

AN ABSTRACT OF THE THESIS OF

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Title FORMATION OF ALKYL- AND DIALKYL CARBENES. THE  
3-CYCLOHEXENYL CARBINYL CARBENE SYSTEM.

Abstract approved Redacted for Privacy  
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The 3-cyclohexenyl carbinyl carbene species was formed by the thermal decomposition of the p-toluenesulfonylhydrazone sodium salt and by oxidation of the hydrazone. Several oxidizing agents were studied. The products were investigated under aprotic and protic conditions and at various temperatures. The diazocompound was formed as an intermediate and found to be relatively stable although extremely sensitive to the conditions. When the diazocompound was decomposed, the azine and the hydrocarbon products, both major and minor, were characterized. Under aprotic conditions the hydrocarbon yield was small and showed a large amount of  $\beta$ -insertion. The  $\beta$ - to  $\gamma$ -insertion ratio decreased as the system became protic. A comparison of the two methods of carbene formation is presented.

FORMATION OF ALKYL- AND DIALKYL CARBENES. THE  
3-CYCLOHEXENYL CARBINYL CARBENE SYSTEM

by

DALE MC CLISH CROUSE

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# FORMATION OF ALKYL- AND DIALKYL CARBENES. THE 3-CYCLOHEXENYL CARBINYL CARBENE SYSTEM.

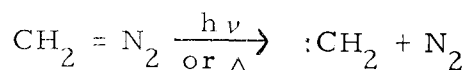
## INTRODUCTION

Of the many intermediates postulated in organic chemistry, perhaps none is more interesting than the divalent carbon (carbene) species,  $\text{:CX}_2$ . The combination of an incomplete electronic octet and a pair of unshared electrons gives to the species both electrophilic and nucleophilic characteristics. Within the past fifteen years there has been an extensive investigation of both the methods for generation of such an intermediate and its fate under various reaction conditions. These investigations have added extensively to studies of both synthetic and mechanistic organic chemistry.

### Substantiation of the Carbene Intermediate

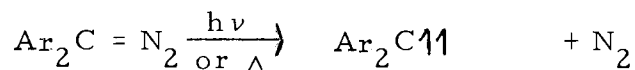
#### Carbene Types

The best evidence for the existence of a carbene intermediate comes from studies of the decomposition of diazomethane, either pyrolytically or photochemically, to give methylene,  $\text{:CH}_2$ , and nitrogen gas.

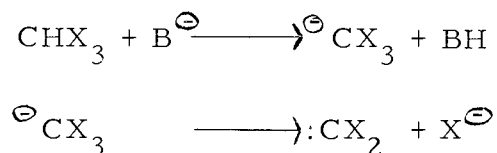


Herzberg (84) observed the vacuum ultraviolet absorption spectrum of two new species in the flask photolysis of diazomethane. One at 140 mμ was subsequently shown to be due to triplet methylene with a linear structure and a bond length of 1.03 Å. The other at 550-950 mμ resulted from singlet methylene with a bond angle of 103° and a bond length of 1.12 Å. To show these new species had only one carbon, 60% C<sup>13</sup> diazomethane was irradiated. Only one new set of lines appeared.

With these physical measurements the divalent carbon species was given a scientific existence. Electron paramagnetic resonance (e. p. r.) measurements have substantiated the existence of triplet diarylcarbenes (172).

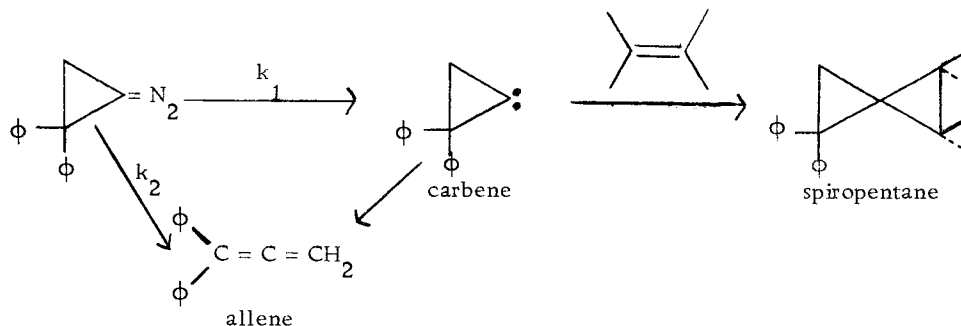


Compelling evidence that dihalocarbenes are intermediates in the basic hydrolysis of haloforms has been demonstrated by Hine and others (47, 88, 89, 90, 92, 159).

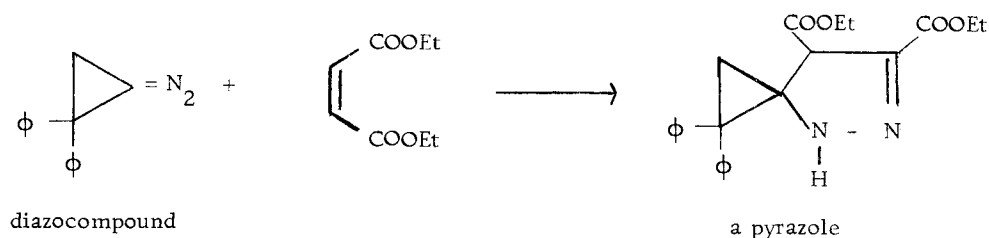


Experiments to demonstrate the existence of alkyl- and dialkylcarbenes are few, and the proof of a "free" carbene intermediate has been illusory. Two types of experiments, one kinetic, the other labeling, have been carried out to show the existence of alkyl- and dialkylcarbenes.

Experiments by Jones and co-workers (97, 98) illustrate kinetic arguments for the intermediacy of a carbene in the decomposition of diazocompounds.



They showed that the allene came from two species and that  $k_1/k_2 = 0.5$ . They also showed by a trapping experiment that the first allene precursor, the diazocompound, was nucleophilic.



Running a series of competitive rate experiments with nucleophilic olefins showed that the intermediate forming the spiropentanes was electrophilic. Presumably this intermediate was the carbene.

Labeling experiments have been used to distinguish alternate mechanisms in carbenoid reactions. Kirmse and co-worker's (109)



Others have used similar experiments (71, 111).

In summary, the formation of dialkylcarbene intermediates has been the subject of much controversy but has not been subjected to much careful mechanistic study. Whiting and co-workers (2, 171) have suggested that in many cases the products can be explained just as easily by a concerted mechanism not involving a carbene. In the remainder of this thesis carbenes will be invoked as intermediates, although not rigorously proven.

### Singlet and Triplet Carbenes

Evidence has accumulated to support the existence of two spin states for carbenes: the singlet state with paired spins ( $\uparrow\downarrow$ ) and the triplet state with unpaired spins ( $\uparrow\uparrow$ ). In addition to the physical methods used to distinguish the two states, several chemical methods have been suggested. These latter methods would be the most convenient for the organic chemist if they are valid.

One suggested chemical method is the use of insertion ratios. With methylene the insertion ratios have been shown by Hammond et al. (115) to be different for the sensitized and unsensitized photolysis of diazomethane (Table I).

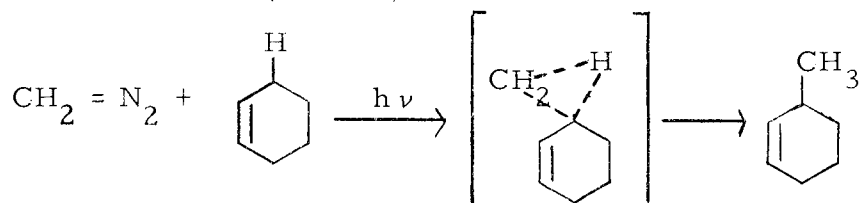
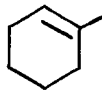
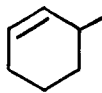
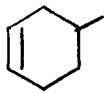


Table I. Methylene Insertion Ratios From  $\text{CH}_2\text{N}_2$ 

Conditions			
Direct photolysis	1.0	0.24	1.3
Thermal at 260°	1.0	0.43	1.7
Sensitized photolysis	1.0	trace	0.42
Thermal Cu catalyst	1.0	0	0
Thermal $\text{Fe}(\text{DRM})_3$ catalyst	1.0	0	0

Because the sensitized photolysis of diphenyldiazomethane was shown by e. p. r. to give triplet carbene (15, 172), Hammond and co-workers assumed that the methylene formed in the presence of a sensitizer is also in the triplet state. They then suggested that the differences in insertion ratios may be attributed to a change in multiplicity; that is, singlet carbenes insert whereas triplet carbenes do not.

A second suggested chemical method for determining spin states is the stereospecificity of carbene addition reactions. Skell and co-workers (159, 160, 162, 185) suggested that singlet carbenes might add stereospecifically to olefins and triplet carbenes non-stereospecifically. Hammond and co-workers (115) presented evidence that addition reactions can be stereospecific (Table II).

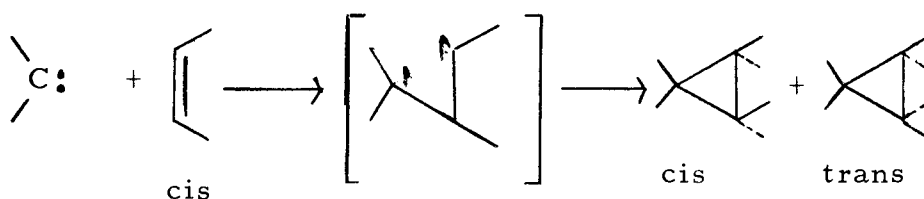
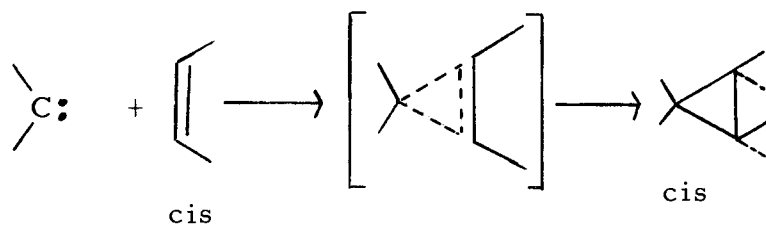






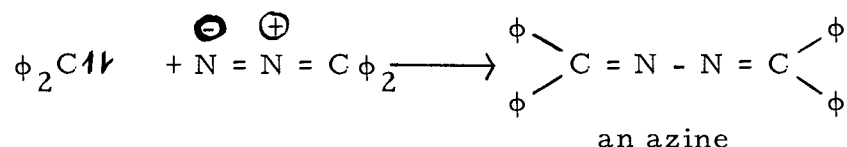


Table II. Methylene Addition Ratios From  $\text{CH}_2\text{N}_2$

Conditions	olefin	 cis	 trans
Direct photolysis		only product	
Sensitized photolysis		2	1
Direct photolysis		only product	
Sensitized photolysis		trace	major product

Using the previous arguments for the spin states of the intermediates the results indicate that Skell's suggestions were partially correct. If all singlet carbenes do add stereospecifically and all triplet carbenes do not, then addition reactions could be used to determine the multiplicity of a specific carbene.

A third chemical method for the determination of spin states is the formation of azines. Zimmerman and Paskovich (186) suggested that azines form from singlet carbenes only.



This work will be further discussed in the azine section of the thesis.

In these chemical methods the spin states of the intermediates were not rigorously proved. Whether the chemical methods are valid in general is also debatable. In spite of these two reservations, many have used addition reactions to determine carbene spin states (48, 54, 143, 159, 160, 162).

A qualitative prediction of the ground state of  $:\text{CX}_2$  is possible theoretically. The X group of  $:\text{CX}_2$  determines the energy of each spin state, the spin state having the lowest energy being the ground state. Bond energies increase with the square of the difference in electronegativities of the bonded atoms; the greater the difference the more the central carbon atom will assume a state in which it has the least electronegativity, that is, a hybrid state containing more p character and less s character. Singlet carbene is presumably  $\text{sp}^2$  hybridized while triplet carbene is sp hybridized. Thus one would expect a singlet carbene ground

state when the X group is more electronegative. From spectroscopic evidence  $\text{:CF}_2$  is a singlet in the ground state,  $\text{:CH}_2$  is a triplet.

As the electronegativity difference decreases, the difference in energy between the singlet and triplet states also decreases; and thus spin inversion becomes more facile. Steric factors, as well as electronic, would certainly have an effect on the energy of the spin states. In some carbenes, namely dialkylcarbenes, the inversion energy may be so small that reaction conditions would favor one spin state over the other. Catalysts may favor one spin state of methylene (Table I) or of dialkylcarbenes (3, 112, 169).

If any differences in chemical reactivity are to be useful to the synthetic organic chemist, the ability to determine the spin state and even change it would be essential. Once the determination is facile then the differences in reactivity between the spin states can be better understood. These differences will undoubtedly be of immense use to the synthetic organic chemist.

