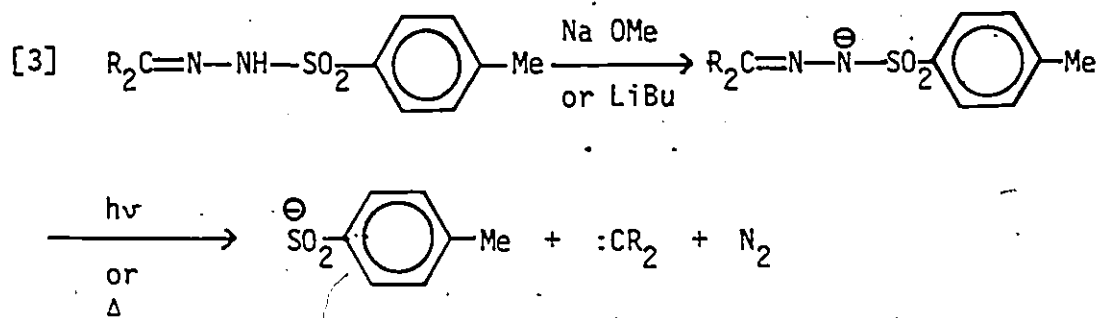
(i) From hydrazones:

Oxidation of hydrazones under mild conditions using lead tetraacetate (L.T.A.) yields diazoalkanes,<sup>4</sup> which can be decomposed directly to carbenes.

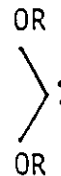
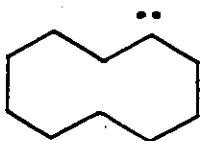
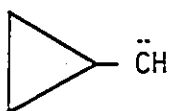


(ii) From toluene-p-sulfonyl hydrazones:

The reaction of Na OMe or LiBu with toluene-p-sulfonyl hydrazones followed by thermolysis<sup>5</sup> or photolysis<sup>6</sup> of the salt yields a carbene:



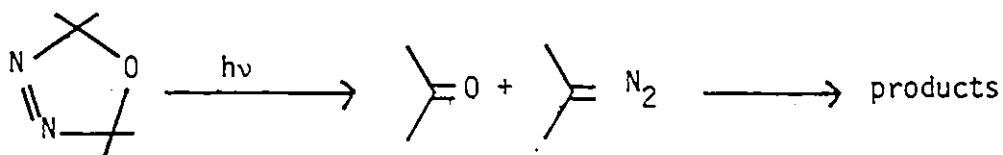
Among the wide range of carbenes generated by this method are:



(iii) From  $\Delta^3$ -1,3,4-oxadiazolines:

Irradiation of  $\Delta^3$ -1,3,4-oxadiazolines results in the formation of diazoalkanes and carbonyl compounds.<sup>7,8,9</sup>

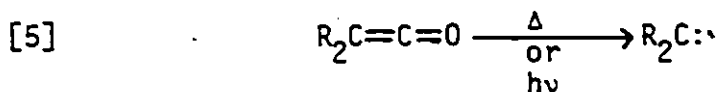
[4]



b) From ketenes

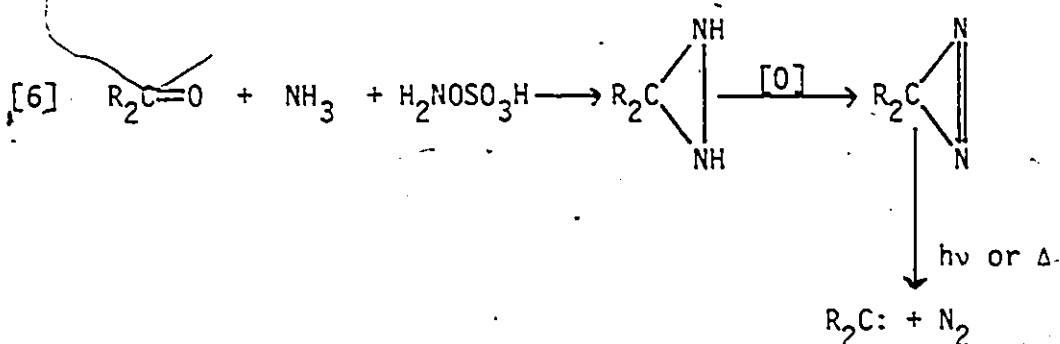
In the case of ketenes, carbon monoxide is lost in the carbene forming process. Substituted ketenes can similarly give carbenes by thermolysis or photolysis. This is not a good

route because ketenes tend to polymerize under the same conditions needed to generate carbenes.<sup>1</sup>



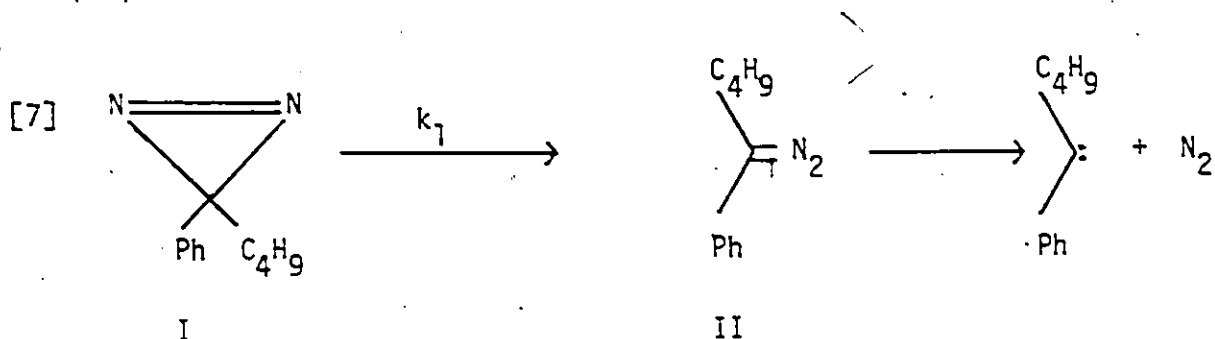
c) From diazirines

The photolysis of diazirines is an excellent procedure for generating carbenes since the diazirine tends to be less hazardous than the isomeric diazoalkane. Diazirines can be synthesized from ammonia, hydroxylamine-O-sulfonic acid and ketones.<sup>10</sup>

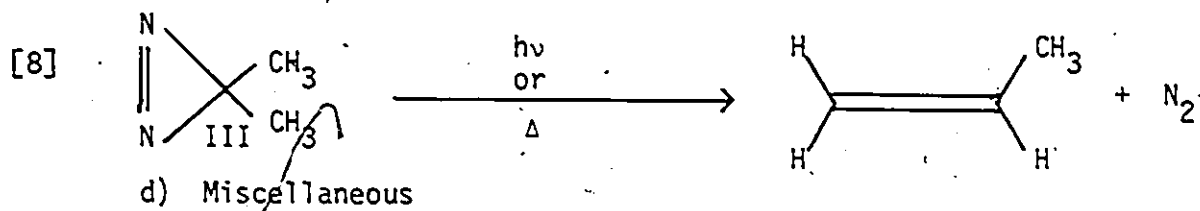


While there is evidence for diazoalkanes being intermediates in the photolysis of diazirines,<sup>11,12</sup> their presence in the thermolysis was not certain<sup>13,14</sup> up to 1976 when 1-phenyl-1-diazopentane (II) was formed<sup>3</sup> from the pyrolysis of 3n-butyl-3 phenyl diazirine<sup>15</sup>(I).

The proposed mechanism is:

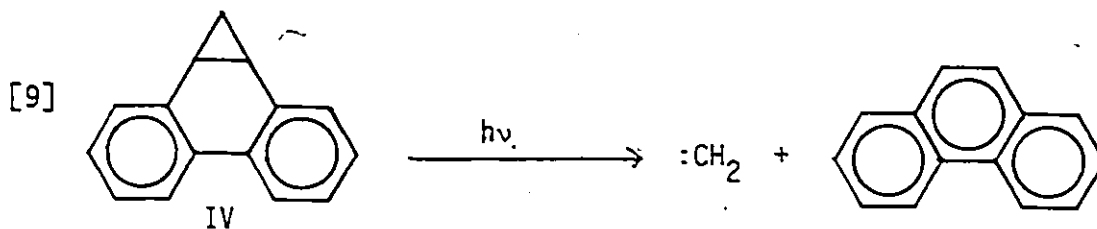


In the case of dimethyl diazirine (III) both photolysis<sup>17</sup> and thermolysis,<sup>18</sup> in the gas phase, yield propene as a major product.

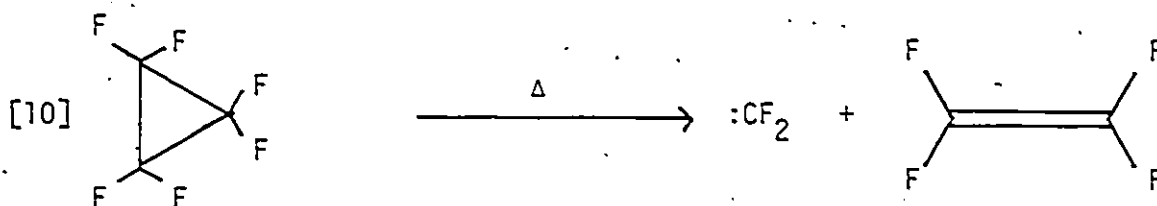


Photolysis of 9,10-dihydro-9,10-methanophenanthrene

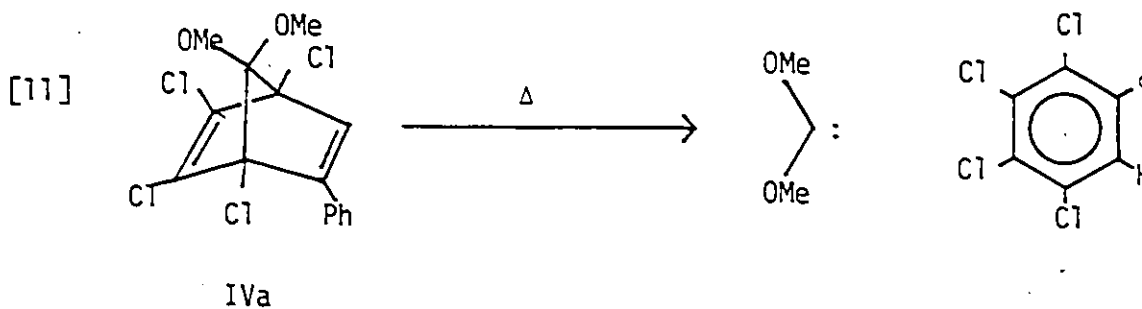
(IV) was shown to generate methylene.<sup>19</sup>

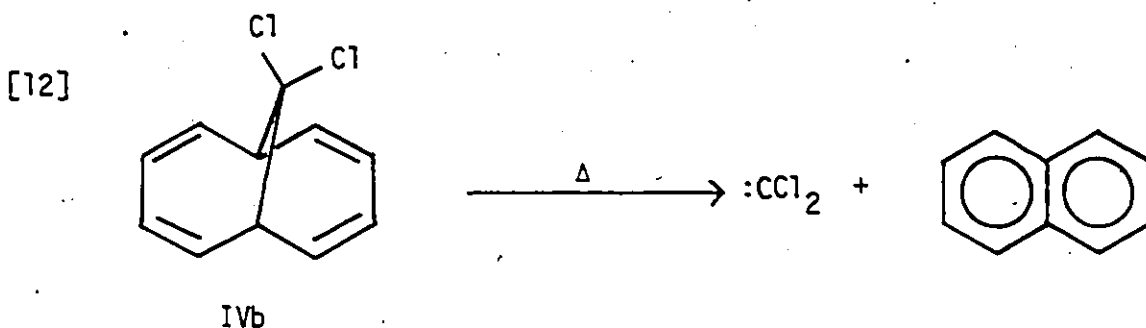


When pyrolysed, hexafluorocyclopropane yields difluorocarbene<sup>20</sup>



Finally, dimethoxy carbene<sup>21</sup> and dichlorocarbene<sup>22</sup> can be generated from the thermolysis of IVa and IVb respectively.





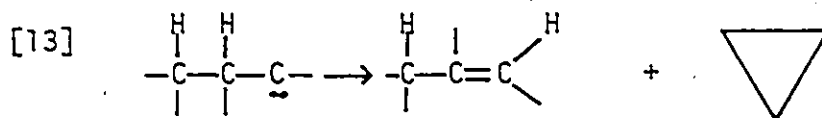
### C: Reactions of Carbenes

The two general reactions of carbenes are insertion reactions and addition reactions. Depending on the substituents, intramolecular or intermolecular insertion or addition can occur.

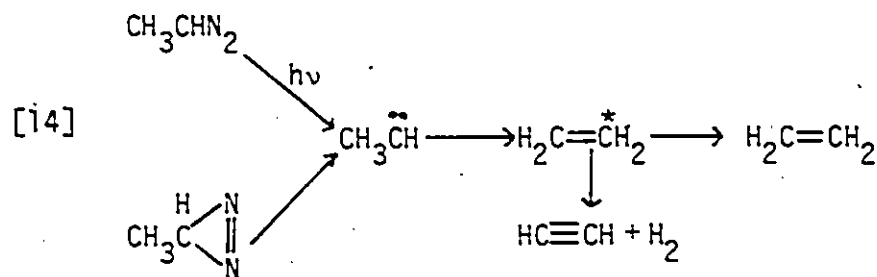
#### a) Insertion reactions

##### (i) Intramolecular insertion

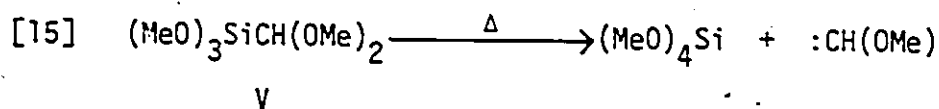
Alkyl and dialkyl carbenes react, predominantly by insertion of the divalent carbon into  $\beta$  and  $\gamma$  C-H bonds, yielding olefins and cyclopropanes.<sup>2,23</sup>



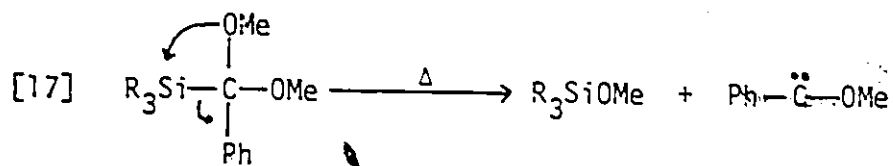
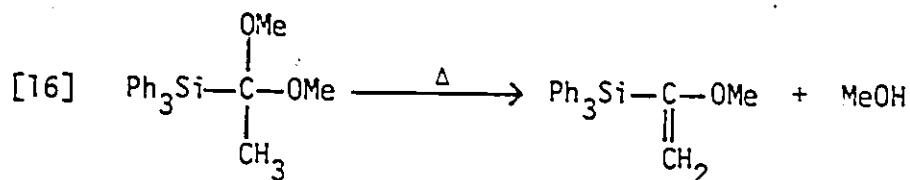
Dimethyl carbene could not be added to olefins, propene being the only product from photolysis and thermolysis of dimethyl diazirine.<sup>17,18</sup> Photolysis of diazoethane<sup>24</sup> and methyl diazirine<sup>25</sup> yielded ethylene and acetylene as major products.