### Stable Carbenes

A discussion of the existence of carbenes is not complete without mentioning the stability of carbenes. Kirmse (107) and Chinoporos (23) in their respective review articles discussed how the X group in  $\text{:CX}_2$  stabilizes the carbene. Diazomethane

and diazoethane are explosive. The dihalocarbenes are very reactive; the most stable  $\text{:CF}_2$  has a half-life of  $10^{-4}$  second. Dialkylcarbenes have never been isolated. Staudinger and Gaule (166) as early as 1916 tried to vary the substituents on the phenyls in diphenyldiazomethane to obtain a stable carbene. Their attempt and subsequent attempts were not successful.

### Formation of Alkyl- and Dialkylcarbenes

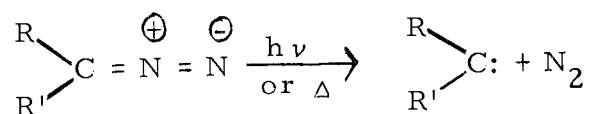
Methods of generating alkyl- $(\text{R}\ddot{\text{C}}\text{H})$  and dialkylcarbenes  $(\text{R}_2\text{C:})$  may be divided into decomposition and elimination reactions.

#### Decomposition

The decomposition reactions may be grouped with respect to the leaving molecule (usually a gas).

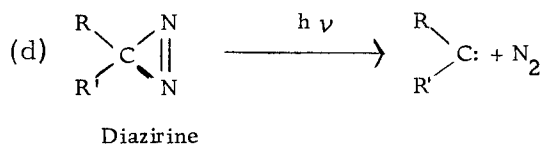
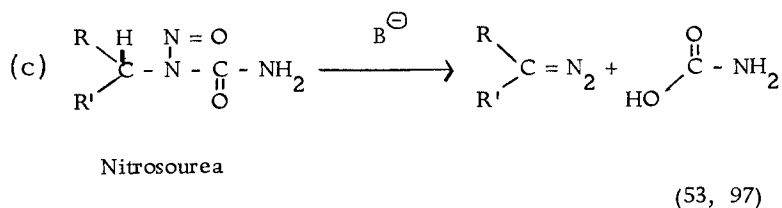
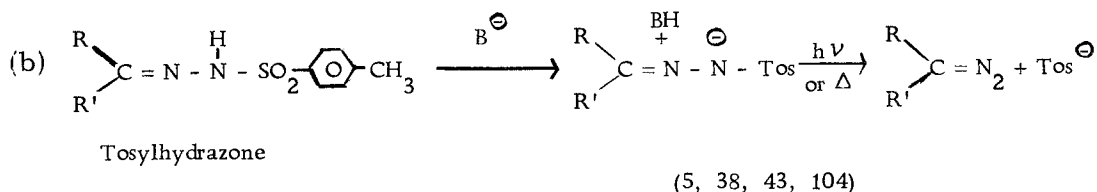
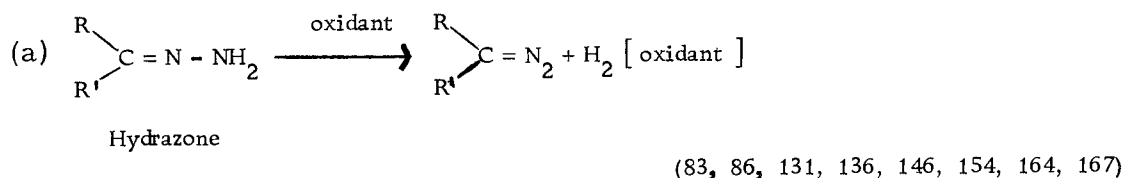
#### Nitrogen Gas

##### Diazocompounds



where R, R' = alkyl or H

There are many ways to form the diazocompound. Some are listed below.



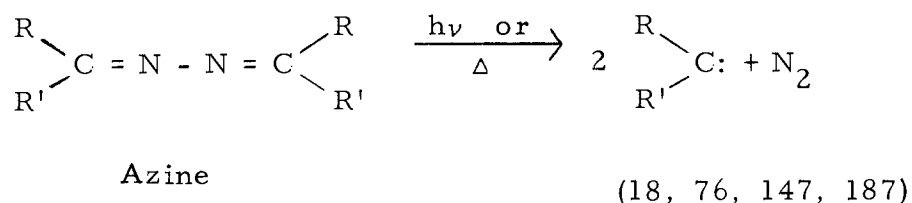
There are other methods for synthesizing diazocompounds starting from amines (1, 41), lithium salts (46), oximes (129), and olefins (16, 17).

Probably the most used method for generation of alkyl- and dialkylcarbenes is the thermal decomposition of the sodium salt of the p-toluenesulfonylhydrazone (tosylhydrazone) of an aldehyde or ketone [ equation (b) above ]. This method in protic solvents, where

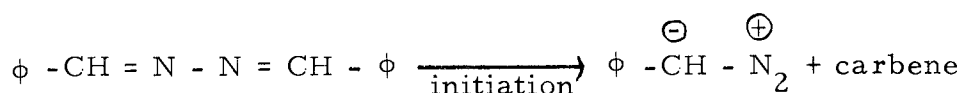
the diazocompound underwent protonation to give products characteristic of a carbonium ion, was used by Bamford and Stevens (5) in 1952. Under aprotic conditions Shechter et al. (104) have distilled out the intermediate diazocompound in high yield. Using the isolated diazocompound reduces the possibility of side reactions, but diazocompounds are sometimes explosive and probably carcinogenic. The presence or absence of a proton source greatly alters the product composition in the Bamford and Stevens Reaction and will be discussed later.

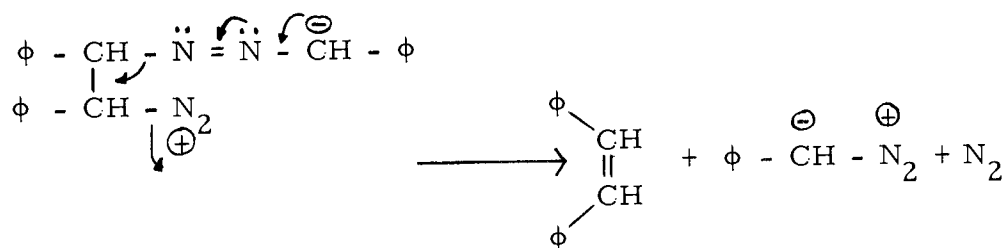
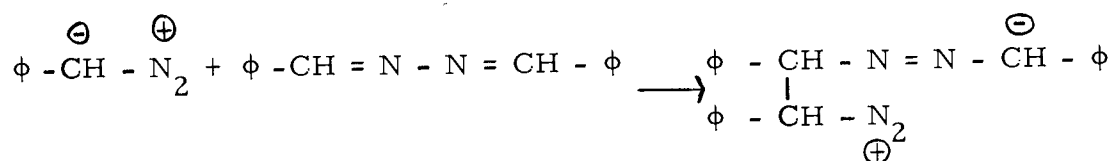
### Azines

The formation of carbenes in the decomposition of azines is uncertain.

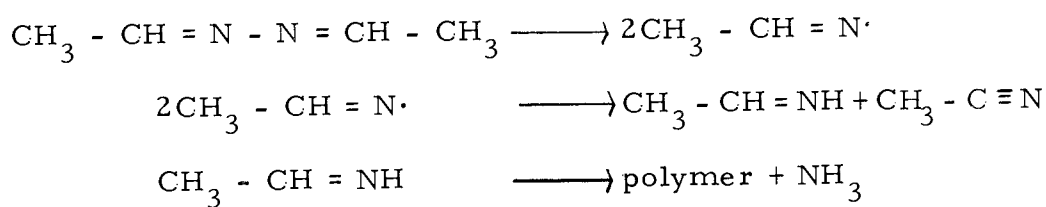


In the thermal decomposition of benzalazine to give stilbene Zimmerman and Somasekhara (187) proposed an ionic chain process.



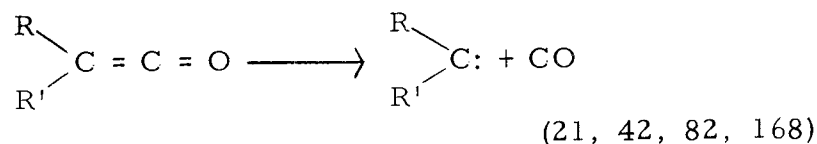


Rice and Glasebrook (147, 148) reported the pyrolysis of acetaldazine but could not prove the intermediacy of a carbene by mirror removal experiments. Brinton (18) reported the photolysis of acetaldazine yielded a small amount of 2-butene and ethylene, but acetonitrile and ammonia were the principal products. This indicated that the major reaction was cleavage of the nitrogen-nitrogen bond.



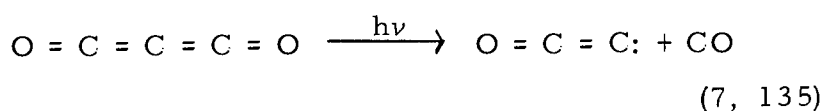
### Carbon Monoxide

#### Ketene



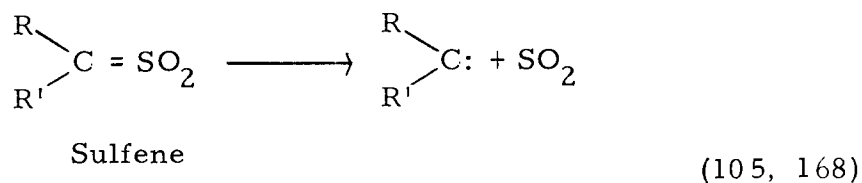
In 1916 Staudinger and Pfenninger (168) decomposed diphenylketene to obtain carbenoid products. Haller and Srinivasan (82) postulated a ketene as an intermediate in the photodecomposition of tetramethylcyclobutan-1,3-dione which yielded some tetramethylcyclopropanone.

#### Carbon Suboxide



Mullen and Wolf (135) presented some evidence for a carbene intermediate by using labeling experiments.

#### Sulfur Dioxide



Staudinger and Pfenninger (168) decomposed diphenylsulfene to obtain carbenoid products. King and Durst (105) have recently reinvestigated this approach to carbenes.

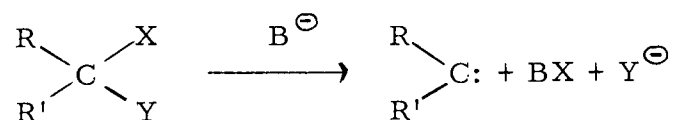
#### Other Methods

Other methods which may have carbenes as an intermediate involve loss of trimethylamine (58), diphenylsulfide (57, 93) and

dimethylsulfide (23).

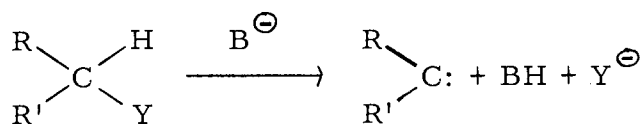
### Elimination

$\alpha$ -Elimination reactions can, in theory, allow an alternative route to carbenes. Such an elimination reaction can be represented by the loss of two groups from the same carbon.



These reactions are generally initiated by base.

In many cases the X group is hydrogen.



$$\text{Y} = \text{Cl}^{\ominus} \quad (25, 26, 29, 30, 32, 59, 71, 111, 153,$$

161, 176)

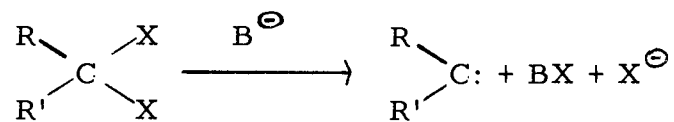
$$= \text{O}^{\ominus} \phi \quad (152)$$

$$= \text{OR}^{\ominus} \quad (34, 35)$$

Bases which have been used are butyllithium (30, 152), sodamide (103, 32), magnesium (123), sodium, potassium, and lithium (111).

It appeared that lithium changed the reaction mechanism (111).

In other cases both X and Y are the same group.

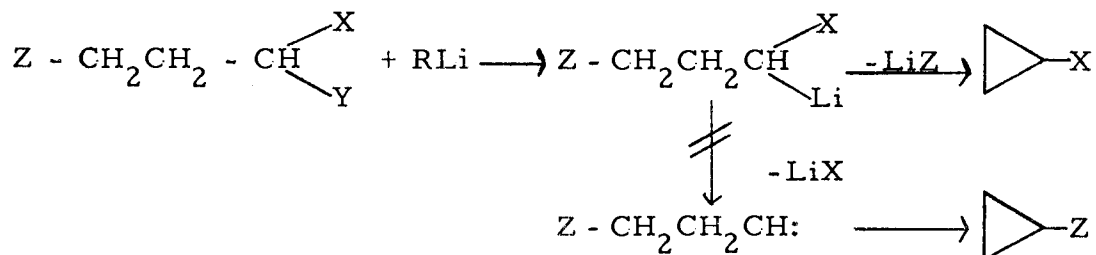


X = C1 (102, 157)

$$= \text{Br} (132, 133, 134, 157, 158)$$
$$= I(3)$$

With gem-dibromocompounds both methyllithium and butyllithium have been used as the base, but with gem-dichlorocompounds only butyllithium was successful (133, 157).