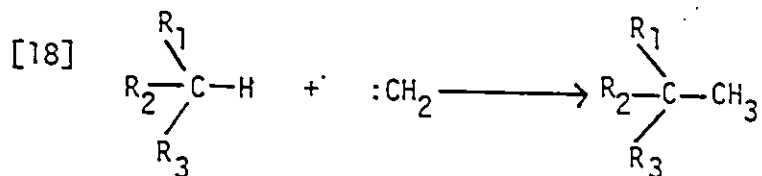
Upon thermolysis of dimethoxymethyl trimethoxysilane (V), methoxy carbene was generated.<sup>26</sup>



This route was used to produce alkoxy carbenes from thermolysis of silyl ketals. Where there was a hydrogen  $\alpha$  to the carbon bearing the alkoxy groups an  $E_2$  process occurred and no carbene was formed.<sup>27</sup>

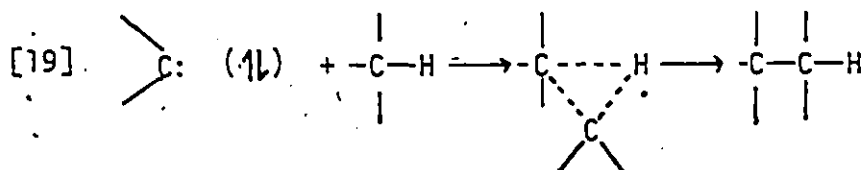


(ii) Intermolecular insertion:

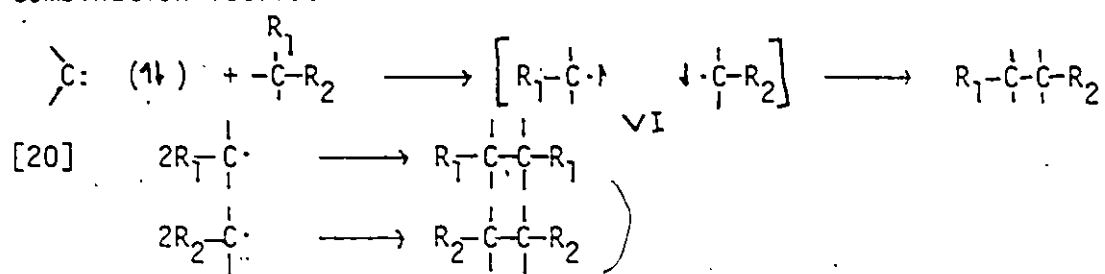


Two different mechanisms can be envisaged for the methylene insertion into a double bond: 1) concerted and 2) non concerted.

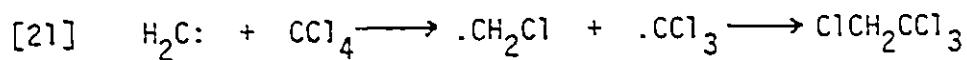
1) The concerted mechanism for a singlet carbene will involve a three-centre transition state.<sup>28</sup>



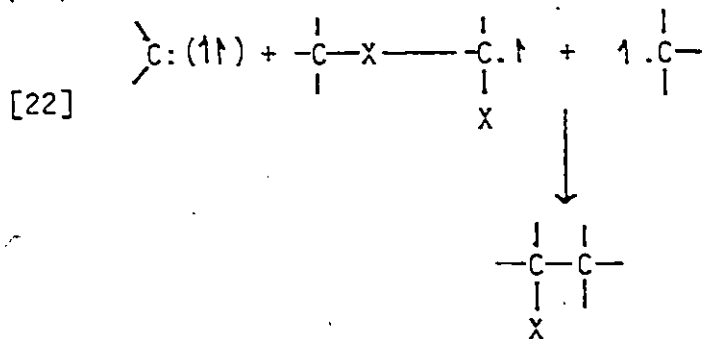
2) The non concerted mechanism involves radical pair formation where the radical pair (VI) undergoes efficient combination because of contributions from ionic states.<sup>29</sup>



For monohaloalkanes, a concerted insertion mechanism can occur; for polyhaloalkanes the insertion mechanism is highly unlikely due to steric reasons. In the latter case a halogen abstraction is followed by a radical coupling reaction.<sup>30</sup>



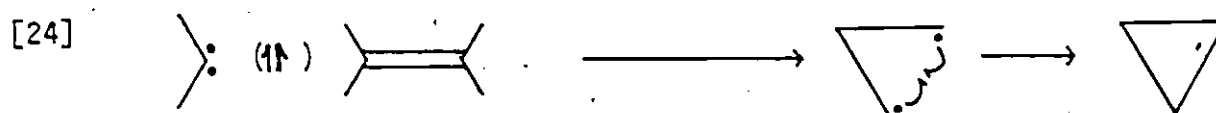
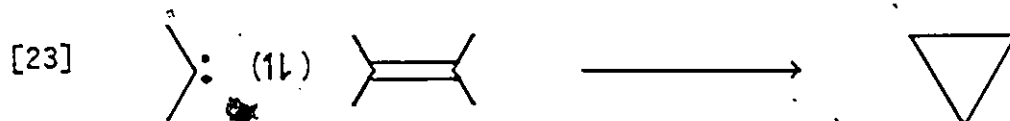
In the case of triplet carbenes a non concerted mechanism is also proposed.<sup>2</sup>





## b) Addition reactions

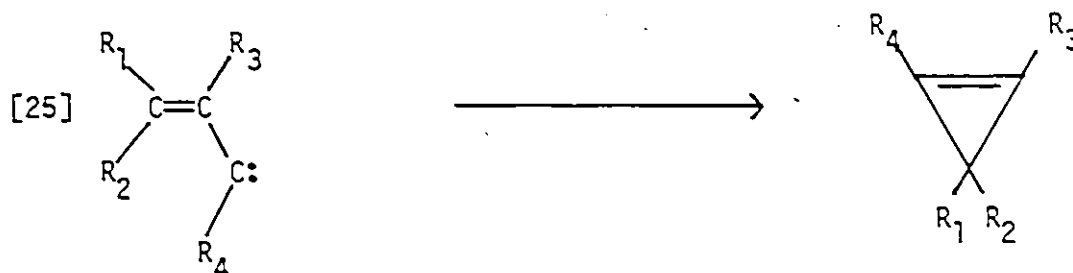
Singlet carbenes and triplet carbenes add to olefins with two different mechanisms. The first one adds in a concerted process, the second one in a non concerted process.



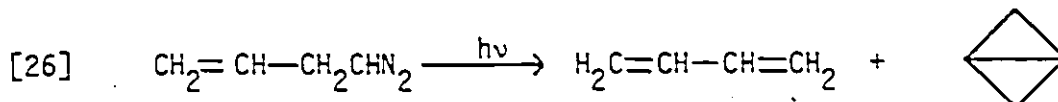
The reactivity of the olefins increases with increased substitution of the double bond with alkyl groups.<sup>2</sup> Like insertion reactions, two different additions can occur; i) intramolecular addition and ii) intermolecular addition.

## (i) Intramolecular addition

A vinylic carbene adds to the double bond to yield a cyclopropene<sup>2</sup> exclusively.



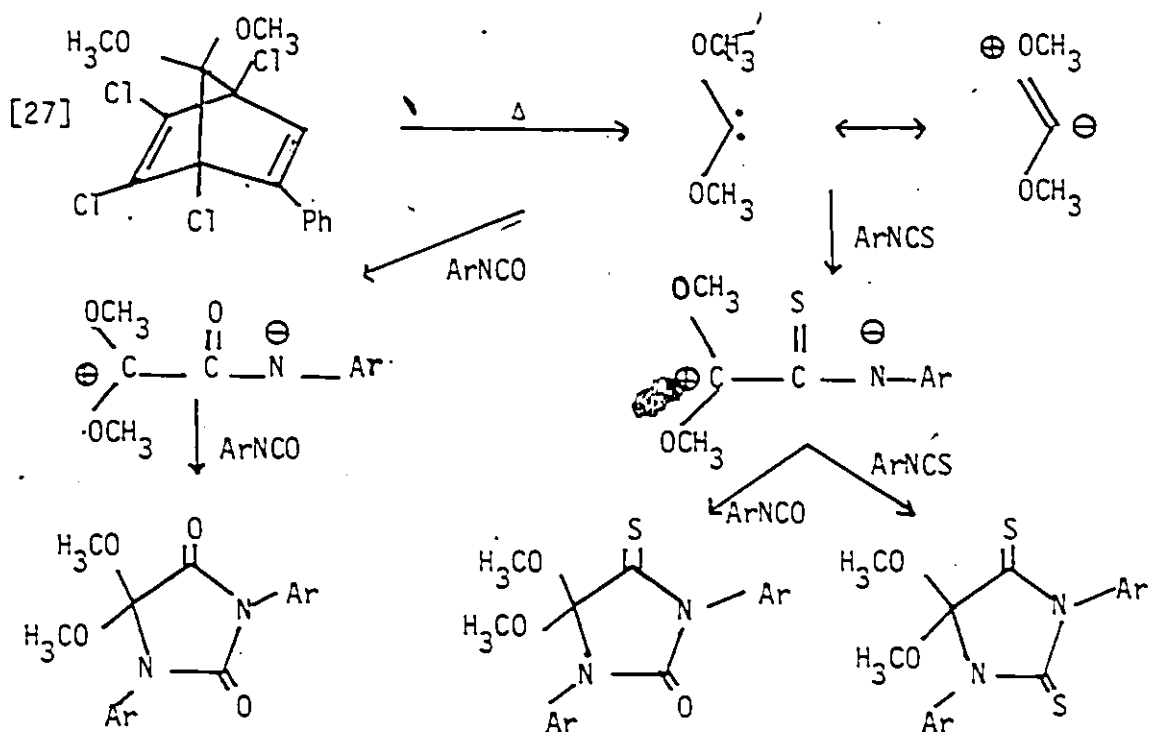
An allylic carbene gives a mixture of intramolecular C-H insertion and intramolecular addition to the double bond.<sup>31</sup>



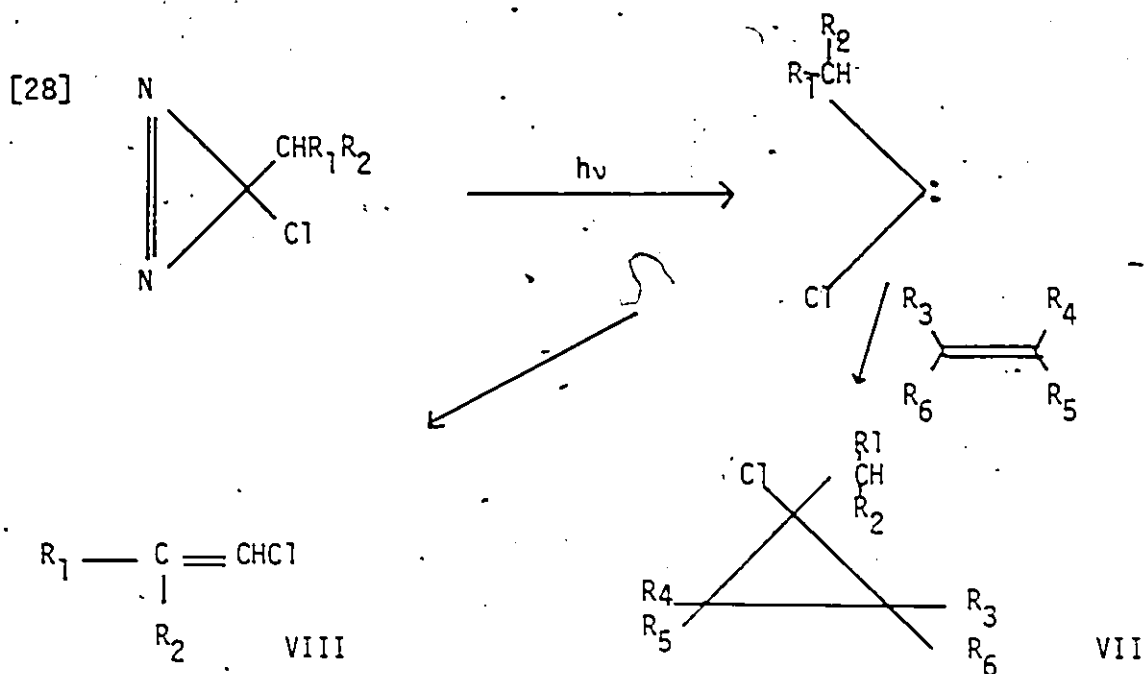
## (ii) Intermolecular addition

Heterosubstituted carbenes can have electrophilic or nucleophilic properties depending on whether or not the substituent is electron withdrawing or releasing. Dichlorocarbene ( $:\text{CCl}_2$ ) shows definite electrophilic properties, while reactions involving diaminocarbene ( $:\text{C}(\text{NH}_2)_2$ ) can be interpreted in terms of nucleophilic intermediates.<sup>32</sup> Carbenes like  $:\text{CF}_2$  and  $(\text{H}_3\text{CO})_2\text{C}:$  can be expected to be on the borderline. Toward olefins difluorocarbene behaves as an electrophile and toward vinylogous esters it shows nucleophilic properties.<sup>33</sup>

In the case of dimethoxycarbene the addition to aryl isocyanates and isothiocyanates gives a positive  $\rho$  value of  $+2.0 \pm 0.5$ . Hoffmann<sup>32</sup> used this positive  $\rho$  value to show the nucleophilic character of the carbene.



Finally, when there is a competition between intra and intermolecular reactions, substituent effects play a big role in determining the product formation.<sup>34</sup> As an example:

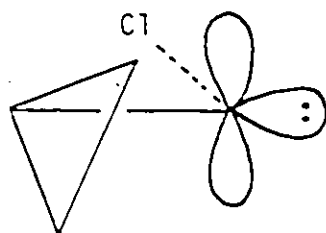


yields of VII and VIII

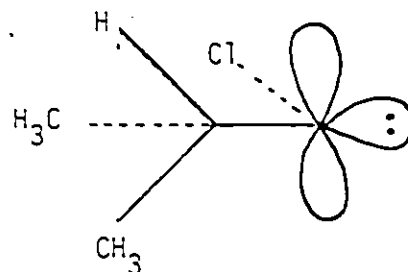
R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>	R <sub>5</sub>	R <sub>6</sub>	VII	VIII
Me	H	Me	Me	Me	Me	30%	54%
Me	Me	Me	Me	Me	Me	—	96%

Generation of isopropylchlorocarbene in the presence of an olefin yields product VIII as a major product, whereas ethylchlorocarbene in the presence of an olefin yields both VII and VIII meaning that the 1,2 hydrogen shift competes with intermolecular addition.

This appears to be consistent with substantial hydride character for the migrant hydrogen, and concomitant positive charge development at the migration origin, stabilization of positive charge is needed for a competitively efficient 1,2-shift and such is the case with isopropylchlorocarbene relative to ethylchlorocarbene. In the cyclopropylchlorocarbene (IX) case addition is the major product, IX probably adopts the bisected conformation, where stabilization factors includes the dual interaction of a chlorine lone pair and the bent  $\sigma$  bonds of the cyclopropyl group, with the p orbital at the carbenic centre. On the other hand, hydrogen migration will result in an increase in strain on the cyclopropyl ring, hence improbable. Isopropylchlorocarbene at relatively low energy cost can adopt conformation such as X to make possible a ready hydride shift<sup>34</sup> which explains the fact that 96% of VIII was obtained.



IX



X

## II: Oxidation of Hydrazones

### A: Use of Lead Tetraacetate (L.T.A)

The first reported use of lead tetraacetate was made by Dimroth in 1923 when lead tetraacetate was used to oxidize malonic esters and aryl substituted methanes to acetoxy derivatives.<sup>36</sup>

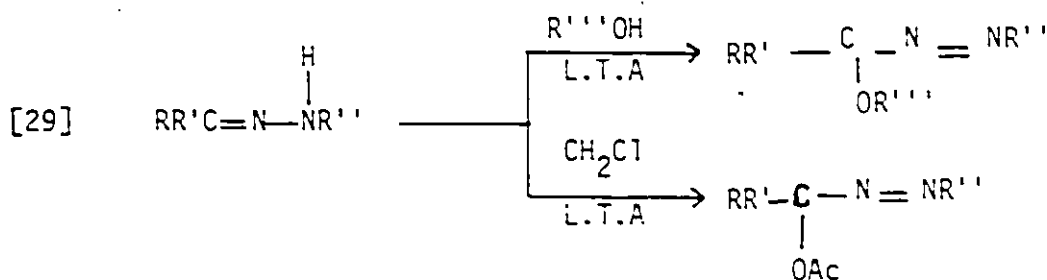
Concurrently, Criegee studied the conversion of olefins to diacetoxo compounds<sup>37</sup> and the use of lead tetraacetate to cleave 1,2 diols.<sup>38</sup>

Lead tetraacetate is a versatile reagent which reacts with sugars,<sup>39</sup> sterols,<sup>40</sup> oximes,<sup>41</sup> semicarbazones,<sup>42-43</sup> hydrazones, azines<sup>45</sup> and many other organic nitrogen compounds.<sup>46</sup> It's versatility and it's synthetic utility have been reviewed extensively.<sup>47-48</sup>

Many attempts have been made for the oxidative cyclization of organic substrates, using potassium permanganate, manganese dioxide and lead tetraacetate. The latter is the most widely used reagent for this purpose. In this discussion the emphasis is on the use of lead tetraacetate in the oxidation of hydrazones.