It is doubtful whether these reactions really involve a free carbene intermediate. The species generated from elimination reactions do not behave like the corresponding carbenes generated from the diazocompound. They add to olefins intermolecularly (134) and, in one case, to an aromatic system (26). A trihalo system was shown to go through a two step process not involving a carbene (106, p. 51).



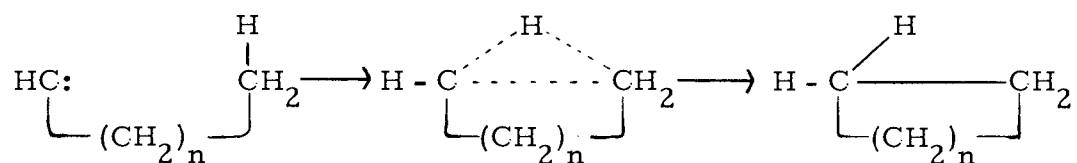
In many instances, however, the products are characteristic of a carbene intermediate (71); thus these reactions are referred to as carbenoid reactions.

### Reactions of Alkyl- and Dialkylcarbenes

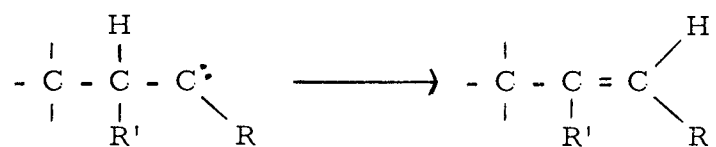
The reactivity of alkyl- and dialkylcarbenes is so high that they usually undergo intramolecular reaction before collision will allow intermolecular reaction. The exceptions to this generalization seem to be carbenes which have some stabilizing feature or which could give only a highly strained system by intramolecular reaction. The intramolecular reactions will be divided into insertion and rearrangement reactions.

#### Insertion

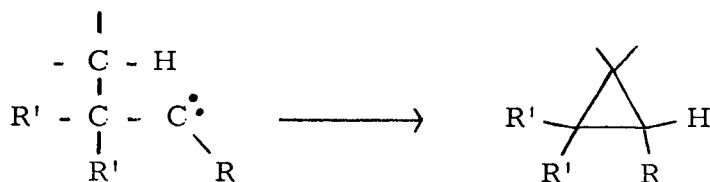
The insertion of a carbene carbon into a carbon-hydrogen bond gives different products depending on the position of the carbon-hydrogen bond.



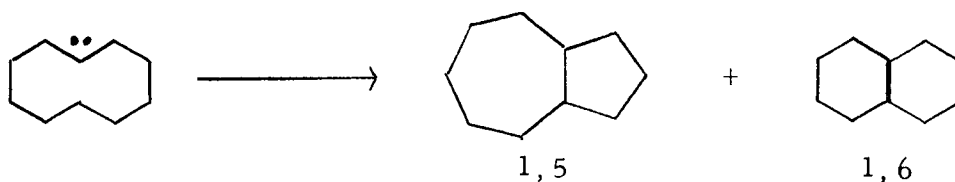
#### $\beta$ -insertion



$\gamma$ -insertion













transannular insertion



The relative yield of cyclopropanes increases with increased branching of the alkyl groups (see compounds 1, 2, 6 or compounds 4, 5 in Table III). Thus,  $\gamma$ -insertion appears to be governed by the proximity of a suitable carbon-hydrogen bond. Kirmse and Wächtershäuser (114) have shown that the formation of cyclopropanes may be consistently explained by a transition state in which the carbene carbon is eclipsed by the  $\gamma$ -carbon-hydrogen bond. The more facile the approach to an eclipsed transition state, the more cyclopropane is formed. Increased branching of the alkyl substituents decreases the energy of activation to the eclipsed transition state thus giving more cyclopropane.

Table III. Alkylsubstituent Effects on Insertion

Compound Number	Reactants Carbene	Products				Reference	
		$\beta$ -insertion	$\gamma$ -insertion	Alkyl Shifts			
1	$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3 - \text{C} - \text{CH:} \\   \\ \text{CH}_3 \end{array}$	0%	92%			(73)	
				7%	1%		
2	$\begin{array}{c} \text{H} \\   \\ \text{CH}_3 - \text{C} - \text{CH:} \\   \\ \text{CH}_3 \end{array}$	62%	38%	0%		(73)	
3	$\begin{array}{c} \text{H} \\   \\ \text{CH}_3\text{CH}_2 - \text{C} - \text{CH:} \\   \\ \text{CH}_3 \end{array}$	63%				0%	(25)
		20%	12%	5%			
4	$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3 - \text{C} - \text{C:} \\   \quad \backslash \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$	52%	47%				(73)
		41%	52%	traces			(108)
				4%	3%		
5	$\begin{array}{c} \text{CH}_3 - \text{CH}_2 - \text{C:} \\ \quad \quad \quad \backslash \\ \quad \quad \quad \text{CH}_3 \end{array}$				0.5%	0%	(73)
		5%	67%	28%			
6	$\text{CH}_3 - \text{CH}_2 - \text{CH:}$	90%	10%	0%		(106, p. 148)	

From Table III various product ratios may be extracted as shown in Table IV.

Table IV. Insertion Ratios

Carbene Type	Ratio Type	Percentage	Number of Hydrogens	Ratio Value	Compound Number From Table III
Alkyl	$\frac{\beta\text{-tert. H}}{\gamma\text{-prim. H}}$	$\frac{62}{38}$	$\frac{1}{6}$	9.8	2
		$\frac{63}{37}$	$\frac{1}{5}$	9.5 corrected	3
	$\frac{\beta\text{-sec. H}}{\gamma\text{-prim. H}}$	$\frac{90}{10}$	$\frac{2}{3}$	13.5	6
	$\frac{\gamma\text{-sec. H}}{\gamma\text{-prim. H}}$	$\frac{17}{20}$	$\frac{2}{3}$	1.3	3
	$\frac{\text{insertion}}{\text{alkyl shift}}$	$\frac{92}{8}$		12	1
Dialkyl	$\frac{\beta\text{-prim. H}}{\gamma\text{-prim. H}}$	$\frac{46}{50}$	$\frac{3}{9}$	2.7	4
	$\frac{\beta\text{-sec. H}}{\beta\text{-prim. H}}$	$\frac{95}{5}$	$\frac{2}{3}$	31	5
	$\frac{\text{insertion}}{\text{alkyl shift}}$	$\frac{93}{7}$		13	4

It can be seen that with  $\gamma$ -insertion a secondary hydrogen is preferred to primary, and with  $\beta$ -insertion this preference is even greater.

Powell and Whiting (144) showed the  $\beta$ -insertion preference between secondary and tertiary hydrogens reversed in the diazodecalins in going from a cis ring juncture to trans.

Ring size leads to varying amounts of insertion as shown in Table V from the work of Friedman and Shechter (75).

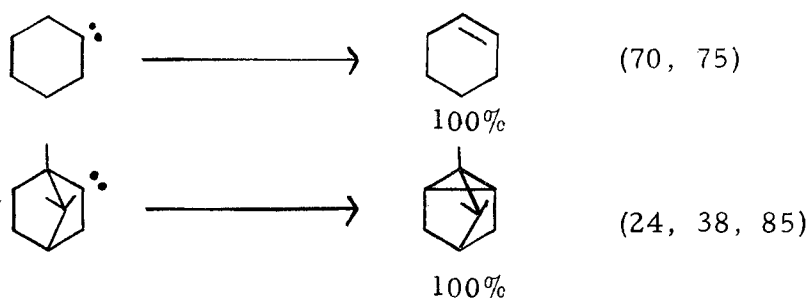
Table V. Ring Size Effects<sup>\*</sup>

Ring Size	Structure	$\beta$ -insertion		$\gamma$ -insertion	1, 4-insertion	1, 5-insertion		1, 6-insertion		Other
		cis	trans			cis	trans	cis	trans	
3										Rearrange- ment C = C = C
4		19%								Ring contraction 80%
5		100%								
6		100%			0%					
7		21%		79%	0%					
8		45%		9%	0%	46%	0%			
9		22%		10%	0%	66%	0%			
10		14%	6%		0%	62%	0%	18%	0%	

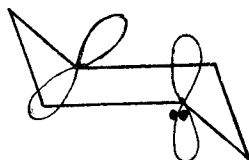
<sup>\*</sup> Tosylhydrazone plus 1.2 eq. NaOMe in diethylcarbitol (DEC); yields 60-70%

Medium rings prefer 1, 3; 1, 5; or 1, 6 insertion probably due to the proximity of the transannular hydrogens. The formation of an exclusive cis ring juncture is consistent with the principle that insertion reactions occur with retention of configuration.

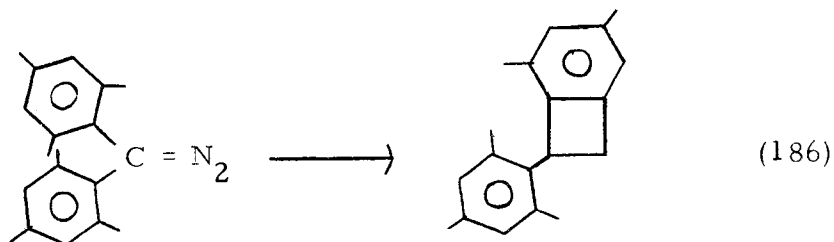
A big difference in  $\beta/\gamma$  insertion ratio is noted when the cyclohexane ring is held in a boat conformation.

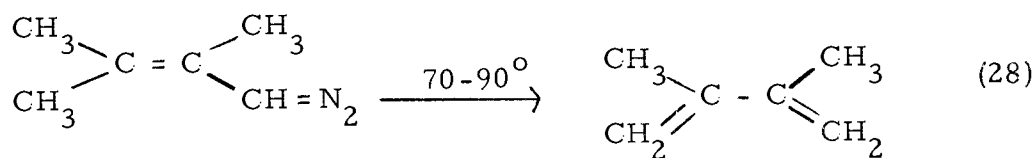
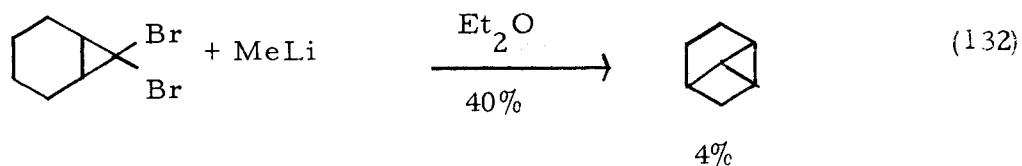


The absence of 1, 4 insertion in Table V may be explained by noting that the stereochemistry does not allow the orbitals to line up.



Only three cases of 1, 4 insertion are known. Zimmerman and Paskovich (186) showed the dimesitylcarbene abstracted a hydrogen atom and then proceeded by a radical mechanism.





The third reaction may also be a radical process. Correlations between spin states and insertion ratios have been sparsely presented in the literature since information regarding spin states is lacking.

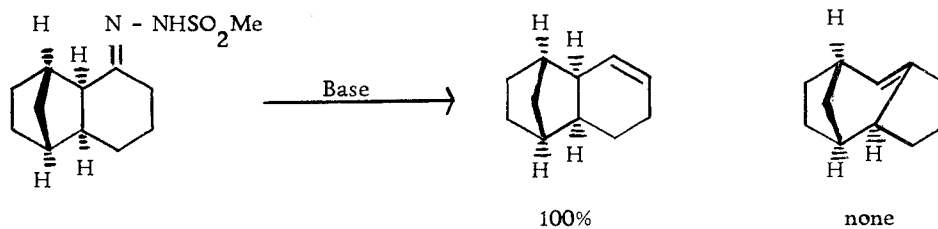
### Rearrangement:

Carbene rearrangements are known and can be placed in two classes.

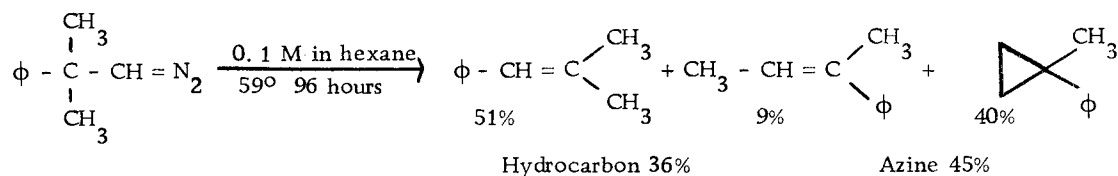
#### Migration



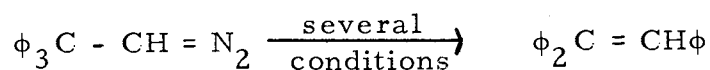
In studying the migration of carbon versus hydrogen Whiting and co-workers (2, 171) showed that hydrogen migration is greatly preferred.