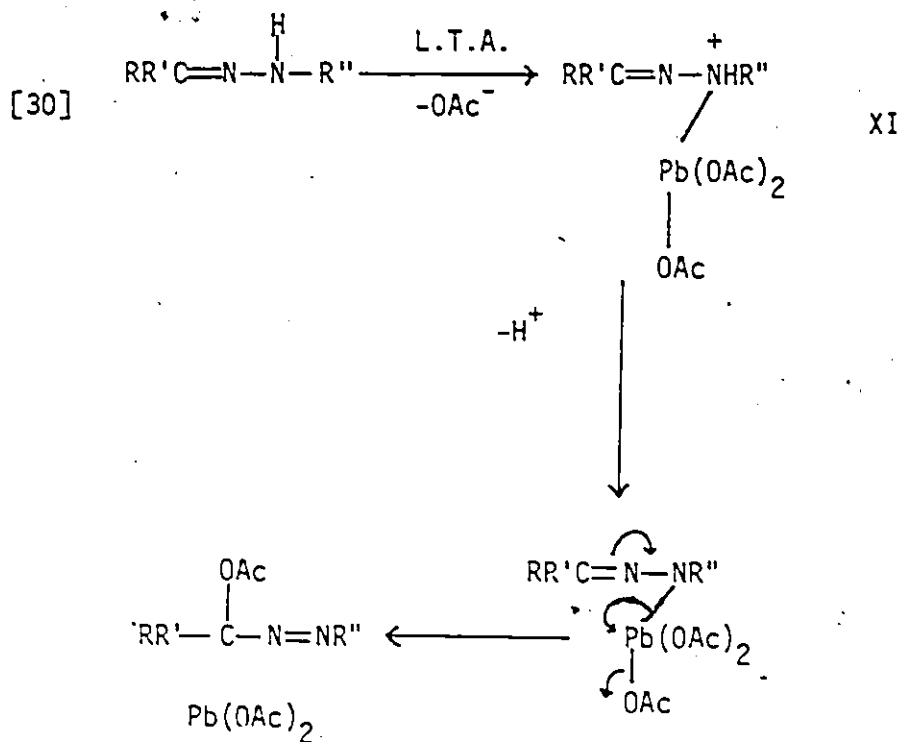
#### B: Reactions with Hydrazones

Aldehyde hydrazones form acyl hydrazines<sup>49</sup> upon treatment with lead tetraacetate, whereas ketohydrazones yield, in general, azoacetates in dichloromethane, and azoethers in alcoholic medium.

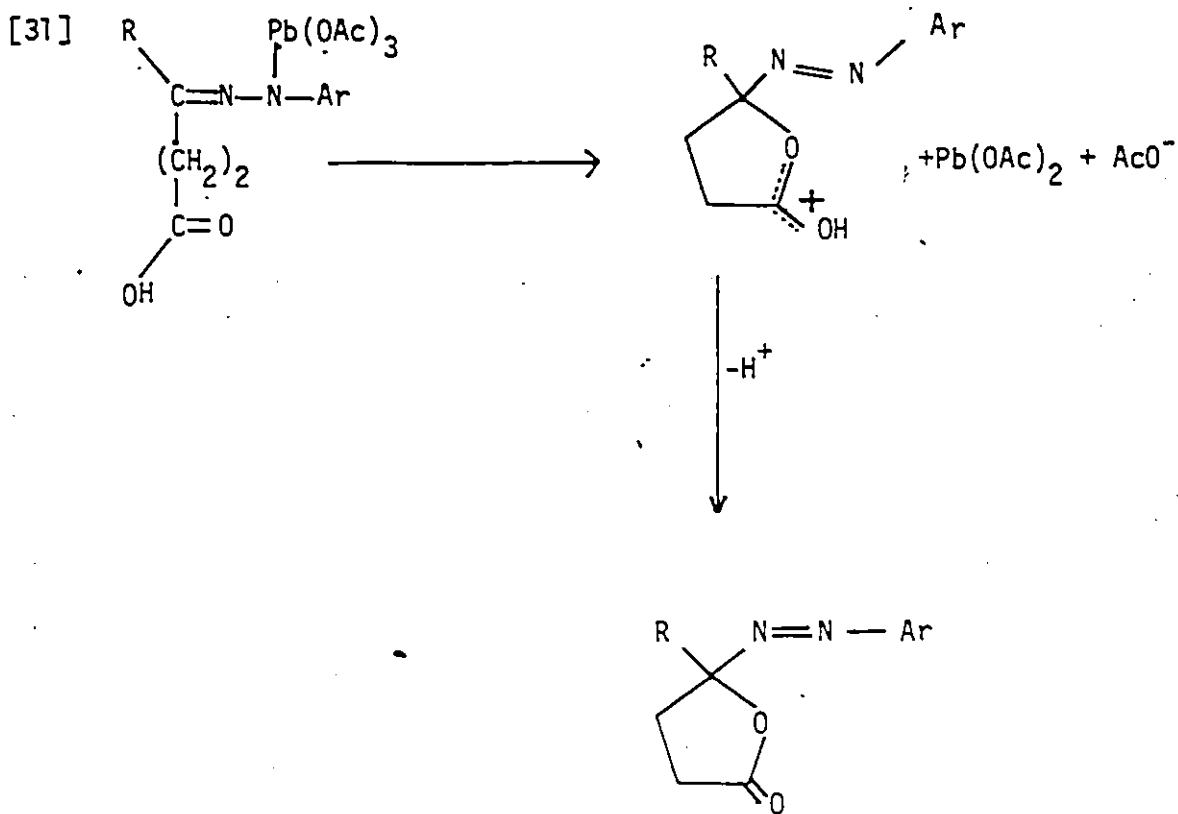


A free radical mechanism was first proposed for the reaction of L.T.A. with ketohydrazones.<sup>4,49,50</sup> Although following the reaction with oximes by E.S.R. spectroscopy shows the presence

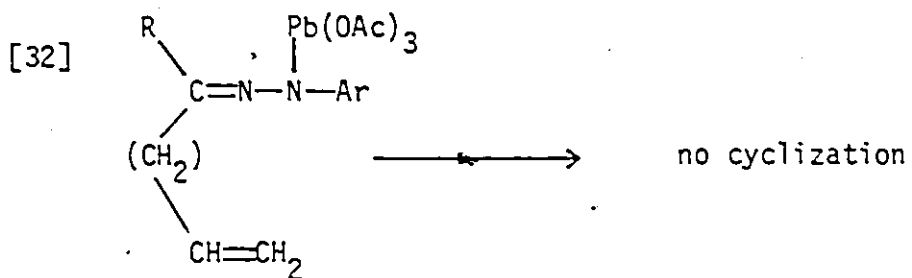
of radicals, there is no evidence for such intermediates in the oxidation of ketone hydrazones. The increased rate of the reaction in the presence of polar solvents suggests a polar mechanism.<sup>51</sup>



When a suitable cyclization site occurs in the ketone substituents of the ketohydrazones, at the 4th or 5th atom from the methine carbon, a cyclic product is obtained.<sup>52</sup> Small amounts of azoacetates are obtained as byproducts. A probable mechanism for the cyclization is a nucleophilic attack by the carbonyl oxygen on the  $sp^2$  carbon of an organolead intermediate.

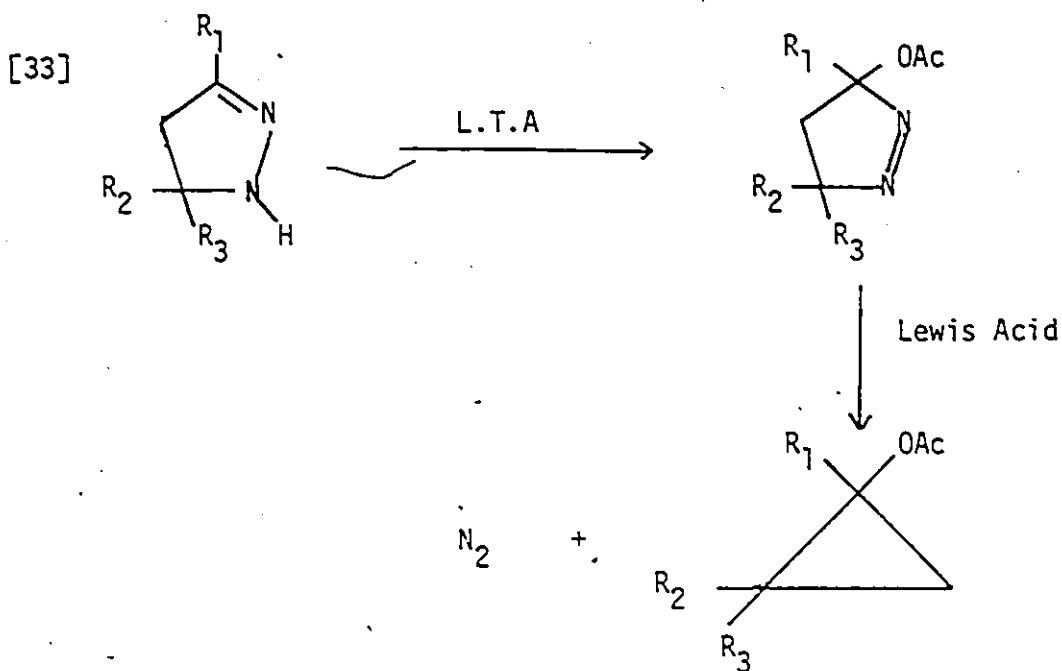


Electrophilic attack of the cation resulting from the loss of  $\text{Pb}(\text{OAc})_3$  in XII on the olefinic  $\pi$  bond is ruled out because no cyclization occurs when the carboxyl group is replaced by a carbon-carbon double bond.

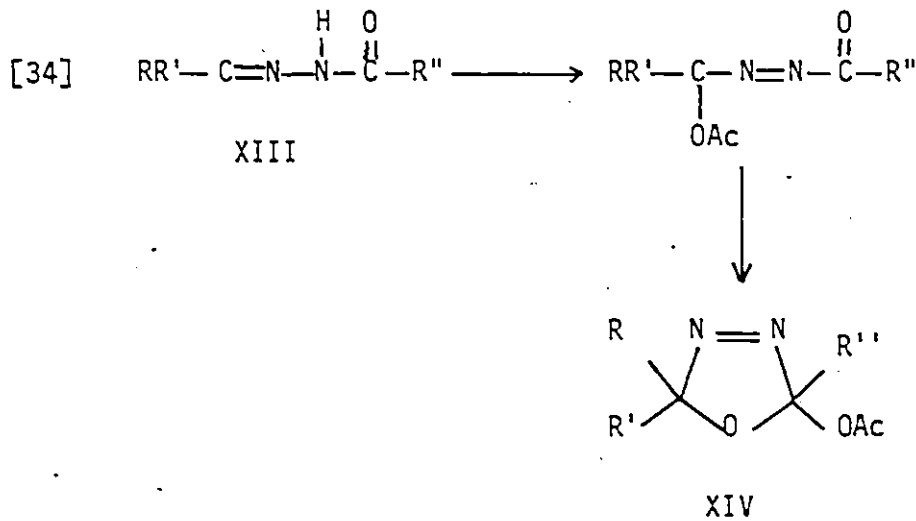


XII

Freeman<sup>53</sup> developed a new route to substituted cyclopropanes using azoacetates in the presence of a Lewis acid.

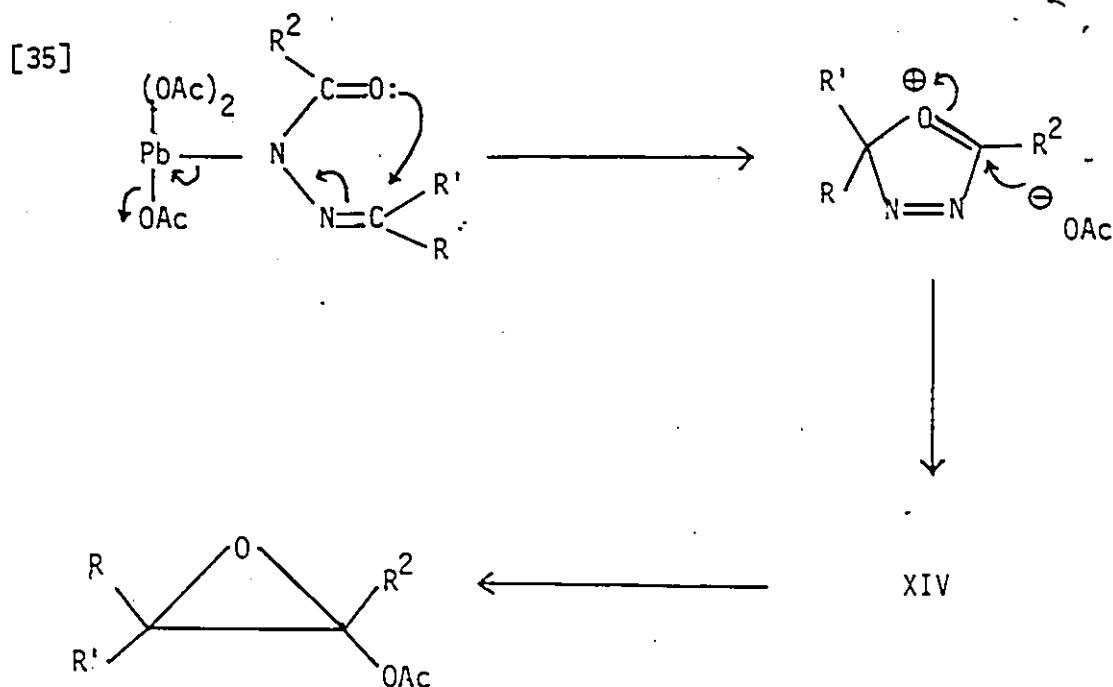


Hoffmann first reported that ketone carbonyl hydrazones of type XIII readily cyclize upon treatment with L.T.A. to  $\Delta^3$ -1,3,4-oxadiazolines XIV<sup>54-56</sup>.



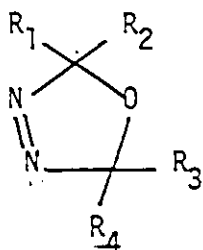


He envisaged an ionic mechanism for the formation of XIV, involving a loss of acetate ion from azoacetate, followed by attack on the resulting carbocation by the carbonyl carbon. Norman has also reported this cyclization.<sup>57</sup> He proposed a polar mechanism that does not involve an azoacetate intermediate.



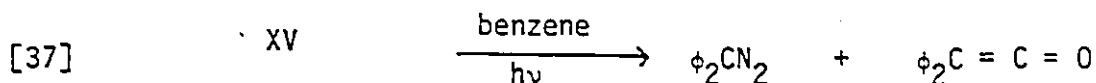
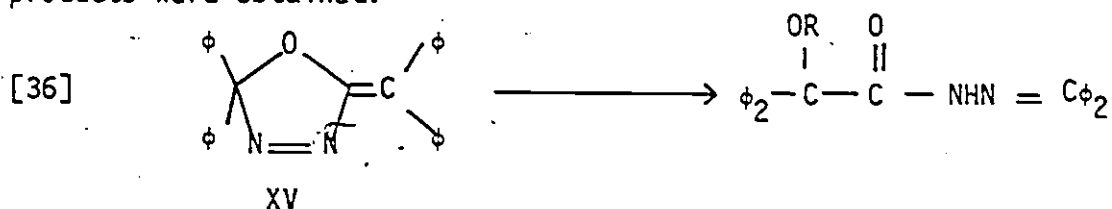
Both workers found that, upon thermolysis,  $\Delta^3$ -1,3,4-oxadiazolines lose nitrogen to form epoxides.