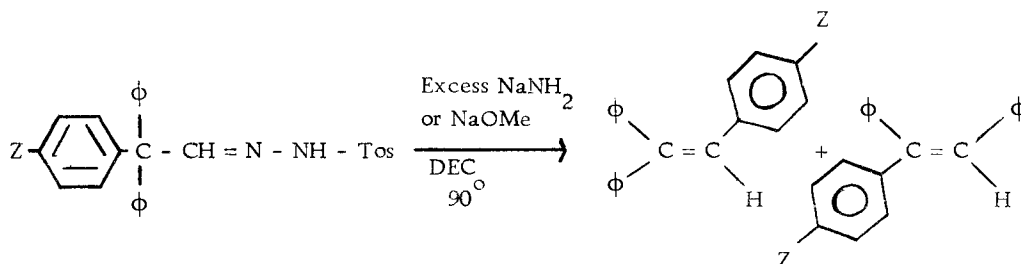
Work carried out by Philip and Keating (142) demonstrated that phenyl/methyl migration aptitude was 10.



Hellerman and Garner (83) found the only product in the following decomposition was given by phenyl migration.

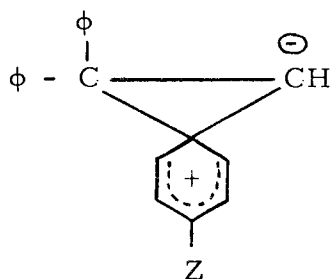


Sargeant and Shechter (149) studied the same reaction with various substituents.



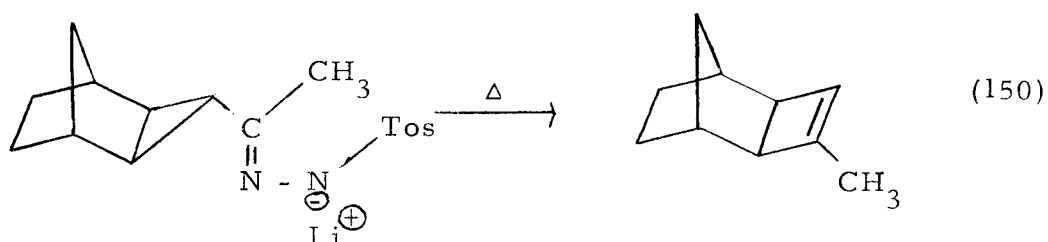
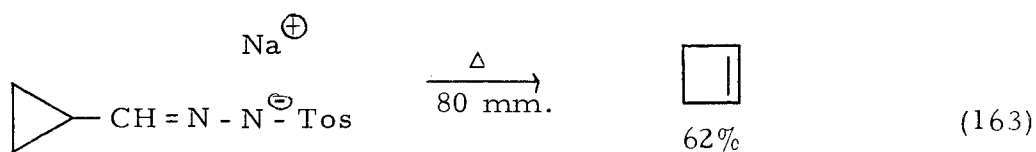
They found the migratory aptitude correlated better with

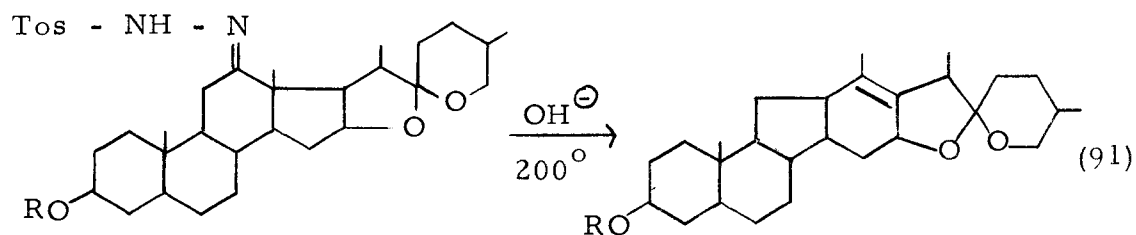
$\sigma_p^\oplus$ ,  $\rho = -0.28$ , and the transition state, represented below, was electrophilic.



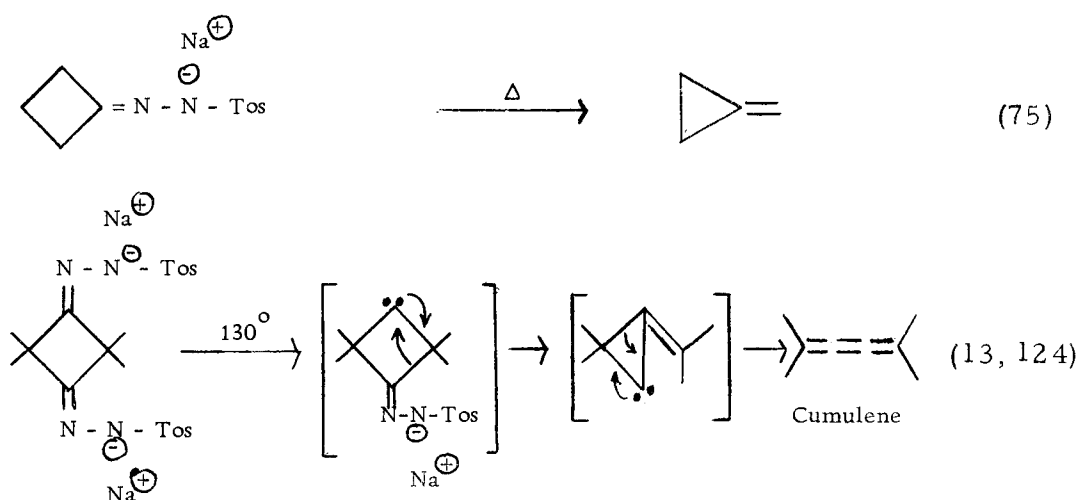
Wilt and co-workers (179, 182) carried out a series of experiments to determine the effect of ring size in the neophyl rearrangement. Their results showed phenyl migration increased as the ring size changed from three to seven. Their work may have involved carbonium ions rather than carbenes.

In reactions involving ring compounds migration can result in ring expansion



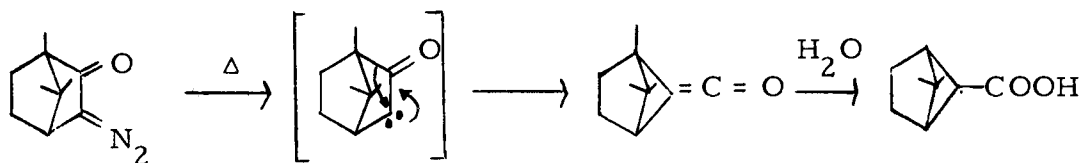


or ring contraction.



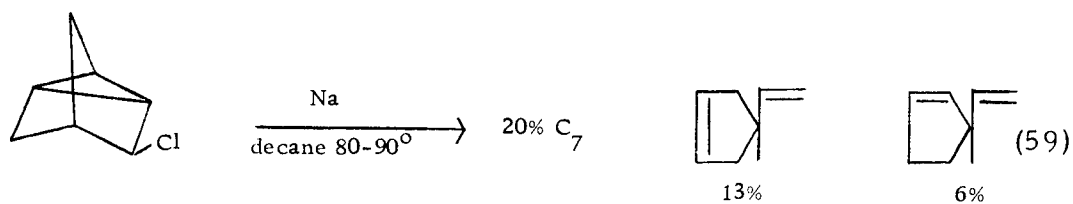
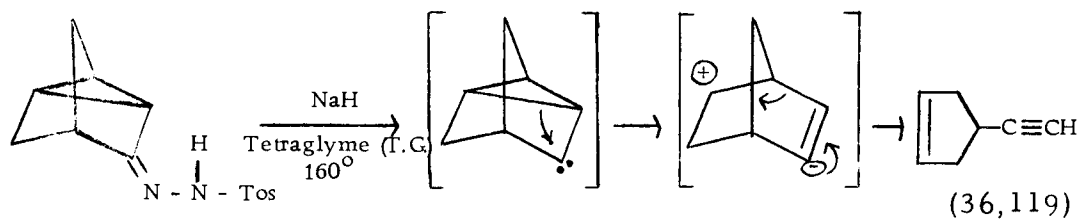
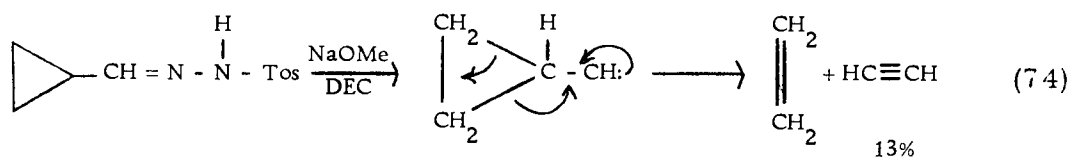
The ring contraction is useful in the synthesis of strained rings.

A widely used example of ring contraction is the Wolff Rearrangement in which the carbene carbon has an  $\alpha$ -keto group.  $\alpha$ -Keto carbenes appear to be stabilized over the unsubstituted analogue and give a ketene by rearrangement.




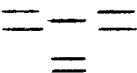


### Fragmentation

Many fragmentations have been observed in carbenoid reactions (19, 67, 68). Some are shown below.



Frey and Stevens (70) demonstrated that the fragmentation increases as the pressure decreases with reactions in the gas phase.

Table VI. Pressure Effects on Fragmentation<sup>\*</sup>

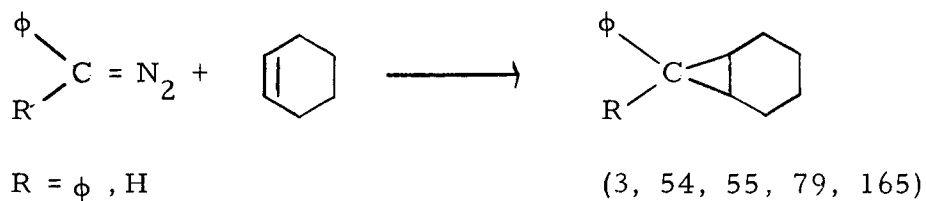
Carbene				Pressure
	88%	8%	2.5%	10.2 mm.
	86%	11%	2.3%	5.9 mm.
	80%	17%	2.1%	3.0 mm.
	71%	26%	1.8%	1.1 mm.
	62%	36%	1.4%	0.34 mm.
	57%	41%	0.9%	0.17 mm.

<sup>\*</sup>Photolysis with Hanovia uvs 500 of diazirine

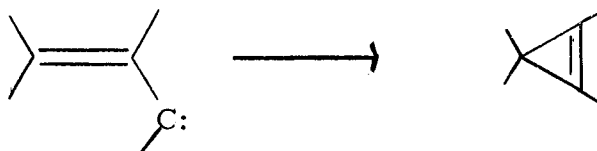
Intermolecular reactions of alkyl- and dialkylcarbenes appear less favorable in many instances and have not been studied as fully as the intramolecular reactions. The classic method of detecting carbene intermediates is trapping by olefins to give cyclopropanes, and this method will be discussed first.

#### Addition

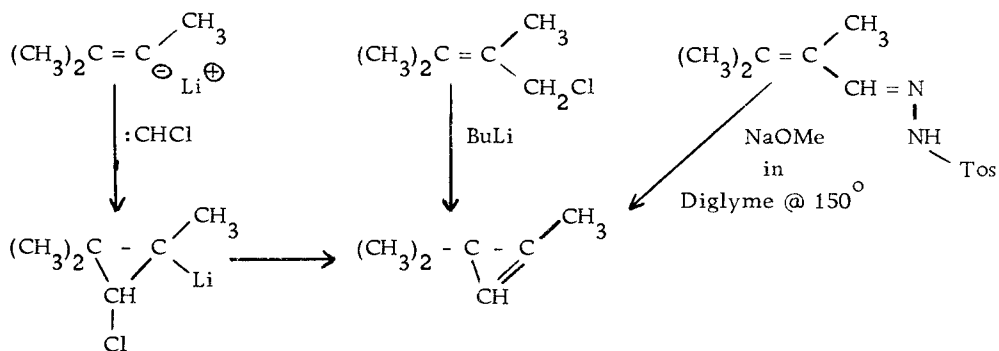
The addition of dihalocarbenes to olefins is well known (47). It is also known that aryl- and diarylcarbenes can be "trapped" with olefins.



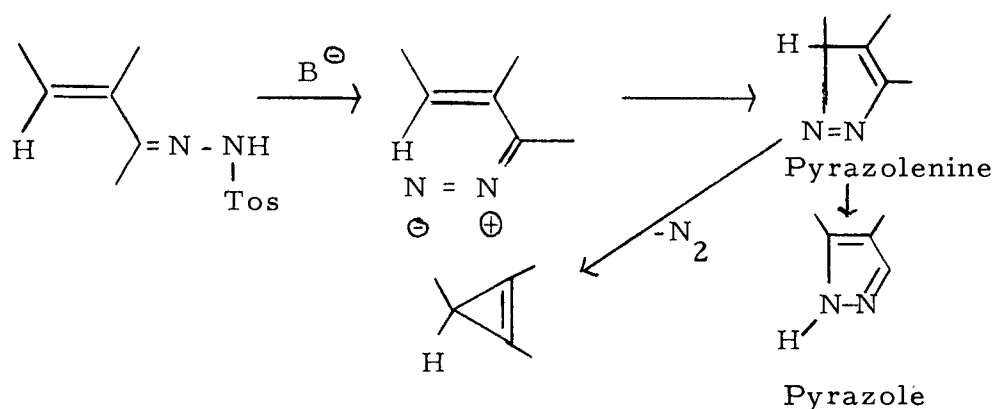
In 1961 Closs and Closs (29) formed cyclopropenes from allylic carbenes by what is formally an intramolecular addition.