### III: Decomposition of $\Delta^3$ -1,3,4-oxadiazolines

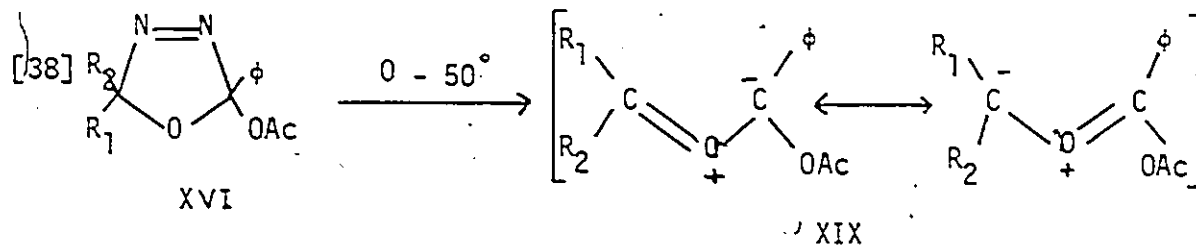


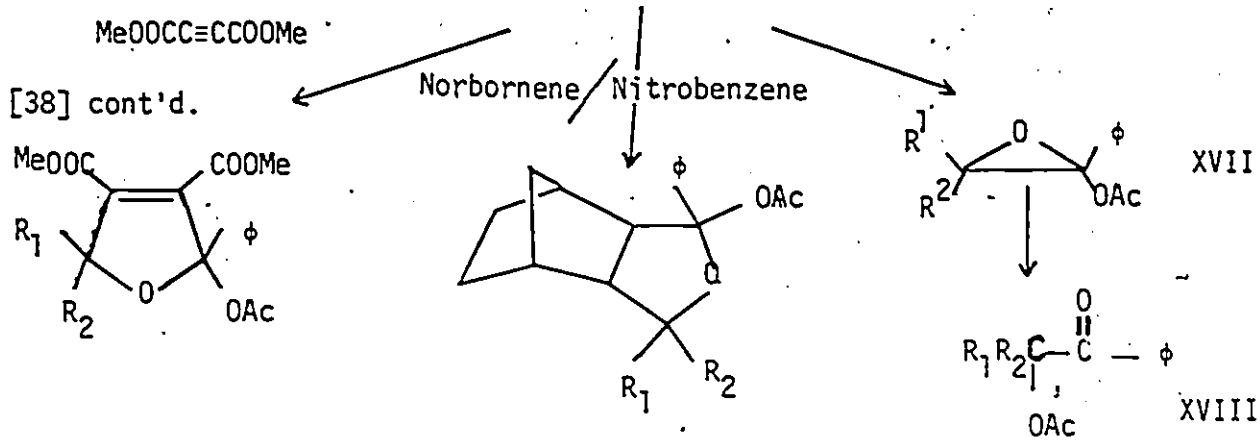
$\Delta^3$ -1,2,3-oxadiazoline

Like diazoalkanes  $\Delta^3$ -1,3,4-oxadiazolines can be decomposed thermally and photochemically. It was first found that photolysis of oxadiazoline XV in benzene yields diphenyldiazomethane and diphenylketene.<sup>7</sup> When hydroxylic solvents were used, addition products were obtained.

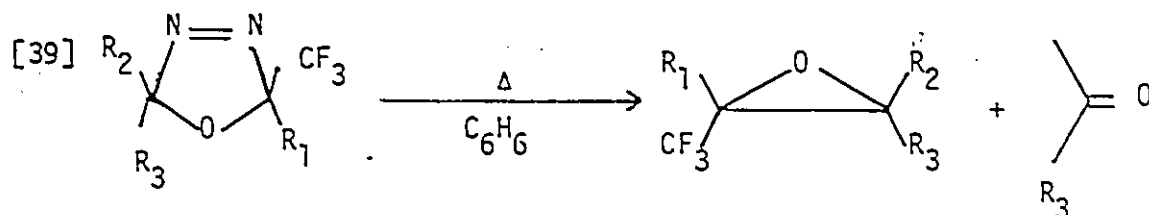


Decomposition of oxadiazolines (XVI) gave epoxyacetates (XVII), which upon heating gave  $\alpha$ -acetoxyketones (XVIII). The decomposition of the oxadiazoline to the epoxyacetate was explained via a carbonyl-ylide mechanism obtained through the loss of nitrogen from (XVI). Intermediate (XIX) was trapped with norbornene and dimethylacetylene dicarboxylate.<sup>8,54-56</sup>

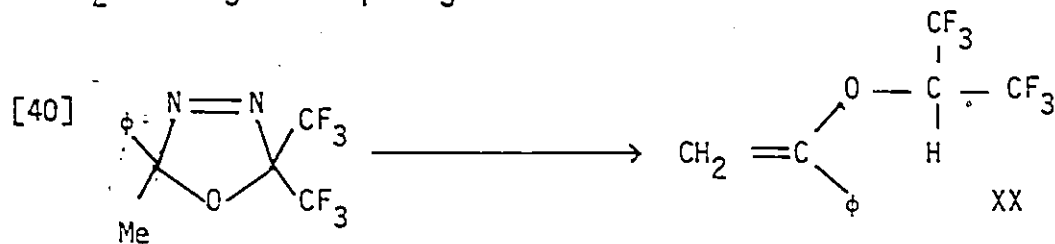




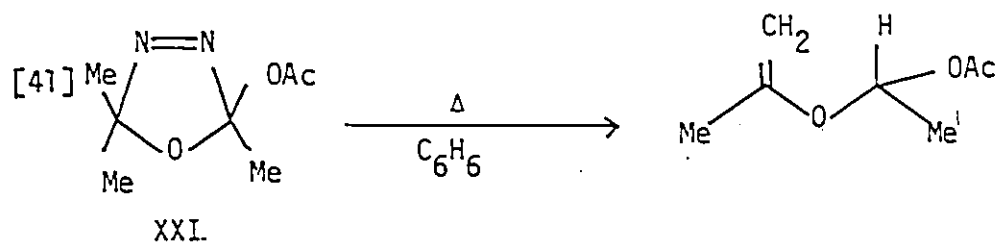
Aromatic diazo compounds react readily with perfluoroacetones to give unexpected cycloadducts,  $\Delta^3$ -1,3,4-oxadiazolines.<sup>58</sup> The thermal decomposition of those oxadiazolines yielded a ketone and an epoxide.



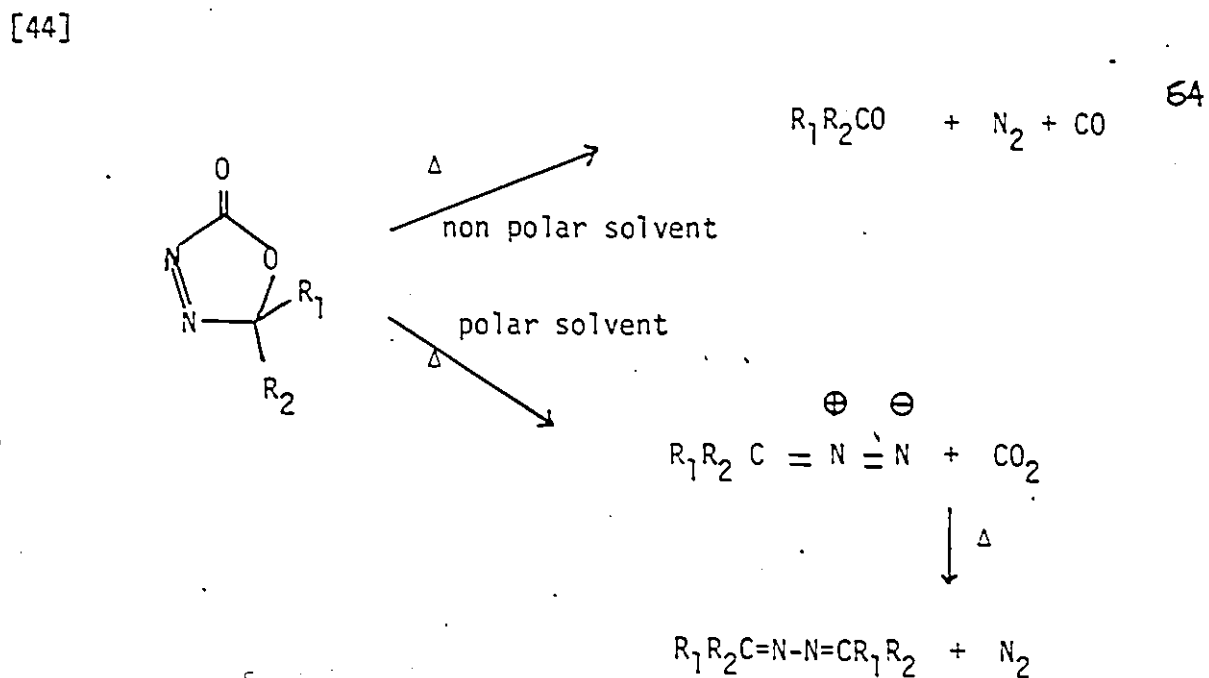
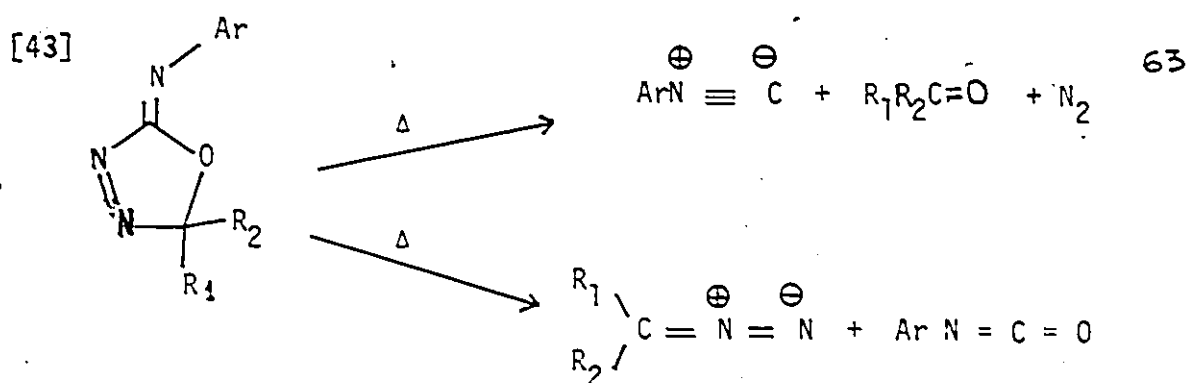
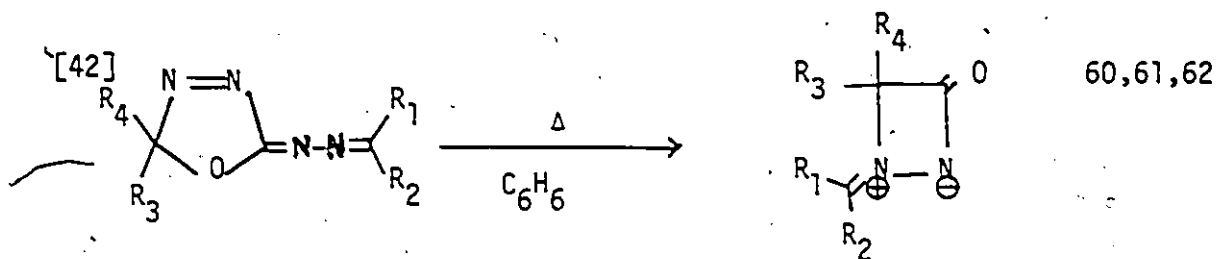
For  $R_2 = Me$ ,  $R_3 = \emptyset$ ,  $R_1 = CF_3$ ; the decomposition product is (XX)



The same type of product was found when decomposing XXI in benzene.<sup>59</sup>



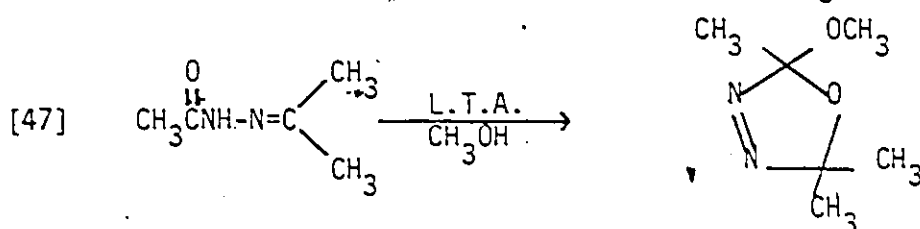
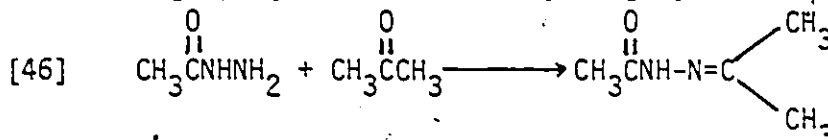
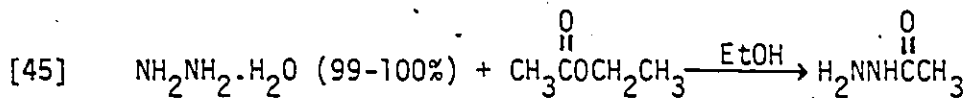
Other examples of decomposition of  $\Delta^3$ -1,3,4-oxadiazolines are shown below.



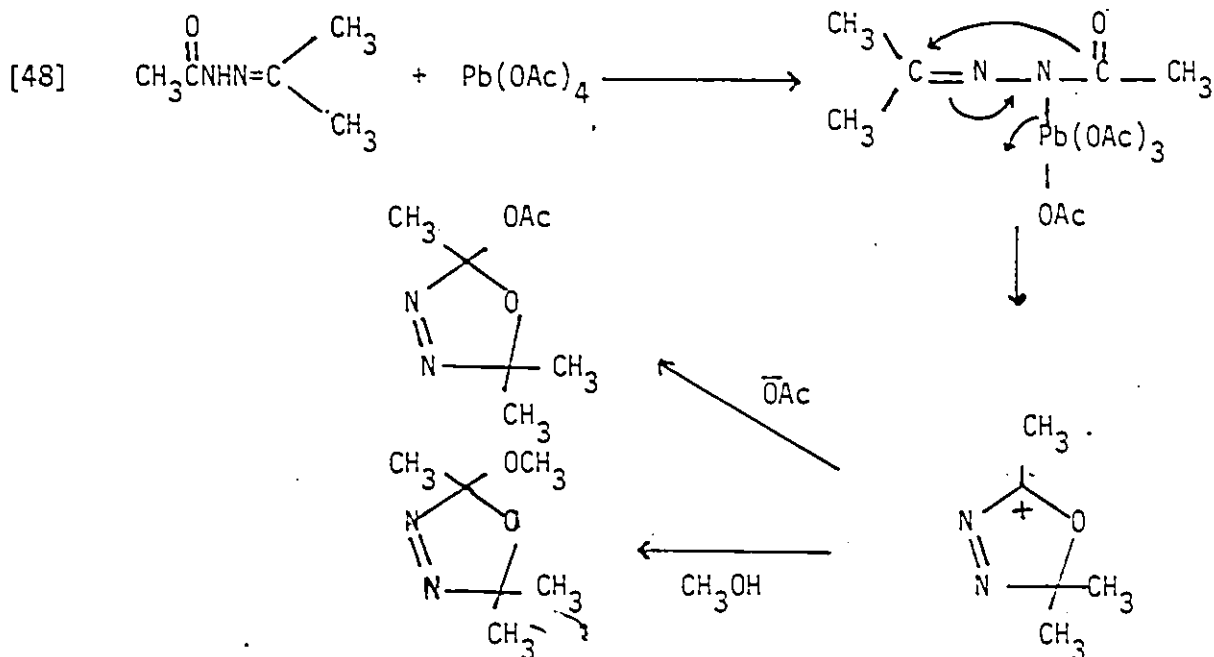
## RESULTS AND DISCUSSION

### I: General

2-Methoxy-2,5,5-trimethyl- $\Delta^3$ -oxadiazoline (XXII) was prepared from the lead tetraacetate oxidation of acetone-N-acetyl hydrazone.



The proposed mechanism for the oxidation is:

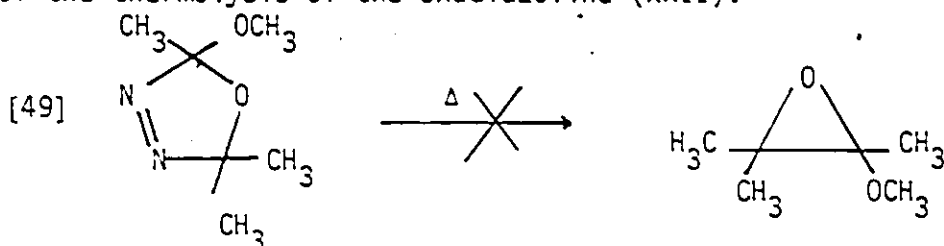


XXII

Oxadiazoline (XXII) was then thermolysed under four sets of conditions:

1. Under air in refluxing  $\text{CCl}_4$
2. In  $\text{CCl}_4$  in an evacuated sealed tube
3. In benzene in an evacuated sealed tube
4. Neat in an evacuated sealed tube

The methoxyepoxide expected on the basis of analogy to the chemistry of oxadiazolines<sup>8,54-56</sup>, eq.[38], was not one of the products of the thermolysis of the oxadiazoline (XXII).



A mechanism consistent with the observed products and with the kinetics is proposed. Finally results of trapping experiments and from the reactions of independently generated dimethyl carbene with  $\text{CCl}_4$  are discussed.

## II. Thermal decomposition of oxadiazoline (XXII)

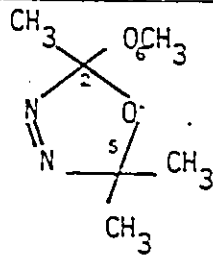
### (i) Under air in refluxing $\text{CCl}_4$

Oxadiazoline (XXII) was thermolyzed in  $\text{CCl}_4$  at  $76^\circ\text{C}$ . After 5 days the solution was distilled (24 mm Hg) and the fraction distilling below  $60^\circ\text{C}$  was collected.

#### 1) Distillate analysis

The P.M.R. spectrum of the distillate showed peaks at  $\delta = 2.0, 2.1, 3.6$  and  $7.3$ , all singlets. Addition, one at a time, of authentic samples of the suspected components to some of the distillate did not give rise to any new P.M.R. peaks. The mixture was separated

Table 1: Synthesis of oxadiazoline

Sample	yield%	M.P. °C	N.M.R. (p.p.m.)	I.R. (cm <sup>-1</sup> )
$\begin{array}{c} \text{CH}_3\text{CNHNH}_2 \\ \text{3} \\ \text{0} \end{array}$	75	65-67	$\delta=1.9$ (S,3)	3452,3328 3200,1679 1632,1370, 1000
$\begin{array}{c} \text{CH}_3\text{CNHN}=\text{C} \\ \text{3} \quad \quad \quad \text{CH}_3 \\ \text{0} \quad \quad \quad \text{CH}_3 \end{array}$	90	139-140	$\delta=1.9$ (S,3) $\delta=2.0$ (S,3) $\delta=2.2$ (S,3) $\delta=9.5$ (S,1)	3200,3097,2948 1617,1400,1369 1340,1250,1134 1042,1011,865
	65	B.P. °C at 10 <sup>-2</sup> mmHg 40-45	<u>P.M.R.:</u> $\delta=1.4$ (S,3) $\delta=1.5$ (S,6) $\delta=3.1$ (S,3) <u>C.M.R.:</u> $\delta=23.4$ $\delta=24.0$ $\delta=25.1$ $\delta=50.4$ (C6) $\delta=119.9$ (C5) $\delta=133.7$ (C2)	2918,2892,2837 1558,1459,1370 1192,1116,1050 990,899, 850,598 550

by gas chromatography and two samples were collected. From the chemical shifts in the P.M.R. spectrum of those samples the first one was thought to be chloroform and the other one a mixture of acetone and methyl acetate. A further experiment was performed to help prove that.

a) Chloroform:

The proton magnetic resonance of the sample showed a singlet at  $\delta = 7.3$ . Some authentic chloroform was added to the reaction product and no new peaks appeared when a P.M.R. was taken. When injected on a 10% D.E.G.S. g.l.c. column heated at  $70^{\circ}\text{C}$ , the authentic chloroform and the reaction product had the same retention time. An I.R. spectrum showed C-Cl bands around  $760\text{ cm}^{-1}$ . Other spectral data are listed in Table 2.

b) Acetone and methyl acetate

The chemical shifts of the sample and a mixture of authentic acetone-methyl acetate mixture were the same with peaks at  $\delta = 2.0, 2.1$  and  $3.6$ ; all singlets. When injected on a 10% D.E.G.S. column at  $70^{\circ}\text{C}$ , authentic acetone and authentic methyl acetate had the same retention times as the first and second peak in the sample, respectively. The infra-red showed an acetone carbonyl stretch at  $1725\text{ cm}^{-1}$ , a methyl acetate carbonyl stretch at  $1748\text{ cm}^{-1}$  and an ester C-O-C stretch at  $1252\text{ cm}^{-1}$ .

2) Residue Analysis

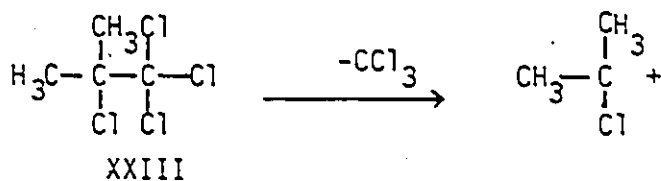
Gas chromatography was used to separate and collect the two major components. The 10% D.E.G.S. column was heated at  $110^{\circ}\text{C}$  and the products were found to be 1,1,1,2-tetrachloro-2-methyl propane (XXIII) and 3,3,3-trichloro-2-methoxy propene (XXIV).

a) Product XXIII

This product was collected as a white solid which sublimed at  $180^{\circ}\text{C}$  (lit.<sup>70</sup>  $178.6^{\circ} - 179.6^{\circ}$ ). P.M.R. singlet at  $\delta = 2.0$  p.p.m.

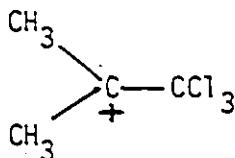


The infra-red spectrum did not show the presence of any carbonyl group or a carbon-carbon double bond. Absorptions at 1390 and 1370  $\text{cm}^{-1}$  are characteristic of gem dimethyl functionality. Absorption at 648  $\text{cm}^{-1}$  is probably due to a C-Cl stretch. In the mass spectrum the parent peak at  $m/e = 77$  for  $^{35}\text{Cl}$  and  $m/e = 79$  for  $^{37}\text{Cl}$  are due to the loss of  $\text{CCl}_3$  from XXIII.

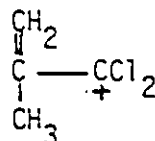


	$^{35}\text{Cl}$	$^{37}\text{Cl}$
m/e	77	79
Intensity ratio	1	0.3

Loss of Cl from XXIII followed by loss of HCl may be responsible for  $m/e = 159$  and 123 respectively.



$m/e = 159$



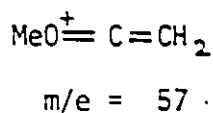
123

The intensity ratios of the peaks at  $m/e = 159, 161$  and 163 (1:1:0.3) suggests the presence of 3 chlorines. The nuclear magnetic resonance spectrum with a singlet at  $\delta = 2.0$  and the infra-red spectrum with bands at 648, 1370 and 1390  $\text{cm}^{-1}$  are in full agreement with the proposed structure of XXIII. Spectra data are listed in Table 2.

b) Product XXIV

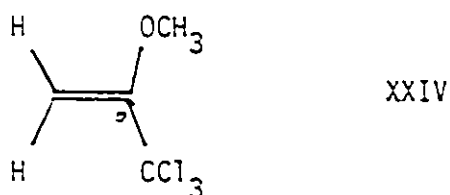
This product was collected under the conditions described under (a) above. Its proton magnetic resonance spectrum showed a pair

of doublets at  $\delta = 4.4$  and  $\delta = 5.2$  and a singlet at  $\delta = 4.0$ . The infra-red spectrum indicated the presence of a carbon-carbon double bond with a band at  $1640 \text{ cm}^{-1}$  and an ether carbon-oxygen absorption band at  $1282 \text{ cm}^{-1}$ . The mass spectrum showed peaks at  $m/e = 57$  (parent peak) and  $m/e = 117$ .



$^+\text{CCl}_3$	$^{35}\text{Cl}$	$1^{37}\text{Cl}$	$2^{37}\text{Cl}$
m/e:	117	119	121
intensity ratios	1	1	0.3

The above data are consistent with the structure of XXIV (3, 3, 3 - trichloro-2-methoxypropene). Mass.spec. gives rise to an ion at  $m/e = 174$ .

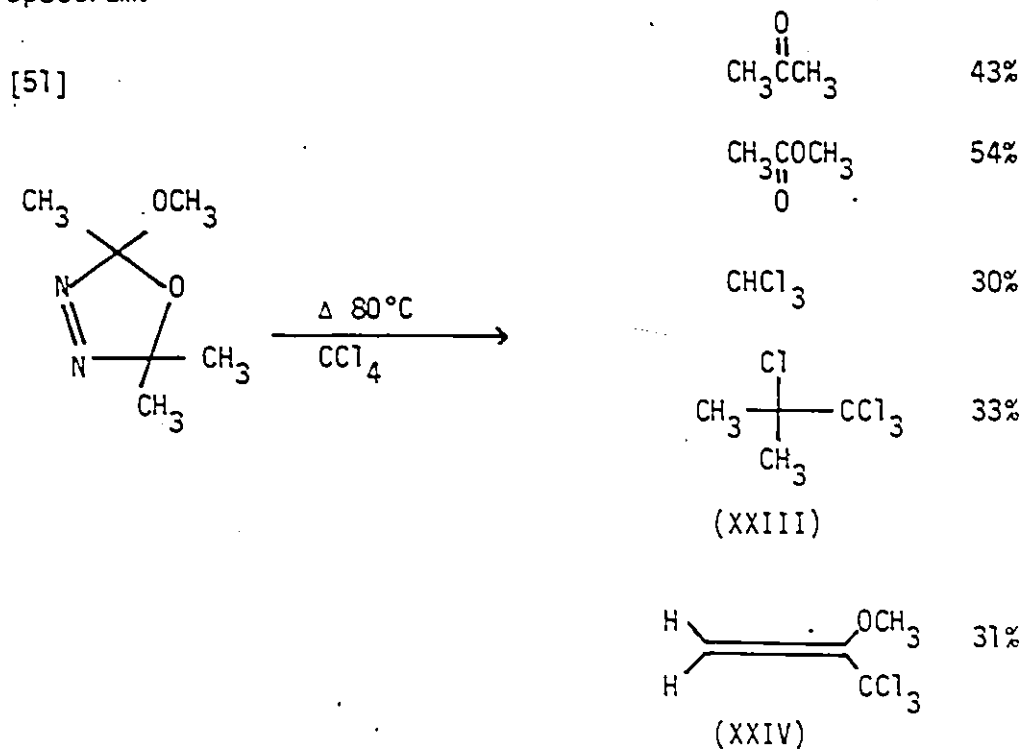


	$^{35}\text{Cl}$	$1^{37}\text{Cl}$	$2^{37}\text{Cl}$
m/e	174	176	178
intensity ratios	1	1	0.3

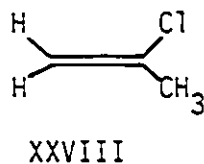
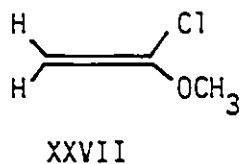
The structure of XXIV is in good agreement with the infra-red, N.M.R. and mass spectra. All spectral data are listed in Table 2.

## 3. Summary

The results of the above experiment are summarized in the equation below. Yields were calculated from peak heights in the N.M.R. spectrum.



Other products which were accounted for in the N.M.R. but which were not isolated are 2-chloro-2-methoxypropene and 2-chloropropene with approximate



yields of 13% and 23% respectively.

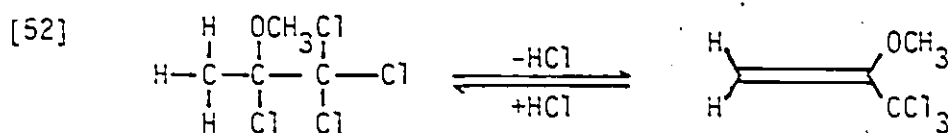
(ii) In  $\text{CCl}_4$  in an evacuated sealed tube

Oxadiazoline (XXII) was thermolysed in a sealed P.M.R. tube at  $80^\circ\text{C}$  for five days, and the product distribution after completion of the reaction was analysed by nuclear magnetic resonance (N.M.R.) spectro-

Table 2: Products from the thermal decomposition of XXII.

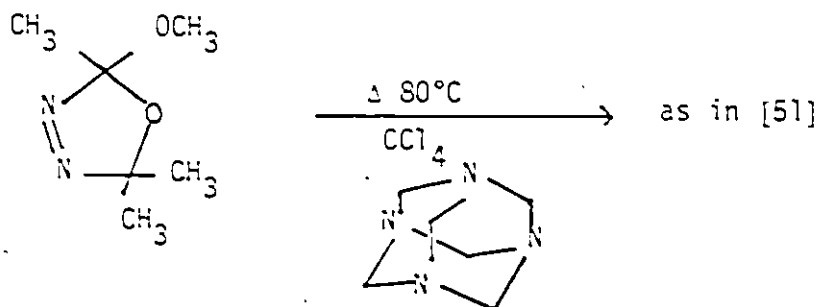
Sample	N.M.R. (ppm)	I.R. ( $\text{cm}^{-1}$ )
$\text{CH}_3\overset{\text{O}}{\parallel}\text{CCH}_3$	$\delta=2.1$	2998, 1725, 1425, 1347, 1239, 1197, 1092, 900
$\text{CH}_3\overset{\text{O}}{\parallel}\text{COCH}_3$	$\delta=2.00$ (S, 3H) $\delta=3.62$ (S, 3H)	2949, 1748, 1450, 1369, 1252 1050, 853
$\text{CHCl}_3$	$\delta=7.3$	2998, 2921, 2852 1222, 760
$(\text{CH}_3)_2\text{CClCCl}_3$	$\delta=2.0$	3097, 2998, 2952 1473, 1390, 1370, 1131 957, 648
$\text{H}_2\text{C}=\text{C}(\text{OCH}_3)\text{CCl}_3$	$\delta=4.0$ (S, 3H) $\delta=4.5$ (d, 1H) J=4Hz $\delta=5.5$ (d, 1H) J=4Hz	3200, 2992, 2944, 2919, 1640, 1451, 1282, 1069, 961

copy. The spectrum was found to be closely similar to that in (i) with the only exception that the yield of 3,3,3-trichloro-2-methoxypropene was much lower in this case, and a new peak at  $\delta = 3.0$  p.p.m. appeared. This result suggested that the vinyl ether (XXIV) was produced later in the open-tube process, from a primary product of the reaction, namely, 1,1,1,2-tetrachloro-2-methoxypropane. The ether was thought to lose HCl in the equilibrium process (eq. 52). In a sealed tube HCl cannot escape which makes a difference between cases (i) and (ii).



In order to check this proposal the experiment was repeated in the presence of a base to trap the HCl produced. If this is, in fact, a reversible process, then the presence of the base should shift the equilibrium to the right and the tetrachloroether should give place to the vinyl ether. The base used was hexamethylenetetramine. At the end of the reaction the product composition was found to be similar to the one in (i) above.