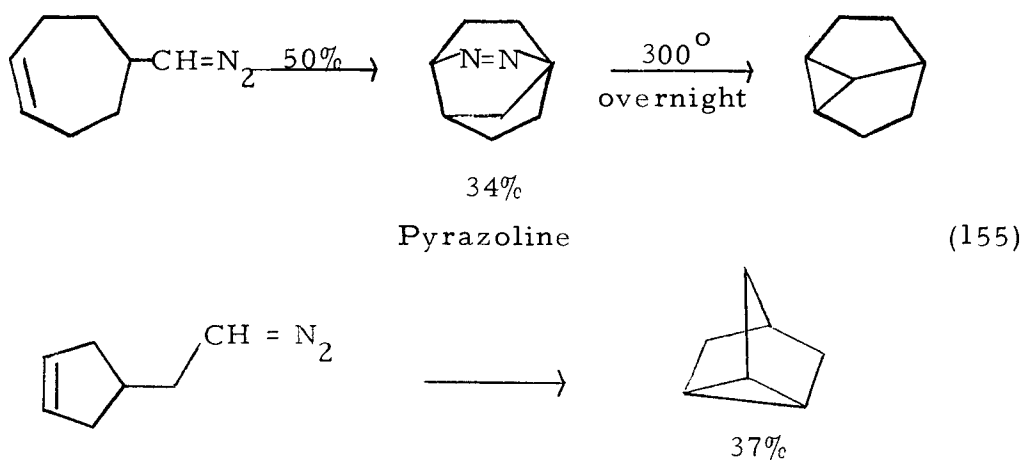
This was not a strict addition for the electrons of the carbene may have overlapped with the double bond. Closs and Closs (27) formed the cyclopropenes by three different carbene routes and correlated the results.



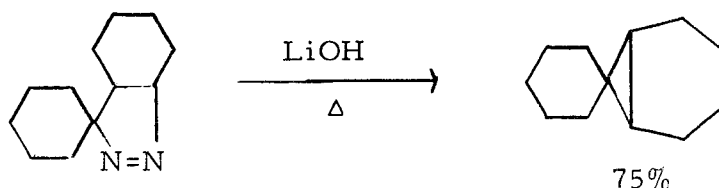
In the tosylhydrazone route the cyclopropene formed has a pyrazolenine precursor rather than a carbene (28). If the pyrazolenine has a  $\beta$ -hydrogen then a stable pyrazole is formed (28, 52).



Cyclopropanes are also formed by intramolecular reactions and seem to go through a pyrazoline intermediate.



Kost and Grandberg (116) demonstrated that the cyclopropane formation was catalyzed by base.



Frey found some intermolecular trapping with low molecular weight diazocompounds (62, 64, 67). Cyclopropylcarbenes generated from gem-dihalides or diazocompounds have been trapped (96, 97, 134). Since then others have reacted carbenes or their precursors with olefins both intermolecularly and intramolecularly (4, 20, 26, 31, 39, 77, 82, 102, 112, 125, 155, 169). The addition is not always successful (123, 175) and depends on the carbene species formed and the conditions of generation. The relation of spin state to stereospecificity in addition reactions has been discussed in great detail without complete agreement.

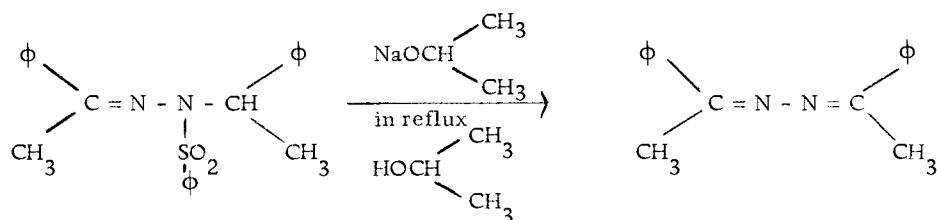
### Other Reactions

Many studies concerning dialkylcarbenes generated from diazo intermediates have not accounted for all of the carbene precursor. The other products which are usually non-hydrocarbons have been seriously neglected.

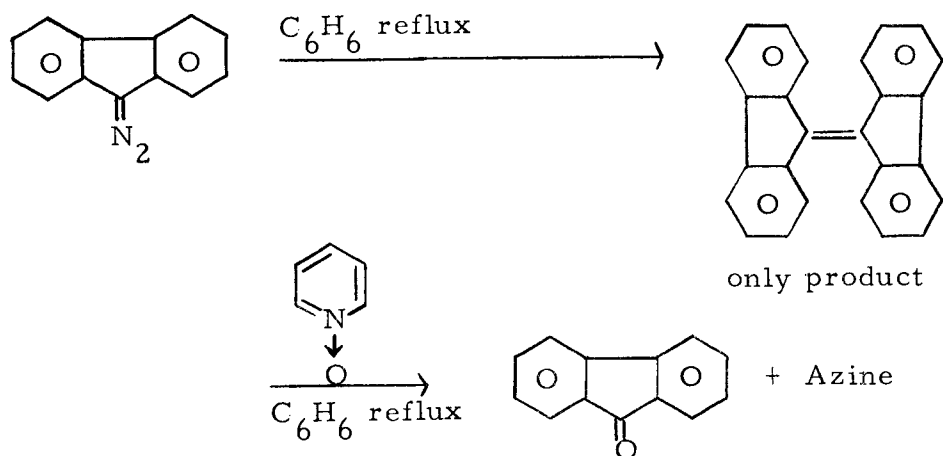
## Azine

In diazo decompositions the azine of the starting material is probably the most common non-hydrocarbon product reported. An azine is almost always found in the decomposition of diaryldiazomethanes (85, 138, 141, 167). Under certain conditions it is the only product. Azines have also been reported in dialkylcarbene reactions where the non-hydrocarbon products were characterized (4, 22, 76, 77, 119, 130, 175).

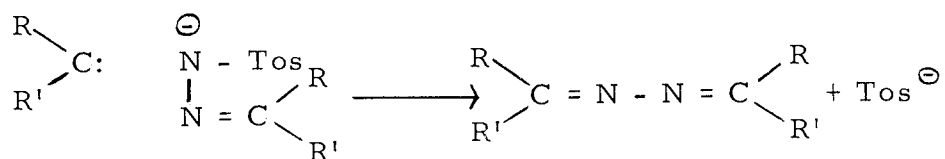
Staudinger and Goldstein (167) found azines in their reaction mixtures as far back as 1916. In 1957 Dornow and Bartsch (52) showed that a product of carbenoid reactions could be converted to an azine by base.



In 1963 Schweitzer and O'Neill (156) provided an interesting example of the formation of azines.



One possible route to an azine is the trapping of the carbene by the sodium salt of the tosylhydrazone (22, 117).

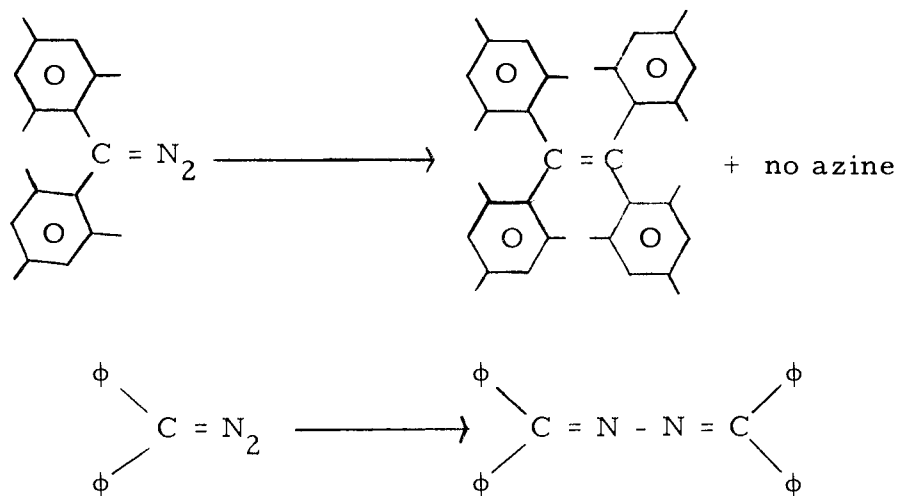


Krapcho and Diamanti (117) provided support for this hypothesis with the following experiments. When the salt was prepared and then heated to  $160^\circ$  in solvent, the azine was obtained in 35% yield; but when sodium hydride was heated to  $160^\circ$  in solvent and the tosylhydrazone added, only 0.6% azine was obtained. They discounted the possibility of the carbene reacting with the diazo-compound, since the diazocompound was supposedly unstable at  $160^\circ$ .

Frey (63) postulated that two diazocompounds reacted together

with loss of nitrogen to form azines. Reimlinger (145) disproved this path in one case by demonstrating that the decomposition of the diazocompound to form azine was first order in nitrogen. In addition, he studied the base catalyzed formation of azine which appeared to be a non-carbenoid process. Azines are also formed by other non-carbenoid processes. One important process is the disproportionation of hydrazone to give azine and hydrazine (6, 86, 122).

Zimmerman and Paskovich (186) demonstrated that dimesityldiazomethane gave no azine whereas diphenyldiazomethane gave azine as the major product.



The sterically hindered carbene can form a dimer; thus pure steric hindrance does not stop azine formation. Zimmerman and Paskovich suggested that sterically hindered carbenes cannot exist

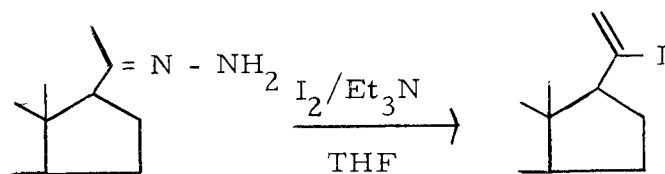
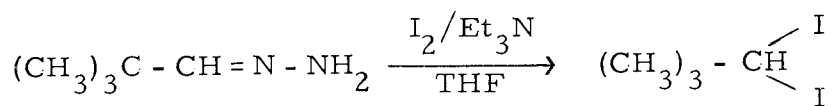
in the singlet spin state. Carbenes in the singlet state are the more electrophilic species (89). Zimmerman and Paskovich concluded that only singlet carbenes form azines. Dimesitylcarbene exists only in the triplet state and thus forms no azine. In summary, azines are probably formed through many pathways, most of which involve a free electrophilic carbene species.

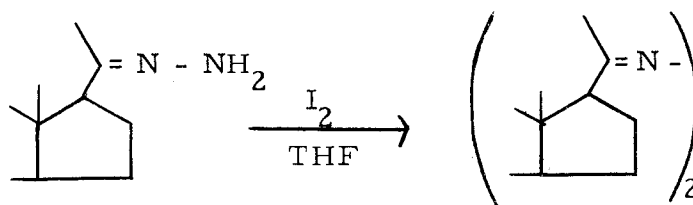
### Diatomic Molecules

Carbenes appear to react with diatomic molecules.

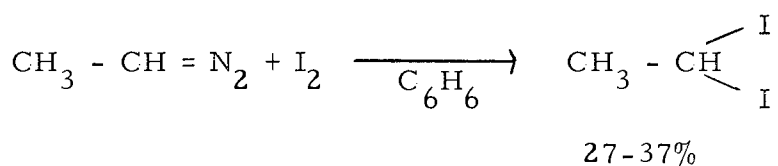


Hellerman and Garner (83) found that iodine catalyzed the decomposition of diazo- $\beta, \beta, \beta$ -triphenylethane. Barton and co-workers (6) found that oxidation of hydrazones in the presence of base yielded gem-diiodides or vinyliodides. In the absence of base the azine was the only product.





Neuman and Rahm (137) recently used the reaction to form gem-diiodides.



Zimmerman and Paskovich (186) showed the reaction of diazocompounds with oxygen took place only while the diazocompound was decomposing presumably to the carbene species. The product of this latter reaction, an aldehyde or ketone, has been reported by others (79, 81, 138, 174, 175). Staudinger (164) allowed the diazocompound to react with various halogens and hydrogen.

### Water

Diazocompounds react with water to give an alcohol plus nitrogen.

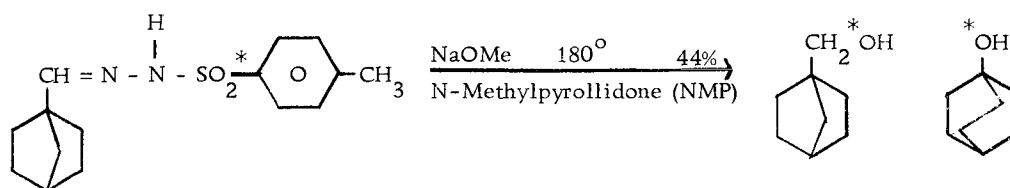


This pathway has been observed by several workers (11, 37, 38, 55, 138, 169, 174). Bethell and Callister (10) showed a change in the kinetics with low water concentrations.