[53]

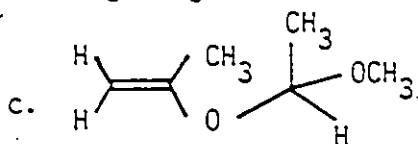
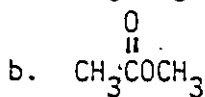
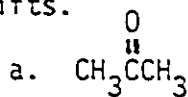


(iii) In benzene in an evacuated sealed tube

In a P.M.R. tube oxadiazoline (XXII) and benzene were mixed together in a 1:10 molar ratio. After thermolysing the solution at 80°C for five days an N.M.R. spectrum was taken and it appeared that propene was a major product (>30%). The N.M.R. signals attributed to propene in the sample were the same as those of an independently-run spectrum of a CCl<sub>4</sub>/propene solution.

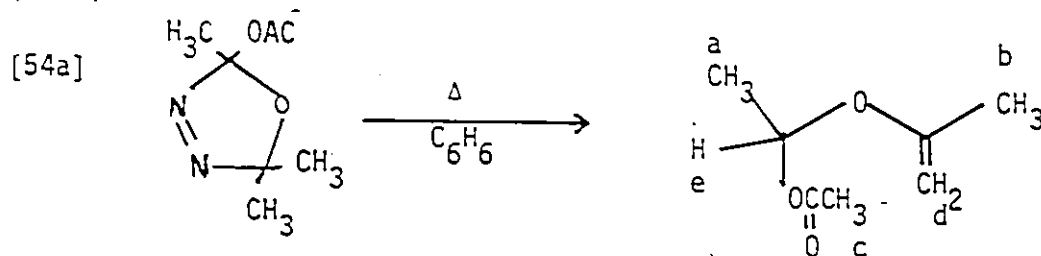
(iv) Neat in an evacuated sealed tube

In a P.M.R. tube oxadiazoline (XXII) was thermolysed for 5 days at 80°C. Three major products were identified from their P.M.R. chemical shifts.



XXV

The structure of product XXV was inferred from its P.M.R. spectrum in comparison with the major product in the decomposition of oxadiazoline (XXVI).<sup>59</sup>



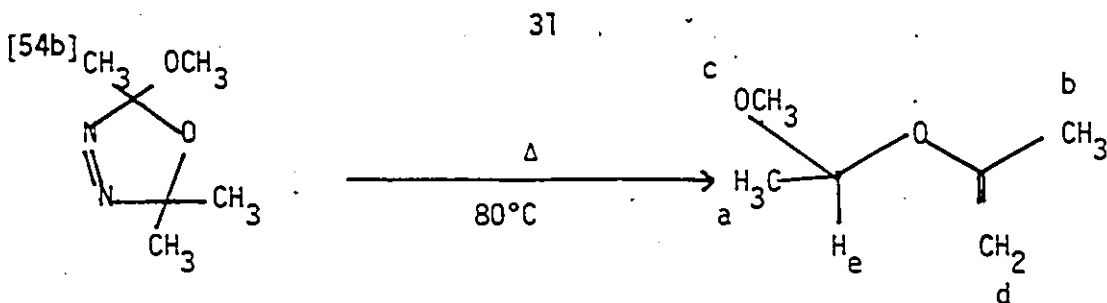
a:  $\delta = 1.50$  doublet, 3H  $J = 6.0$  Hz

b:  $\delta = 1.85$  doublet, 3H  $J = 1.0$  Hz

c:  $\delta = 2.08$  singlet, 3H

d:  $\delta = 4.05$  multiplet, 2H  $J = 1.0$  Hz

e:  $\delta = 6.07$  quartet, 1H  $J = 6.0$  Hz



- a:  $\delta = 1.25$ , doublet 3H,  $J = 6.0$  Hz  
 b:  $\delta = 1.80$ , doublet 3H,  $J = 1.0$  Hz  
 c:  $\delta = 3.20$ , singlet, 3H  
 d:  $\delta = 4.00$ , multiplet 2H  
 e:  $\delta = 5.10$ , quartet 1H  $J = 6.0$  Hz

### III. Rate constant calculations:

The thermal decomposition of oxadiazoline XXII in carbon tetrachloride at  $80^\circ\text{C}$  was followed by P.M.R. spectroscopy using dichloromethane as an internal standard for peak height measurements. The P.M.R. spectra were recorded every 4-5 hours. Reaction was stopped by quickly cooling the P.M.R. tube in cold water and the time outside the bath was not counted. Peak heights of the P.M.R. signal were normalized with respect to dichloromethane. The reaction was followed to 73% of completion. The rate constant was calculated by plotting the  $\ln$ . value of the ratio of the peak height of the starting material to the peak height of dichloromethane, versus the time. The best line was drawn, the slope of which was the rate constant.

$$k = 6.81 \pm 0.3 \times 10^{-6} \text{ sec}^{-1} \quad (0.3 = \text{standard deviation}).$$

The values used in the plot are listed in Table 3

Time (hours)	$\ln A$
0	0.6268
12	0.8404
28	1.2292
36	1.4563

Time (hours)	ln A
52	1.9061

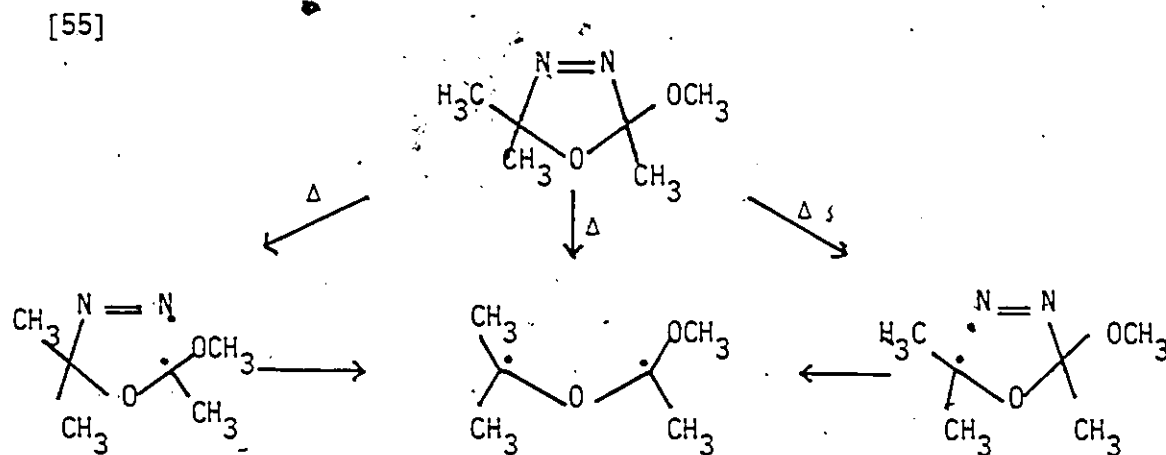
A =  $\frac{\text{peak height of starting material}}{\text{peak height of standard}}$

#### IV: Mechanism of decomposition

The fact that from the thermolysis of oxadiazoline (XXII) chlorinated products were obtained indicates that the intermediates reacted with the solvent, carbon tetrachloride. The experimental evidence on which this mechanism is based includes:

- (i) First order kinetics
- (ii) Identity of the products
- (iii) Same types of products from a process known to involve  $\text{Me}_2\text{C:}$  as intermediates.

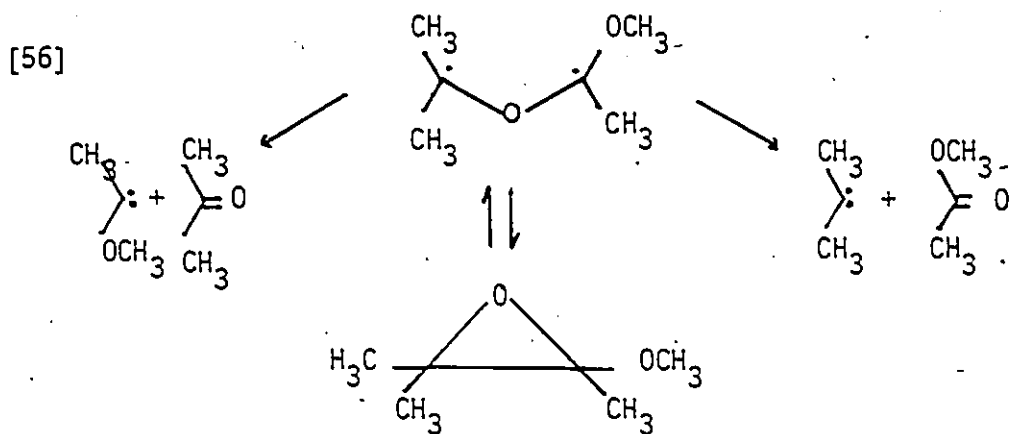
The rate determining step might be the loss of nitrogen in a concerted or non concerted fashion.



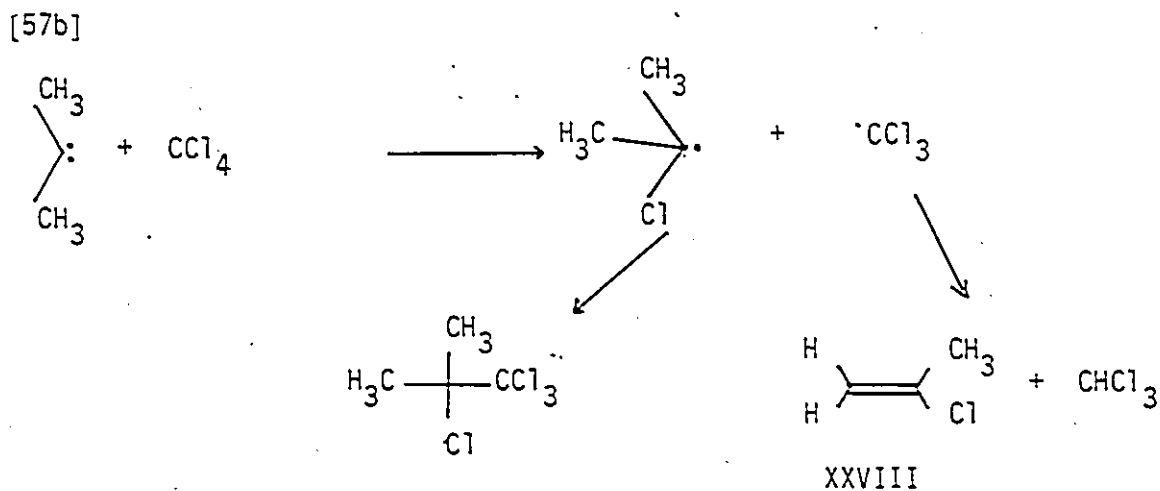
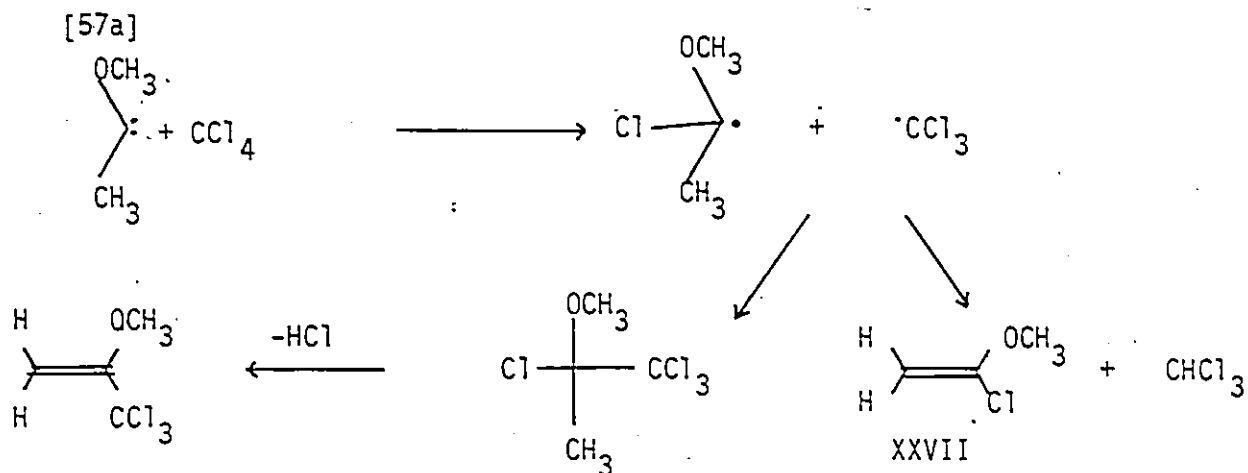


The 1,3 diradical could be going to the methoxyepoxide in a reversible process, although no evidence was found to prove this point.

The diradical could break in two ways:



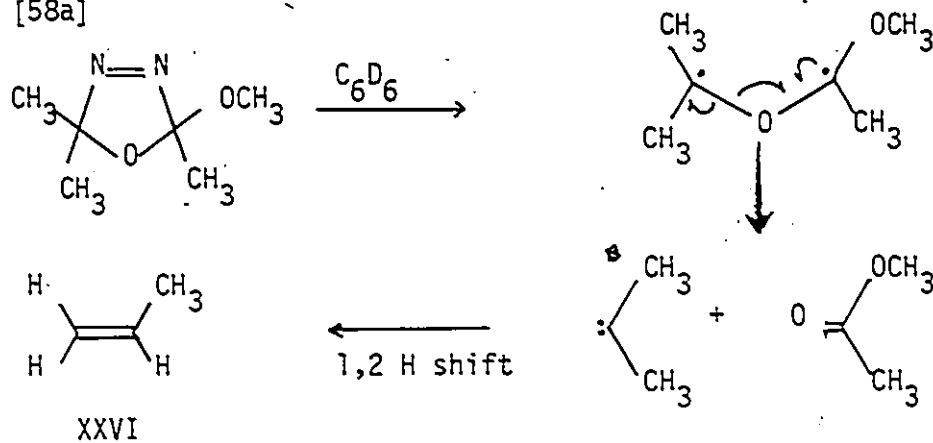
The carbenes thus formed could react as follows:



Products XXVII and XXVIII were not isolated, their yield was calculated from the P.M.R. spectrum. In the case of the decomposition in benzene, the production of propene was a good sign in favour of the carbene

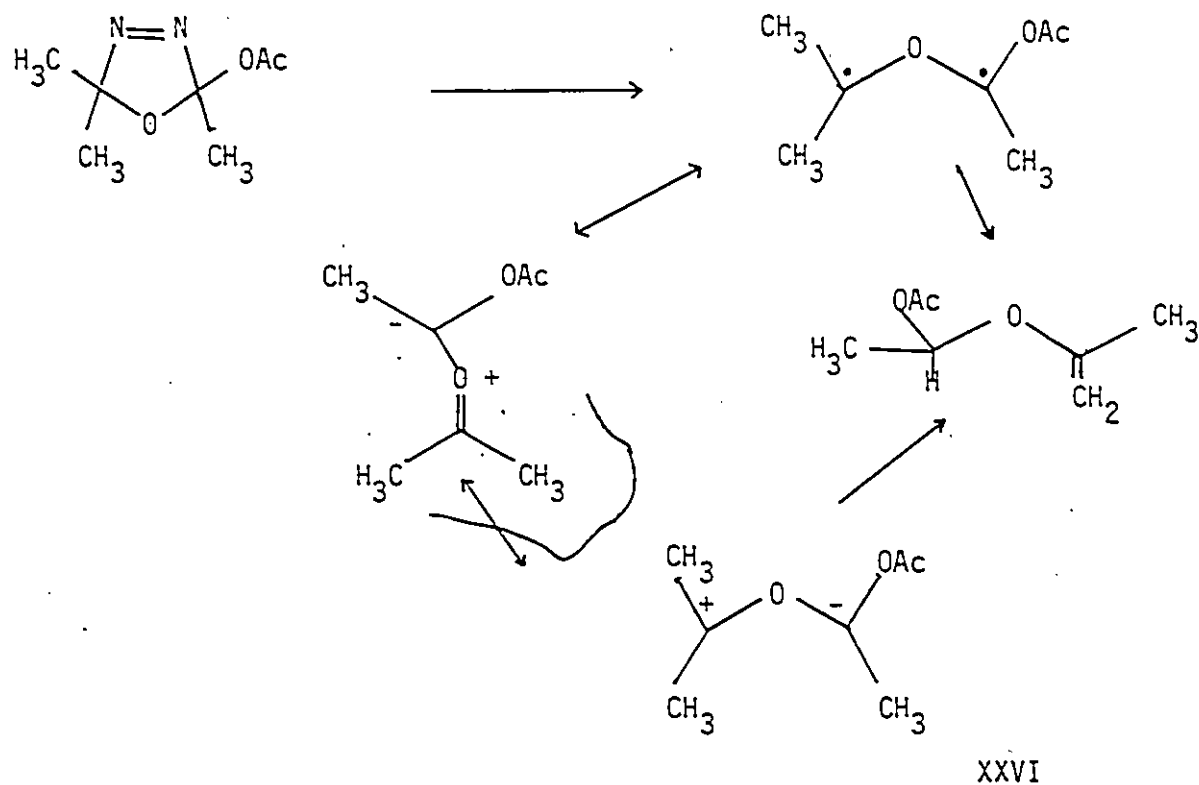
mechanism.

[58a]



The proposed mechanism for the decomposition of XXI is shown below:<sup>66</sup>

[58b]



This work so far suggests that the mechanism of the decomposition of the oxadiazoline (XXII) in carbon tetrachloride is completely different from the mechanism of the decomposition of oxadiazoline (XXI). In the latter carbenes are involved as intermediates, namely: methoxymethyl carbene and dimethyl carbene. In order to support or discredit this proposal two experiments were performed.

1. Trapping experiment with a known carbene trap
2. Reaction of independently generated dimethylcarbene with

$\text{CCl}_4$ .

V: Trapping the Carbenes with 1,1-diphenylethylene

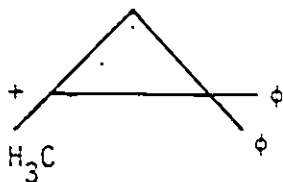
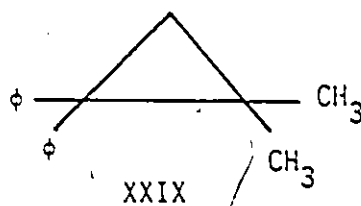
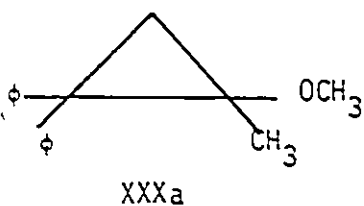
Oxadiazoline XXII and 1,1-diphenylethylene were heated together (40 mg: 350 mg), at 82°C. After 72 hours the reaction mixture was analyzed. The P.M.R. spectrum showed the presence of acetone and methylacetate in a 1:2 ratio, plus a multitude of peaks and some unreacted starting material. Distillation of the mixture at 60°C (24 mm Hg) gave those two compounds which had the same P.M.R. spectrum and the same G.C. retention time on a 10% D.E.G.S. column heated at 70°C, as authentic acetone and methyl acetate. The residue was distilled at high vacuum (0.1 torr at 100°C to remove any polymeric material. Two major products were obtained, separation of which was carried out by preparative thin layer chromatography: 1,1-diphenyl-2,2-dimethylcyclopropane (XXIX) and 1,1-diphenyl-2-methoxy-2-methylcyclopropane (XXX).

(i) Product XXIX

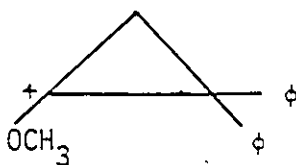
This product was obtained from the band at lower  $R_f$  value. Its P.M.R. spectrum was consistent with 1,1-diphenyl-2,2-dimethylcyclopropane. It showed peaks at  $\delta=1.12$  (singlet, 2H);  $\delta=1.25$  (singlet, 6H) and at  $\delta=7.2$  (distorted singlet, 10H).

## (ii) Product XXX

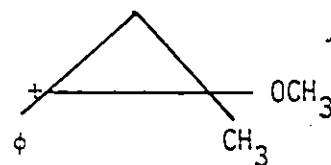
The P.M.R. of this compound showed a broad singlet at  $\delta = 1.16$  (4H) a doublet at  $\delta = 1.25$  (1H,  $J = 9.0$  Hz.), a singlet at  $\delta = 3.10$  (3H) and a multiplet at  $\delta = 7.30$  (10H). It was obtained from the band with the higher  $R_f$  value on a thin layer plate. The mass spectrum showed a molecular ion at  $m/e = 238$ . Losses of 15 and 31 units suggest the loss of methyl and methoxy respectively. A peak at  $m/e = 77$  shows the presence of a phenyl ring. Finally a peak at  $m/e = 161$  suggests the loss of a  $C_6H_5$  unit.



$m/e$  207



223



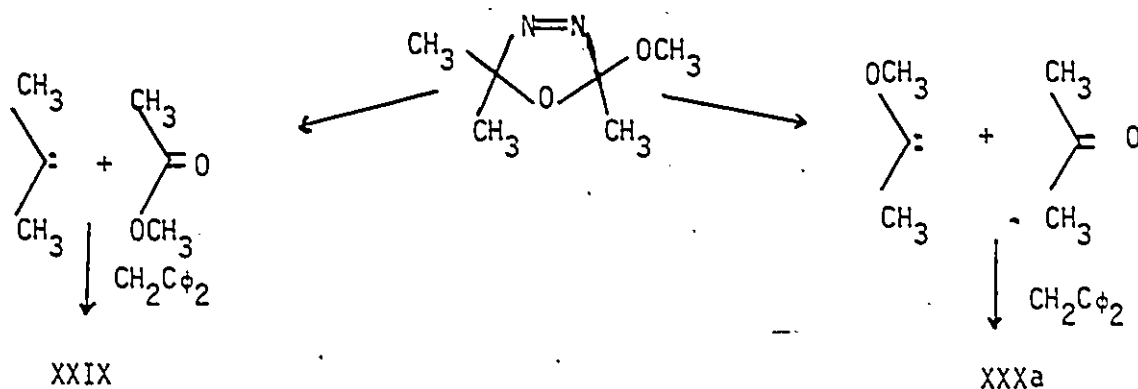
161

The P.M.R. peaks responsible for the gem hydrogens were at  $\delta = 1.16$  and  $\delta = 1.25$ . When the peak at  $\delta = 1.16$  was irradiated, the doublet at  $\delta = 1.25$  collapsed to a singlet. Two different mechanisms can be proposed for this trapping reaction, one involving a carbene addition to the olefin, and the other one involving a cycloaddition reaction of diazoalkanes and 1,1-diphenylethylene.

## (i) Carbene mechanism:

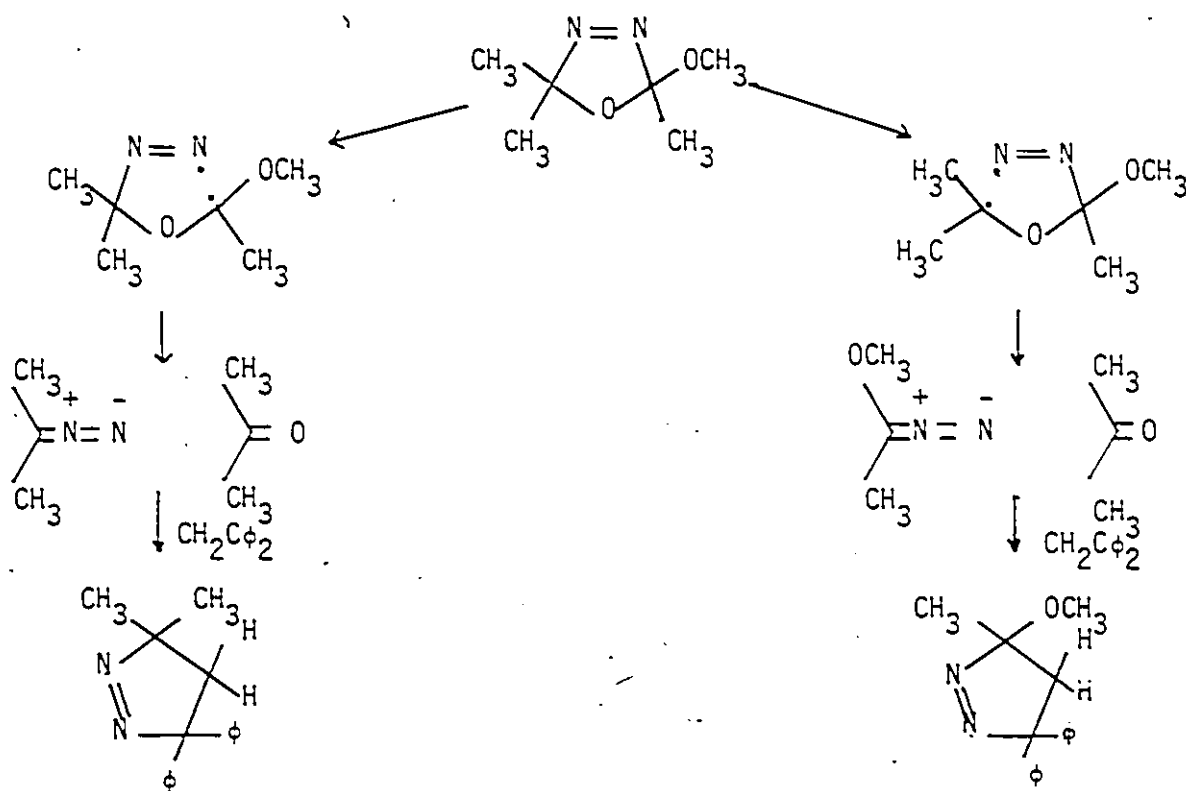
The mechanism involving carbenes as intermediates is shown

below:

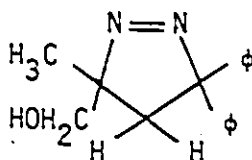


## (ii) Cycloaddition reaction

Another mechanism can be proposed with no loss of nitrogen from the oxadiazoline(I) hence giving trapping products containing nitrogen.



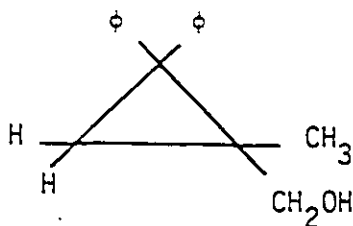
The mass spectrum of those 1-pyrazolines could be very similar to those of the cyclopropanes because it was found<sup>65</sup> that in similar compounds molecular nitrogen is often lost and the molecular ion appears at 28 mass units below what is expected for the parent ion. The N.M.R. spectrum of pyrazoline XXXI shows:<sup>65</sup>



XXXI

- $\delta = 1.13$  3H singlet  
 $\delta = 2.29$  2H doublet, doublet  
 $\delta = 3.20$  1H singlet  
 $\delta = 3.81$  2H doublet, doublet  
 $\delta = 7.3$  10H singlet

And in the corresponding cyclopropane<sup>65</sup> XXXII

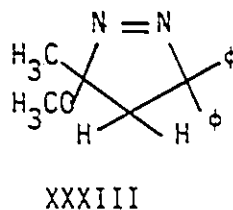
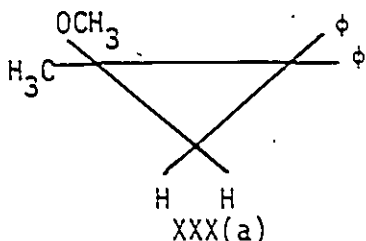


- $\delta = 1.06$  3H singlet  
 $\delta = 1.18$  2H doublet-doublet  
 $\delta = 1.43$  1H singlet  
 $\delta = 3.28$  2H doublet  
 $\delta = 7.26$  10H multiplet

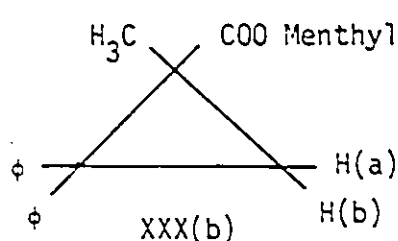
The three important conclusions are:

1) The aromatic protons appear as a singlet in the pyrazoline and as a multiplet in the cyclopropane.

2) The gem protons in the pyrazoline case appear at  $\delta = 2.29$  and in the cyclopropane case at  $\delta = 1.18$ . In the trapping experiment the aromatic protons in product (XXXa), appear as a multiplet and the gem protons appear at  $\delta = 1.16$  and  $\delta = 1.25$ . The product then is XXX(a) and not XXXIII.



3) The cyclopropane hydrogens have a reasonable chemical shift when compared to those of model compound XXX(b).<sup>65</sup>



	$\delta_{Ha}$	$\delta_{Hb}$
XXX(a)	1.16	1.25
XXX(b)	1.37	

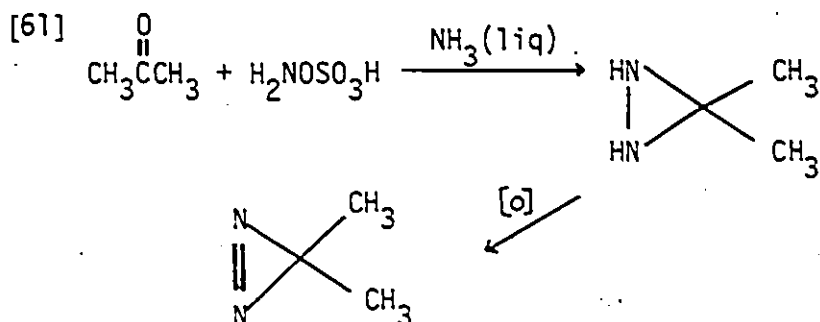
4) The pyrazolines formed are known to be stable<sup>65</sup> so their absence in the products rules out the possibility of their decomposition forming the 3-membered ring.

#### VI Reaction of independently generated dimethylcarbene with $CCl_4$

Dimethyl carbene is known to be generated from the thermal and photochemical decomposition of dimethyldiazirine.<sup>2</sup> When produced in the gas phase it undergoes a 1,2-hydrogen shift to yield propene as a major product.<sup>25</sup>

The generation of this carbene from the corresponding diazirine was done photochemically and thermally in the presence of  $CCl_4$ . Dimethyldiazirine

was prepared from dimethyldiaziridine from the procedure of Shmitz and Ohme.<sup>10</sup>



i) Photodecomposition:

In a sealed tube a 1:10 ratio of dimethyl diazirine and  $\text{CCl}_4$  were irradiated ( $\lambda_{\text{max}} = 300 \text{ nm}$ ). The reaction was followed by taking P.M.R. spectra every hour for 12 hours. After this time 80% of the starting material had reacted. The P.M.R. spectrum showed the presence of chloroform ( $\delta = 7.30$ ) propene ( $\delta = 1.65$ , doublet of doublets, 3H;  $\delta = 4.85$  multiplet, 2H; and  $\delta = 5.70$ , multiplet, 1H);  $(\text{CH}_3)_2\text{CCl} \text{CCl}_3$  ( $\delta = 2.0$ ) and  $\text{CCl}_3 \text{CH}_2\text{CHClCH}_3$  ( $\delta = 1.70$ , doublet, 3H;  $\delta = 3.20$ , multiplet, 2H;  $\delta = 4.35$ , multiplet, 1H).