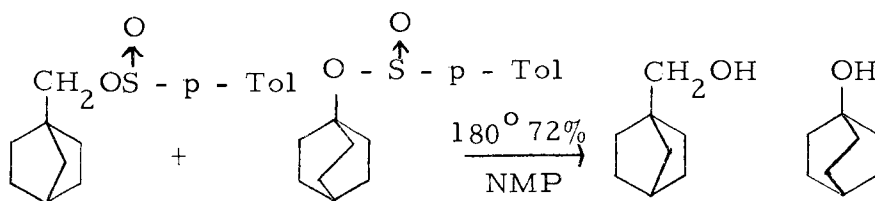
### Sulfinate Esters, Sulfones, and N-alkyltosylhydrazones

Four major papers have been devoted to the non-volatile products in the decomposition of the tosylhydrazone sodium salt. Alcohols, formed by reaction of the diazocompound with water, were also found in anhydrous decompositions of the tosylhydrazone (180).

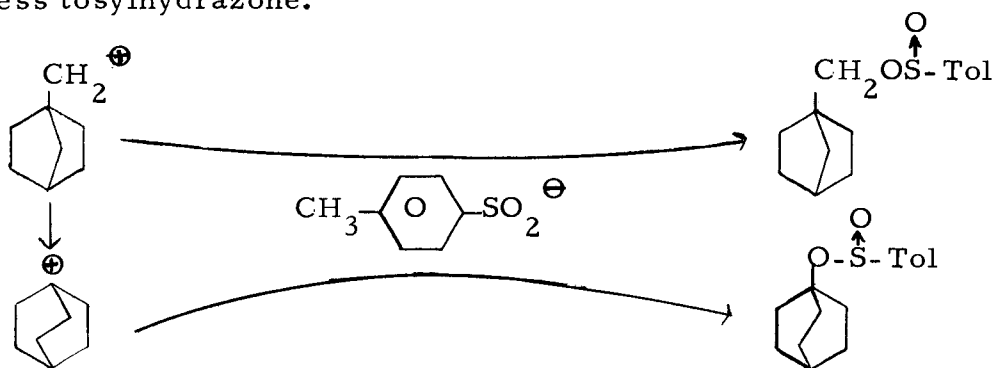
In a recent paper Wilt and co-workers (183) found by labeling techniques that the oxygen of the alcohol came from the sulfonyl oxygen of the tosylhydrazone.



After proving that sulfinate esters were intermediates in these reactions, they demonstrated that the sulfinate ester decomposed to the alcohol under reaction conditions.

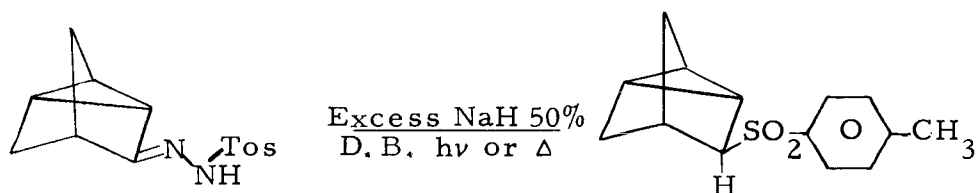


The sulfinate esters were obtained from the reaction of the carbonium ions with the sulfinate anion, the proton source being excess tosylhydrazine.



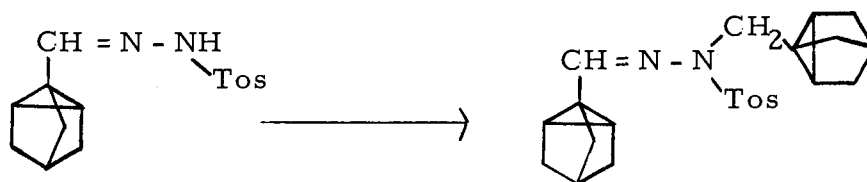
Wilt et al. found no sulfones in these cationic reactions.

Lemal and Fry (119) did extensive work on the formation of sulfones. They reported that as the system became more aprotic the yield of the sulfone increased.

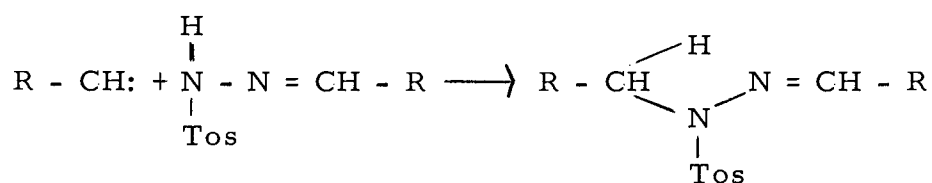


Others have also found sulfones in tosylhydrazone decompositions (5, 76).

Dauben and Willey (38) found sulfur containing products in the decomposition of a tosylhydrazone without base. Dornow and Bartsch (52) found N-alkyltosylhydrazones formed from diazoalkanes and aldehyde tosylhydrazones. Wilt et al. (182) found only one aldehyde which gave this product.



They suggested that it was formed by carbene insertion into the nitrogen-hydrogen bond of the tosylhydrazone.

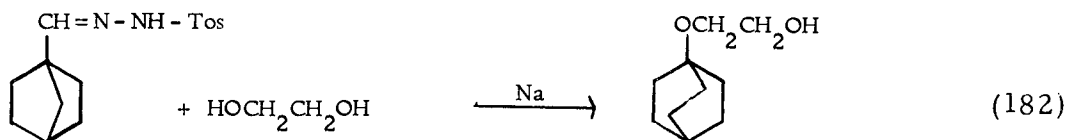
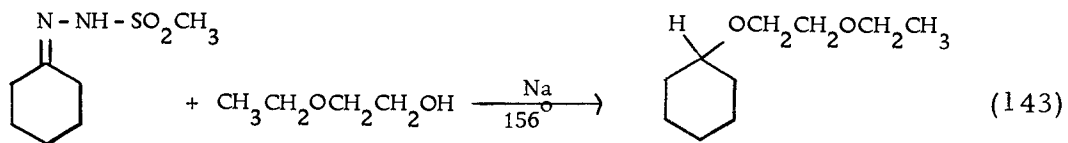
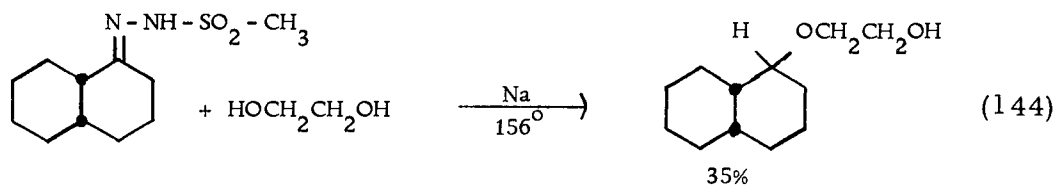


Lemal and Fry (119) traced the formation of this type product to the presence of excess tosylhydrazone. Stechl (169) also identified this type of product.

Nozaki et al. (138) studied the formation of the three above mentioned products in various solvents. The sulfone yield was highest in an ether solvent; the N-alkyltosylhydrazone yield was highest in aromatic solvents and did not form in water.

### Alcohol

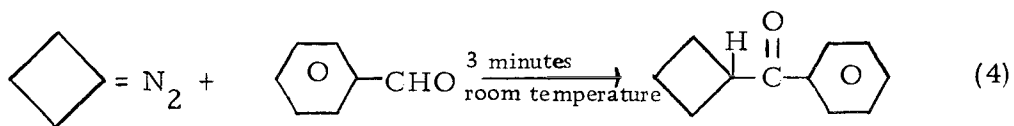
In carbenoid reactions run in alcoholic media (the Bamford and Stevens Reaction) the intermediate was sometimes trapped by the alcohol.



The higher molecular weight alcohols were more reactive than methanol.

### Aldehyde or Ketone

When a diazocompound was added to an aldehyde or ketone, an immediate reaction occurred (151).



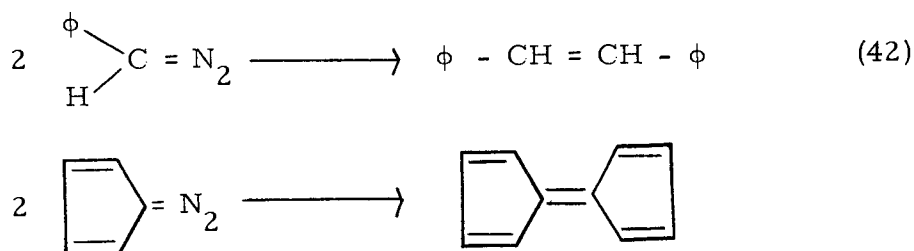


### Acid

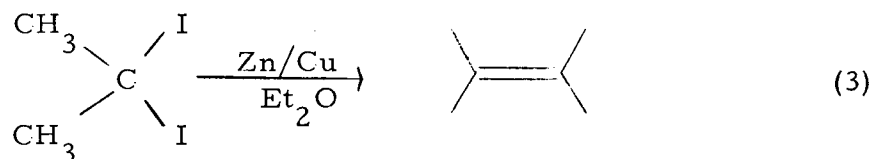
In the decomposition of diazoalkanes the amount of diazoalkane was routinely determined by titrating with acid and measuring the nitrogen evolution or ester formation (53, 131). The reaction has been studied by several workers (4, 33, 83, 95, 164, 168).

### Dimers

Products that appeared to be dimers of carbenes have been detected in aromatic (3, 52, 138, 145) and aliphatic systems (3, 42, 62, 64, 169).



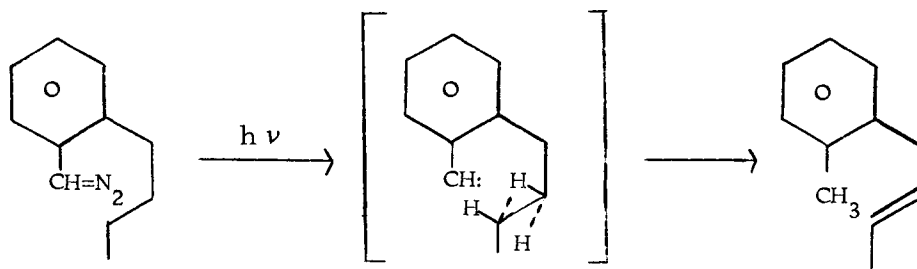
The formation of dimers was aided by catalysts suggesting a preferred spin state (3, 169).



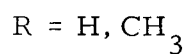
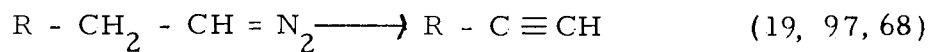
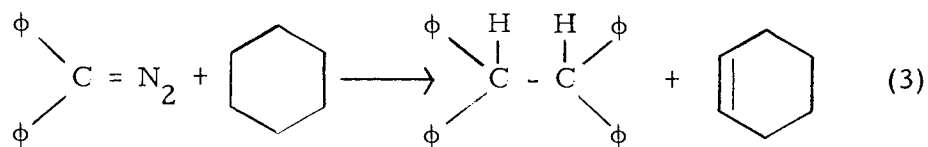
Dimers were produced when the carbenes were stabilized (174), but their formation was subject to solvent effects (138).

### Vincinal Hydrogen Abstraction

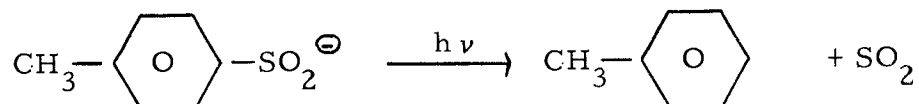
Gutsche and co-workers (79, 80, 81) reported the abstraction of vincinal hydrogens to form an olefin in carbenoid reactions.



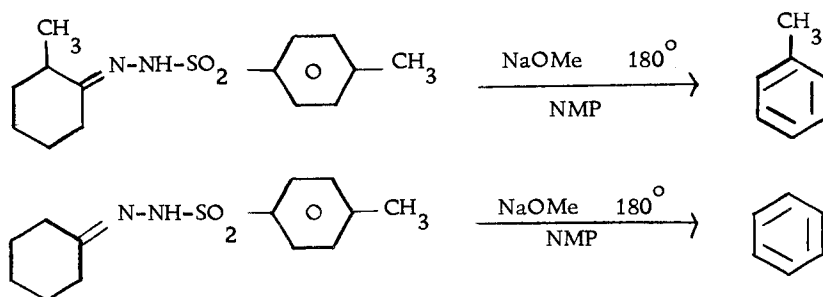
They proposed that the intermediate carbene abstracted the vicinal hydrogens. The loss of hydrogen from two adjacent carbons has been observed in other systems.



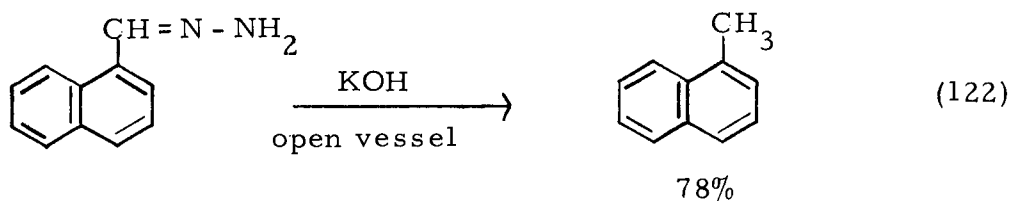
Dauben and Willey (38) found toluene in the photodecomposition of the tosylhydrazone sodium salt of camphor. They suggested that the sulfinate anion decomposed upon irradiation.



Toluene, detected by Wilt and Wagner (181) in the methylcyclohexanone tosylhydrazone system, could be attributed to the sulfinate anion; but the benzene found in the cyclohexanone tosylhydrazone system must be attributed to aromatization of the cyclohexane moiety. These conditions were protic.

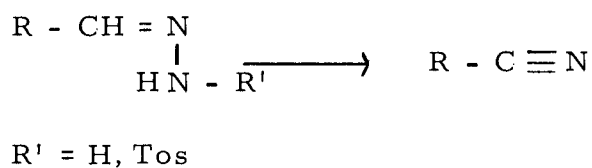


Whether Gutsche and co-worker's results can be interpreted as a new reaction of alkyl- and dialkylcarbenes or merely the standard Wolff-Kishner reduction of aldehyde or ketone hydrazone with base has not been clearly determined.

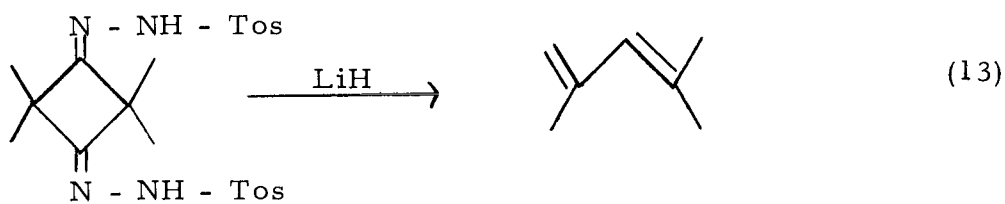


### Nitrile

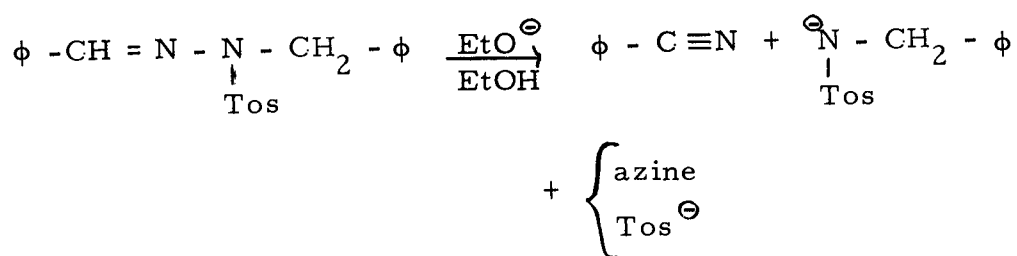
Nitriles have been observed in carbenoid reactions (13, 81, 91).



Bond and Bradway (13) suggested a three step process for the loss of cyanide as a one carbon fragment: fragmentation, elimination, and radical decomposition of a diazosulfone intermediate.



Of related interest is the formation of a nitrile in the basic reaction of N-alkyltosylhydrazones.



### Sulfur Dioxide and Phosgene





Staudinger and co-workers formed adducts with  $\text{SO}_2$  (168) and  $\text{COCl}_2$  (165) in the decomposition of diazocompounds.

### Areas of Research Interest

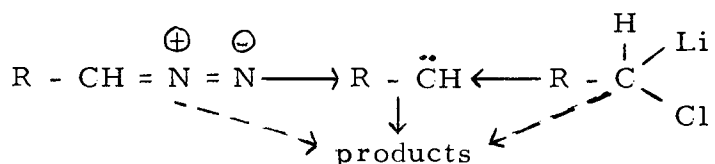
#### Mode of Generation

In spite of widespread study many problems concerning alkyl- and dialkylcarbenes remain to be solved. Table VII shows the various product compositions which result from different modes of generation of ethylmethylcarbene.

Table VII. Comparison of Modes of Generation

Carbene Precursor					Reference
$  \begin{array}{c}  \text{CH}_3 - \text{CH}_2 - \underset{\text{H}}{\underset{ }{\text{C}}} - \text{CH}_3 \\  \text{Ts} - \underset{ }{\text{N}} - \text{N} \\  \text{H}  \end{array}  \xrightarrow[\Delta]{\text{NaOMe}}  $	5%	67%	28%	0.5%	(73)
$  \begin{array}{c}  \text{CH}_3 - \text{CH}_2 - \underset{\text{N}=\text{N}}{\underset{ }{\text{C}}} - \text{CH}_3 \\  \text{N}=\text{N}  \end{array}  \xrightarrow[\text{h}\nu]{\Delta}  $	4%	67%	29%	0.4%	(66)
	23%	38%	36%	2.4%	(66)
$  \begin{array}{c}  \text{CH}_3 - \text{CH}_2 - \underset{\text{Br}}{\underset{ }{\text{C}}} - \text{CH}_3 \\  \text{Br}  \end{array}  \xrightarrow{\text{MeLi}}  $	1%	74%	25%	-	(106, p. 55)

The highly reactive carbene precursors, such as the diazo-compound or the chlorolithium intermediate, could conceivably give rise to the isolated products directly.

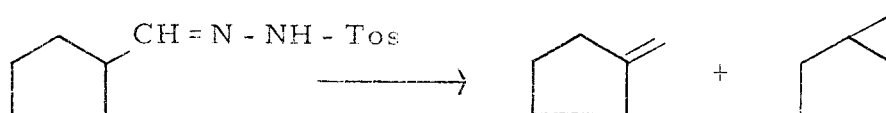


The actual existence of a free carbene species has not been demonstrated unequivocally. Even if the free carbene species is formed, the mode of generation may change its spin multiplicity and vibrational excitation (possibly explaining the photochemical results in Table VII).

The problems implicit in the various methods used for carbene formation will be discussed first.

#### p-Toluenesulfonylhydrazones

Decomposition of sodium salts of tosylhydrazones has become the most used method for dialkylcarbene studies. The method of preparing the sodium salt affects the products of the decomposition. In one decomposition the major hydrocarbon products were reversed.

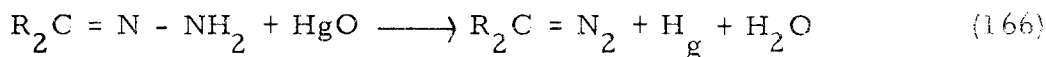


When the tosylhydrazone was added to sodium methoxide in refluxing diglyme, the major product (73%) was the cyclopropane (114). When the dry sodium salt was decomposed without solvent, the major product (65%) was the olefin (14).

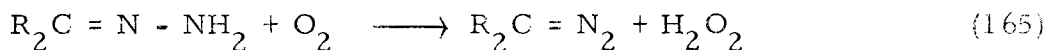
Understanding the effect that changing reaction conditions have on product composition would allow greater synthetic utility of carbene reactions.

### Hydrazones

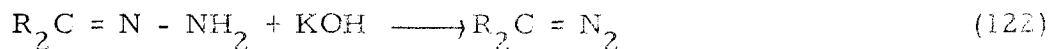
One mode used to generate carbenes is the oxidation of hydrazones. Staudinger et al. did some preliminary work in this area (164, 165, 166, 167, 168). They used several oxidants, but mercuric oxide gave the best results.



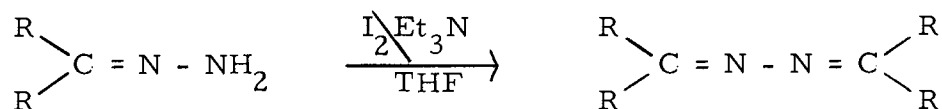
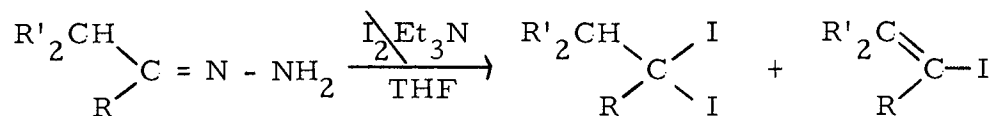
R = H, alkyl



Mercuric oxide has subsequently been used by others (42, 81, 112, 128, 184). Other oxidizing agents have been used with varying success.

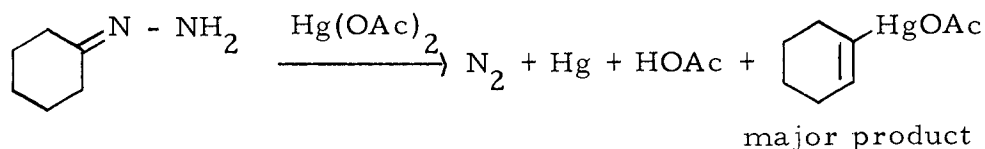






Reusch et al. (24, 146) found the hydrocarbon products of the oxidation with HgO to be solvent independent. Schroeder and Katz (154), on the contrary, show solvent effects with yellow HgO but show none with Ag<sub>2</sub>O.

Certain mercury oxidants lead to many types of organomercury compounds (136).



Temperature

To preserve the integrity of heat sensitive molecules, lowering the temperature of decomposition of the tosylhydrazone would be desirable. However, lowering the temperature may change the product composition. Whiting and co-workers (24, 143) have studied temperature effects in the camphor hydrazone and tosylhydrazone decompositions. They found an increase in temperature increased the yield of tricyclene. Zimmerman and Paskovich (186) observed


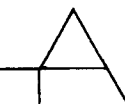


an increase in dimer products with a decrease in temperature.

Farnum (55) attempted to lower the temperature of tosylhydrazone decompositions by changing the leaving group. He observed no significant effect suggesting that the stability of the forming diazocompound determines the temperature of decomposition.

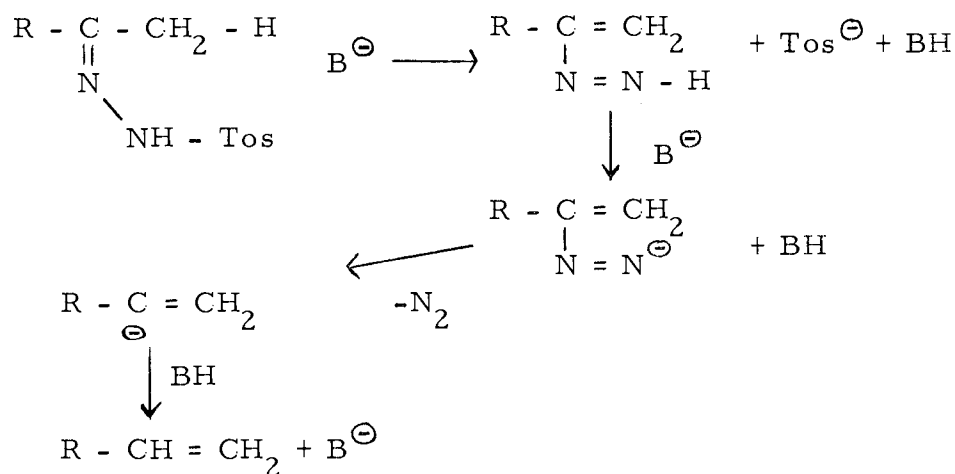
### Base

Several important papers have recently been published on the effect of base in tosylhydrazone decompositions. Kirmse et al. (109) published the results in Table VIII.

Table VIII. Effect of Different Bases





$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3 - \text{C} - \text{C} = \text{N} - \text{N} - \text{Ts} \\   \quad \quad \quad \backslash \\ \text{CH}_3 \quad \quad \quad \text{CH}_3 \end{array}$				
Na glycol in glycol	6%	2%	56%	36%
NaOMe in diglyme	41%	52%	4%	3%
LiH in decalin	39%	40%	13%	8%
NaH in decalin	80%	18%	1%	1%
NaNH <sub>2</sub> in decalin	100%	-	-	-

They then proposed that reactions involving NaH or NaNH<sub>2</sub> as the base do not proceed through a carbene but through a carbanion alternative.



Smith, Shechter, Bayless, and Friedman (163) varied the amount of NaOMe and found the striking results abstracted in Table IX.

Table IX. Effect of Base Concentration<sup>\*</sup>

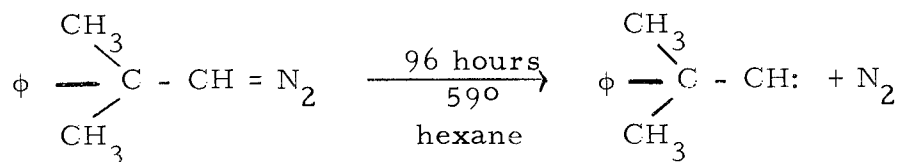
 CH = N - NH - Tos	Equivalents of NaOMe	Hydrocarbon Yield				HC≡CH	H <sub>2</sub> C = CH <sub>2</sub>
	1.8	89%	41%	39%	3%	8%	9%
	1.1	85%	83%		3%	5%	5%
	1.1	80%	85%	3%	2%	4%	4%
	1.0	95%	82%	3%		5%	5%
	0.8	55%	26%	6%	57%	4%	7%

<sup>\*</sup>Decomposed in purified Diethyl Carbitol at 180°

In excess base, fragmentations were important; and in excess tosylhydrazone the non-hydrocarbon products were appreciable. To obtain the free carbene one must use equimolar amounts of base and tosylhydrazone.