The presence of chloroform suggested that not all the dimethyl carbene produced formed propene. Some of it reacted with  $\text{CCl}_4$ .

ii) Thermolysis

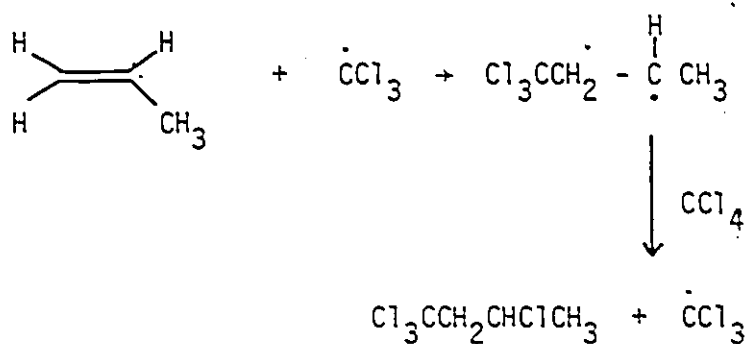
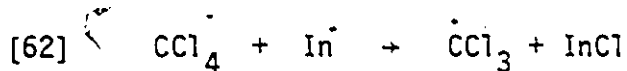
In a sealed tube dimethyldiazirine and  $\text{CCl}_4$  were thermolyzed at  $100^\circ\text{C}$ . After 4 days the P.M.R. spectrum did not show any sign of propene but the amount of  $\text{CCl}_3\text{CH}_2\text{CHClCH}_3$  was larger compared to the other products in the reaction mixture ( $\text{CHCl}_3$  and  $\text{CCl}_3\text{CCl}(\text{CH}_3)_2$ ). The amounts were compared by peak heights.

iii) Interpretation of results

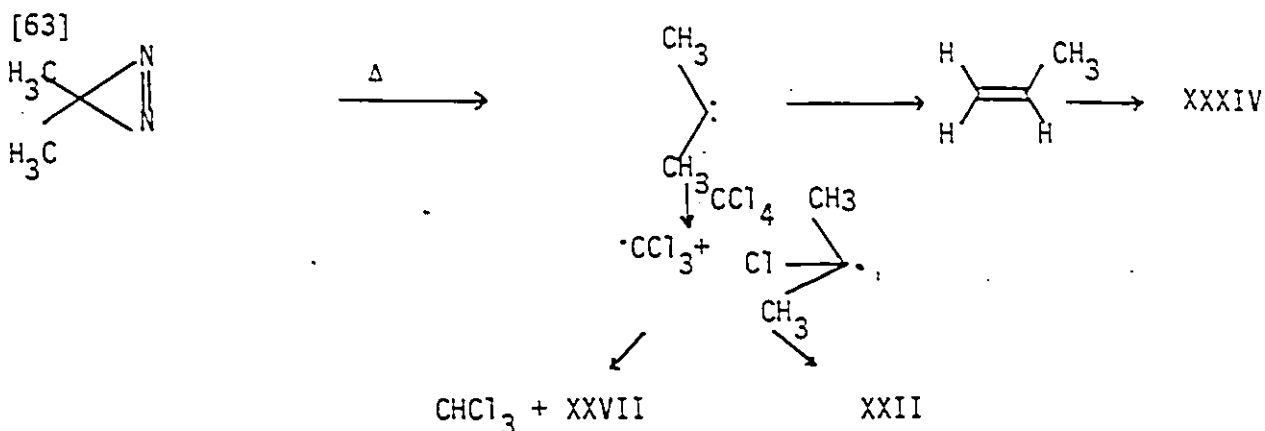
The presence of propene in the photoreaction and its absence in the thermal reaction suggests that it reacts thermally with carbon



tetrachloride to give  $\text{Cl}_3\text{CCH}_2\text{CHClCH}_3$ . An attempt to react  $\text{CCl}_4$  directly with propene under thermolysis conditions failed. No reaction occurred. On the other hand when the sealed tube from the photoreaction was heated, the 20% starting material left over initiated the reaction. Propene disappeared and the peaks due to  $\text{Cl}_3\text{CCH}_2\text{CHClCH}_3$  increased which suggests a radical type initiated reaction of propene with  $\text{CCl}_4$ .



The presence of chloroform in the products suggests a reaction of dimethylcarbene with carbon tetrachloride. Where in the gas phase dimethyldiazirine decomposes to give 90% yield of propene,<sup>24,25</sup> in the presence of carbon tetrachloride there is at least one process that can compete with the fast 1,2-hydrogen transfer. The reaction of dimethyl carbene with carbon tetrachloride is shown below:



### VII: Conclusion

Decomposition of  $\Delta^3$ -oxadiazolines often goes via a 1,3-diradical which rapidly closes yielding an epoxide (eq. 38)<sup>8,54-56</sup>.

In the case of the decomposition of oxadiazoline (XXII) the evidence so far is in good accord with the carbene mechanism. There is no direct evidence for the presence of the methoxyepoxide. The presence of diazoalkanes as intermediates is ruled out because it is known that they would react via a cycloaddition reaction with 1,1-diphenylethylene to give a stable pyrazoline, which is not the case.<sup>65</sup>

Pyrolysis of oxadiazoline (XXII) generates dimethylcarbene and methoxymethyl carbene. When generated in the presence of  $\text{CCl}_4$ , benzene and 1,1-diphenyl ethylene, the carbenes give products in good accord with the proposed mechanism.

### VIII: Summary

2-Methoxy-2,5,5-trimethyl- $\Delta^3$ -1,3,4-oxadiazoline was prepared from the lead tetraacetate oxidation of acetone-N-acetyl hydrazone in methanol.

The decomposition of the oxadiazoline is believed to involve carbene intermediates which react with the solvent, carbon tetrachloride, to give chlorinated products.

A trapping experiment with 1,1-diphenylethylene led to 1,1-diphenyl-2,2-dimethyl cyclopropane and 1,1-diphenyl-2-methoxy-2-methyl cyclopropane, in support of a carbene mechanism.

Finally, dimethyl carbene was generated from dimethyl diazirine in the presence of carbon tetrachloride and the production of chloroform and 1,1,1,2-tetrachloro-2-methyl propane suggests that one intermediate from thermolysis of the oxadiazoline is indeed dimethylcarbene.

### III: Experimental

#### 1: Instrumental

Proton magnetic resonance (P.M.R.) spectra were obtained from Varian T.60 and Varian E.M. 390 instruments. Carbon tetrachloride and chloroform-d were used as solvents. Tetramethylsilane (T.M.S.) was used as a reference. Infra-red spectra were recorded on a Perkin-Elmer, model 283, instrument. Solutions were made with carbon tetrachloride and spectra were taken in 0.1 mm NaCl cells. Mass spectra were obtained from a high-resolution Consolidated Electrodynamics Corporation (C.E.C.), 21-110 instrument. Melting points were determined on a Thomas Hoover capillary melting-point apparatus. Gas chromatograms were obtained using a Varian Aerograph instrument, model A90-P3. Starting materials were all commercially available, and were used without further purification unless otherwise specified.

#### 2: Synthesis reactions

##### (i) Preparation of lead tetraacetate

The method used was that of Fieser.<sup>67</sup> Acetic acid (1200 ml) and acetic anhydride (800 ml) were mixed in a three litre, three-necked, round bottom flask. The mixture was heated to 55°C and stirred vigorously with a mechanical stirrer. Red lead oxide (1400 g) was added in portions of 15-20 g over a period of five hours. A fresh addition was made only after the orange colour due to the preceding portion had mostly vanished. The temperature was maintained between 55°C and 60°C. At the end of the reaction the thick slurry was filtered, washed with cold acetic acid and recrystallized from hot acetic acid, (700 g, 79% yield)

## (ii) Preparation of acethydrazide

The procedure of Allen and Bell was followed, except for minor modifications.<sup>68</sup> Hydrazine hydrate (100g/99%) was added over a period of 10 minutes to a mixture of ethyl acetate (150 ml) and ethanol (150 ml/95%), in a one litre, three-necked, round-bottomed flask. After boiling the mixture for 48 hours the solvent was evaporated with a rotatory evaporator, and this was followed by distillation under reduced pressure (24 mm Hg). The product which distilled between 140°C and 150°C was collected. The condenser was heated with steam to prevent the solidification of the product. Recrystallization from ethanol gave acethydrazide of satisfactory purity; m.p.: 65°C - 67°C. (litt.<sup>71</sup>: 66°C - 67°C). Spectral data are reported in table 1.

## (iii) Preparation of acetone-N-acetyl hydrazone

Acetone (29g, 0.5 mole) and acethydrazide (36 g, 0.48 mole) were dissolved in dichloromethane. Sodium sulfate ( $\text{Na}_2\text{SO}_4$ ) was added as a drying agent to remove the water produced in the reaction. The mixture was stirred for two hours. The product was recovered after filtration of the mixture, followed by evaporation of dichloromethane. Recrystallization from ethanol gave sufficiently pure acetone-N-acetyl hydrazone; m.p.: 139°C-140°C (litt.<sup>72</sup>: 139.5° - 140°C) 51g, 90% yield. Spectral data are reported in table 1.

(iv) Preparation of 2-Methoxy-2,5,5-trimethyl- $\Delta^3$ -1,3,4-oxadiazoline

The lead tetraacetate (L.T.A.) was first washed with pentane to remove traces of acetic acid, under an atmosphere of dry nitrogen to avoid hydrolysis. L.T.A. (44.3 g, 0.1 mole) was added to a stirred solution of absolute methanol (500 ml) containing trifluoroacetic acid (25 ml). Acetone -N-acetyl hydrazone (11.4 g,

0.1 mole) was added to the mixture and the temperature was maintained at 0°C. The disappearance of the yellow colour was taken as evidence that the oxidation was complete. Most of the methanol was evaporated at reduced pressure (24 mm Hg), and the acetic acid was neutralized by adding a 5% solution of sodium bicarbonate. The mixture was then transferred to a separatory funnel and the oxadiazoline was extracted with dichloromethane. The solution was dried and the dichloromethane was evaporated. The residue was distilled at 25 mm Hg, and the fraction boiling between 35°C-45°C, was collected (65% yield). Other data are found in Table 1.

(v) Preparation of dimethyldiaziridine

Dimethyl diaziridine was prepared according to the procedure of Schmitz and Ohme.<sup>10</sup> In a three necked flask cooled to -78°C, liquid ammonia (34 c.c.) was mixed with acetone (17 c.c.) and methanol (20 ml). Hydroxylamine-O-sulfonic acid (13g) was added in portions. After the mixture had been stirred for two hours, it was left overnight for the excess ammonia to evaporate at room temperature. Extraction with cold ether was followed by an extraction of the ether solution with conc. H<sub>2</sub>SO<sub>4</sub>. The acidic solution was made alkaline and saturated with KOH pellets. Vacuum distillation (1 mm Hg) gave dimethyldiaziridine; mp. 40°C - 42°C (litt.<sup>10</sup>: 41° - 42°C); 10% yield. The I.R. spectrum was the same as in the litt.<sup>73</sup>

(vi) Preparation of dimethyldiazirine

The procedure of Schmitz and Ohme<sup>10</sup> was followed. Dimethyldiaziridine (3.5 g, 0.05 mole) was dissolved in 80 ml of a 2N aqueous NaOH solution, and added over a period of three minutes to a solution of 30 g of Ag NO<sub>3</sub> in H<sub>2</sub>O. The diazirine (litt.<sup>10</sup>: b.p.: 20° - 22°C) collected in a round bottomed flask cooled at dry ice methanol temperature. (50% yield). The I.R. spectrum was the same as in the litt.<sup>74</sup>

### III: Decomposition reactions

(i) Thermolysis of oxadiazoline (XXII) in  $\text{CCl}_4$  under reflux:

The reaction was carried out in a round-bottomed flask fitted with a reflux condenser. The molar ratio of (XXII) to carbon tetrachloride was approximately 1:10. The flask was heated with an oil bath for five days at the boiling point of  $\text{CCl}_4$  ( $76.7^\circ\text{C}$ ). During this time the colourless solution became dark yellow. Distillation at reduced pressure (24 mm Hg) at  $50^\circ\text{C}$  gave a mixture of acetone, methyl acetate and chloroform.

The distillate was analyzed by gas chromatography using a 10" x 0.25" of a 10% D.E.G.S. column, at  $70^\circ\text{C}$ .

The residue was analyzed in the same fashion with the same column heated at  $110^\circ\text{C}$ . Spectral data are listed in Table 2.

(ii) Thermolysis of oxadiazoline (XXII) in  $\text{CCl}_4$  in a sealed tube.

Oxadiazoline XXII ( $10^{-4}$  mole) and  $\text{CCl}_4$  (1.00 ml) were mixed together in an N.M.R. tube. After several degassifications, at liquid nitrogen temperature, the tube was sealed under vacuum ( $5 \times 10^{-1}$  mm Hg). The thermal decomposition was carried out in a temperature controlled oil bath at  $80^\circ \pm 0.5^\circ\text{C}$  for 5 days.

(iii) Thermolysis of oxadiazoline (XXII) in benzene in a sealed tube.

Oxadiazoline XXII ( $10^{-4}$  mole) and benzene (1.00 ml) were mixed together in an N.M.R. tube. After several degassifications at liquid nitrogen temperature, the tube was sealed under reduced pressure ( $5 \times 10^{-3}$  mm Hg). The tube was heated for 5 days in an oil bath kept at  $80^\circ\text{C} \pm 0.5^\circ\text{C}$  before the N.M.R. spectrum was taken.

(iv) Thermolysis of neat oxadiazoline

In an N.M.R. tube some oxadiazoline (XXII) was degassed at liquid nitrogen temperature, sealed and heated in a constant temperature oil bath at  $80\text{ C} \pm 0.5^\circ\text{C}$  for five days. The reaction was stopped and an N.M.R. spectrum was recorded.

(v) Kinetics of the thermolysis of oxadiazoline (XXII) in  $\text{CCl}_4$

In an N.M.R. tube oxadiazoline (XXII) (20 mg) and carbon tetrachloride (1 ml.) were mixed together. Hexamethylenetetramine (10 mg) was added, the tube was degassed at liquid nitrogen temperature and sealed under reduced pressure ( $5 \times 10^{-3}$  mm Hg). The tube was heated at  $80^\circ\text{C}$ . The reaction was followed by N.M.R. and spectra were recorded every 2-3 hours.

(vi) Thermolysis of oxadiazoline (XXII) in the presence of 1,1-diphenylethylene

Oxadiazoline (XXII) and 1,1-diphenylethylene were mixed together in a 1:5 molar ratio. After the mixture was degassed the thick walled tube was sealed under reduced pressure ( $5 \times 10^{-3}$  mm Hg). The reaction was carried out at  $82^\circ\text{C}$  for 72 hours and the tube was opened and the mixture was worked up. The distillate collected up to  $50^\circ\text{C}$  (24 mm Hg) was analyzed by P.M.R. and Gas Chromatography. The residue was diluted with dichloromethane and 100 mg portions were applied on silica gel plates (1 mm thick). After eluting with dichloromethane two major strips were scraped from the glass. The support was extracted with dichloromethane and the solvent evaporated. Proton magnetic resonance spectra and infra-red spectra were taken to identify the products.

(vii) Photochemical decomposition of dimethyl diazirine in  $\text{CCl}_4$ .

Dimethyldiazirine (0.0005 mole) and  $\text{CCl}_4$  (1.00 ml) were mixed together in a pyrex N.M.R. tube. After degassing the tube at liquid nitrogen temperature, it was sealed under reduced pressure ( $5 \times 10^{-3}$  mm Hg). A Rayonette apparatus ( $\lambda_{\text{max}} = 300$  nm) was used as a light source and the photodecomposition was carried out at  $50^\circ\text{C}$ . The tube was checked for disappearance of starting material every hour, by running an N.M.R. spectrum. After 12 hours 80% of the starting material signal (1.0 ppm) had disappeared.

(viii) Thermal decomposition of dimethyldiazirine in  $\text{CCl}_4$

Dimethyldiazirine (0.0005 mole) and  $\text{CCl}_4$  (1.00 ml) were mixed together in a tube. After several degassifications at liquid nitrogen temperature, the tube was sealed at reduced pressure ( $5 \times 10^{-3}$  mm Hg). The reaction was performed in an oil bath where the temperature was maintained at  $100^\circ\text{C}$  for 96 hours. After this time the reaction was stopped and an N.M.R. was taken.

In all those reactions 2 drops of T.M.S. were used as an internal standard for N.M.R. spectra. Peak heights for yield calculations are relative to the T.M.S. peak height. Finally all spectral data are reported in Table 1 and 2 and in the results and discussion portion of this thesis.



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