### Rate of Decomposition

Diazocompounds decompose at extremely different rates. Diazomethane and diazoethane have been known to explode. Farnum (55) accelerated the diazocompound decomposition with an acid or base, but the reaction presumably proceeds through a non-carbenic pathway. The time required for the uncatalyzed decomposition through a carbene intermediate is a very important consideration. In one case a purified diazocompound required 96 hours to decompose (142).



The formation of carbenes may be an exceedingly slow process.

### Solvent

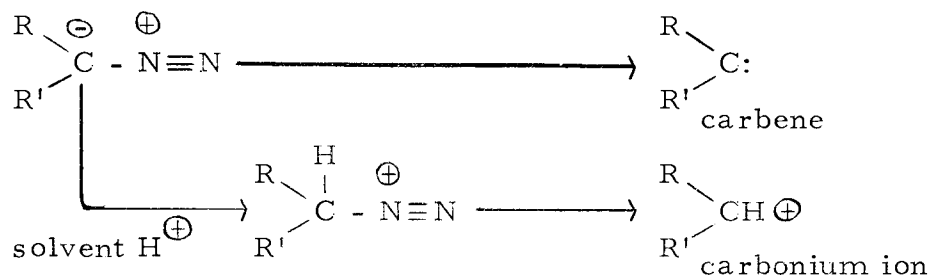
The diphenyldiazomethane decomposition illustrates the amazing effect solvent has on the products in carbenoid reactions

(Table X).

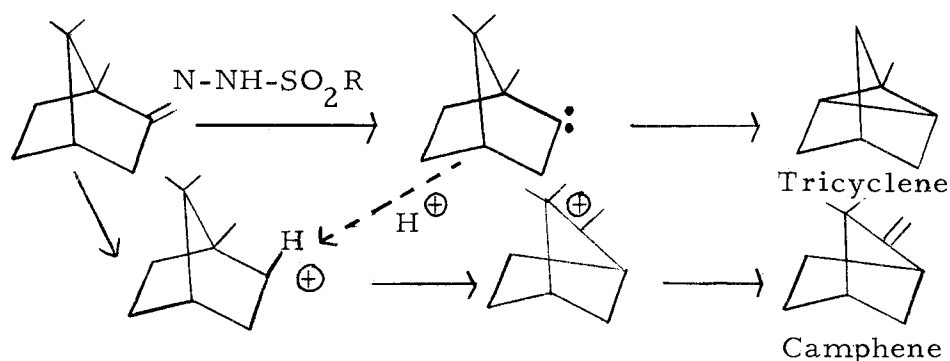
Table X. Solvent Effects on Diphenyldiazomethane Decomposition

Solvent	Yield N <sub>2</sub>	$\begin{array}{c} \phi \\ \diagdown \\ \text{C} = \text{N} - \text{N} = \text{C} \\ \diagup \\ \phi \end{array}$	$\begin{array}{c} \phi \\ \diagdown \\ \text{CH} - \text{CH} \\ \diagup \quad \diagdown \\ \phi \quad \phi \end{array}$	Reference
Benzene	75 %	45 %	negligible	(113)
Benzene 80°		74 %	none	(141)
Cyclohexane	80 %	21 %	29 %	(113)
Pet Ether 120°		23 %	23 %	(141)
Toluene	87 %	13 %	35 %	(113)
Cyclohexene	100 %	negligible	40 %	(113)

Probably the most serious difficulty in decomposing the diazo-compound to the carbene is the competition of decomposition to the corresponding carbonium ion in the presence of a proton source. The reaction of the diazocompound with a proton is very rapid (4, 95).



In 1959 Powell and Whiting (143) used the camphor system to distinguish between carbonium ion and carbene intermediates. The products in this system were thought to be indicative of the intermediate.



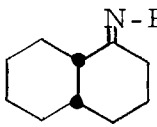
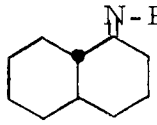
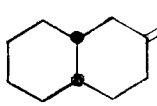
As the medium became less protic, the ratio of tricyclene to camphene became larger. Diazocamphor has special features, however, which may make protonation difficult. Apparently tricyclene can form in 99-100% yield in weakly protonating solvents such as acetamide.

Dauben and Willey (38) also worked with camphor tosylhydrazide and reported results similar to Powell and Whiting's. Note in Tables XI and XII, as well as Table IX, that as the conditions became more protic the hydrocarbon fraction decreased. Since the remainder of the diazocompound which has been converted to the carbonium ion by the solvent is trapped by the nucleophile present, the total yield remains constant.

Table XI. Solvent Effects on Hydrocarbon Yield in the Camphor System

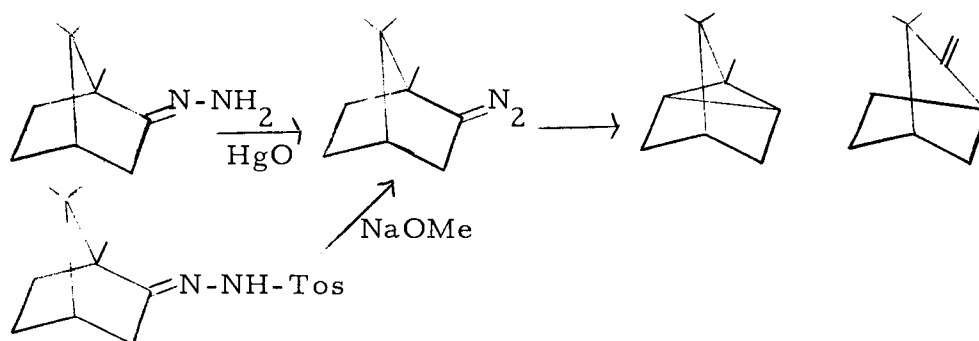
Solvent	Light source	Yield hydrocarbon	Other	% Tricyclene	% Camphene
aqueous 0. 1N KOH	filtered	8%	alcohols	18	82
	unfiltered	trace			
MeOH 0. 1N KOH	filtered	44 %	Me ethers	36	64
	unfiltered	36 %		20	80
diglyme 0. 1N NaOMe	filtered	70 %		87	13
	unfiltered	93 %		99	1

Table XII. Solvent Effects on Hydrocarbon Yield in the Decalin System

Substrate	Solvent	% Yield Hydrocarbon	%Yield Total
	acetamide	67	67
	ethylene glycol	26	61
	acetamide	72	72
	ethylene glycol	36	70
	ethylene glycol	43	71

\* R = NH - SO<sub>2</sub> CH<sub>3</sub>

Clark, Whiting, Papenmeier, and Reusch (24) compared the hydrazone oxidation with the tosylhydrazone decomposition again using the camphor system.



Their results are reported in Table XIII.

Table XIII. Solvent Effects of Hydrazone Oxidation and Tosylhydrazone Decomposition

Solvent	Temperature	% Tricyclene	
		Hydrazone	Tosylhydrazone
$\text{CH}_3\text{CH}_2\text{OH}$	79	75	
	138		86
$\text{CF}_3\text{CH}_2\text{OH}$	76	13	
$\text{HOCH}_2\text{CH}_2\text{OH}$	138	57	
	138		25
$\text{HOCH}_2\text{CH}_2\text{CH}_2\text{OH}$	80	75	
	132		46
$\text{CH}_3\text{OCH}_2\text{CH}_2\text{OH}$	80	62	
$\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}$	132		92
$\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_3$	81	98	




These authors felt that the  $\text{HgO}$  oxidation was insensitive to solvent effects since the solvents used were not strongly protonating. The only exception was trifluoroethanol. The tosylhydrazone was very sensitive to the protonating solvent. The decomposition of the

intermediate diazocompound was catalyzed by HgO as evidenced by the ethylene glycol to ethanol ratio which was 1.5 for the hydrazone and 18 for the tosylhydrazone.

For many years it was felt that the formation of cyclopropanes indicated a carbene intermediate. This feeling has greatly prejudiced the workers in the dialkylcarbene field until recently. Now several papers have clearly established that carbonium ions give cyclopropanes under certain conditions, that is, the conditions of carbenoid decompositions (8, 33, 75). Cations in aprotic media have enhanced reactivity which reflects decreased solvating character of the media (101).

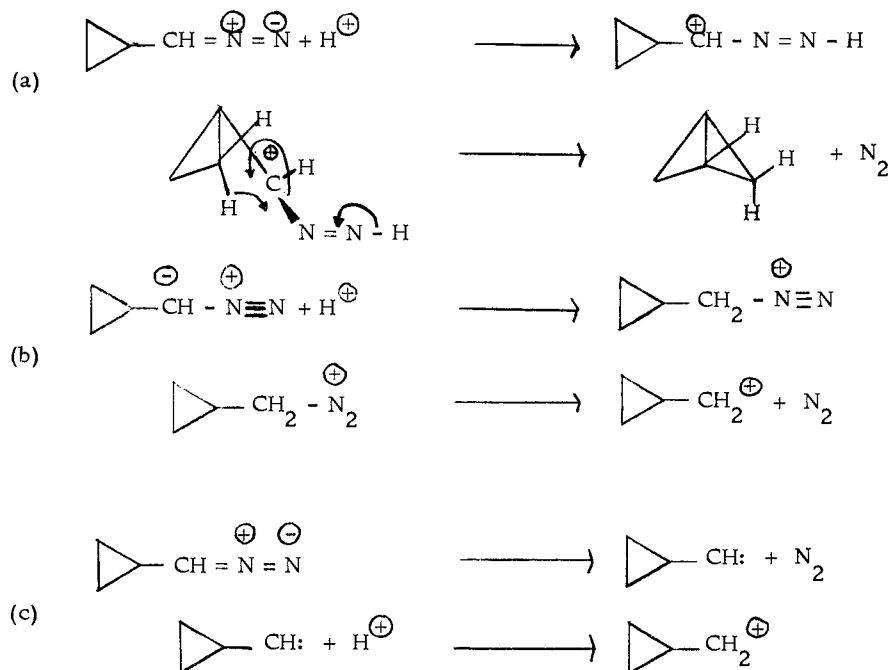
From the paper by Smith, Shechter, Bayless, and Friedman (163) the startling results in Table XIV were reported for the decomposition of the cyclopropane carboxaldehydetosylhydrazone.

Table XIV. Cyclopropanecarboxaldehyde Tosylhydrazone

Solvent	eq. of NaOMe	Yield of N <sub>2</sub>				HC≡CH	H <sub>2</sub> C = CH <sub>2</sub>
Diethyl Carbitol	1.0	95 %	82 %	3 %		5 %	5 %
Diethyl Carbitol	0.8	55 %	26 %	6 %	57%	4%	7 %
Using the isolated salt							
Diethyl Carbitol (a)	1.0	62-71%	34 %	32 %	16%	8 %	7 %
Diethyl Carbitol (b)	1.0	76 %	50 %	3 %	34%	4%	10 %
Diethyl Carbitol (c)	1.0	68 %	28 %	8 %	64%		
Ethylene glycol	1.0	53 %	15 %	6 %	74%		
Pyrolysis (80 mm.)	1.0	60 %	62 %	38 %			
Pyrolysis (760 mm.)	1.0	100 %	33-0 %	44-100 %		0-10 %	0-13%

(a) plus one MeOH of crystallization (b) plus 1.25% water added  
(c) plus 10% ethylene glycol added

The cyclopropane, bicyclobutane, appears to arise only in the presence of a proton source such as water, methanol, tosylhydrazone, and p-toluenesulfonic acid. The deamination of cyclopropylcarbinylamine with amyl nitrite in acetic acid gave bicyclobutane as 97% of the hydrocarbon product (9). Several protonating paths have been proposed for the tosylhydrazone decomposition.


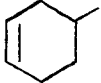




Wiberg and Lavanish (177) demonstrated that the (b) pathway was inconsistent with the results of labeling experiments.

## General Interest

Of general theoretical interest is knowledge concerning the selectivity of dialkylcarbenes. Methylene is known to be non-selective in the liquid phase inserting at every collision (39).

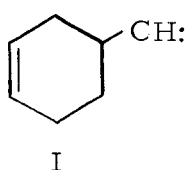
Table XV. Non-selective Methylene Insertion

$\text{CH}_2 = \overset{\oplus}{\text{N}} = \overset{\ominus}{\text{N}}$	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	$\text{C}_4\text{H}_9 - \underset{\text{CH}_3}{\underset{ }{\text{CH}_2}}$ 48%	$\text{C}_3\text{H}_7 - \underset{\text{CH}_3}{\underset{ }{\text{CH}}} - \text{CH}_3$ 35%	$\text{C}_2\text{H}_5\underset{\text{CH}_3}{\underset{ }{\text{CH}}}\text{C}_2\text{H}_5$ 17%
$h\nu @ 25^\circ$ or $-75^\circ$		26% 	26% 	11% 

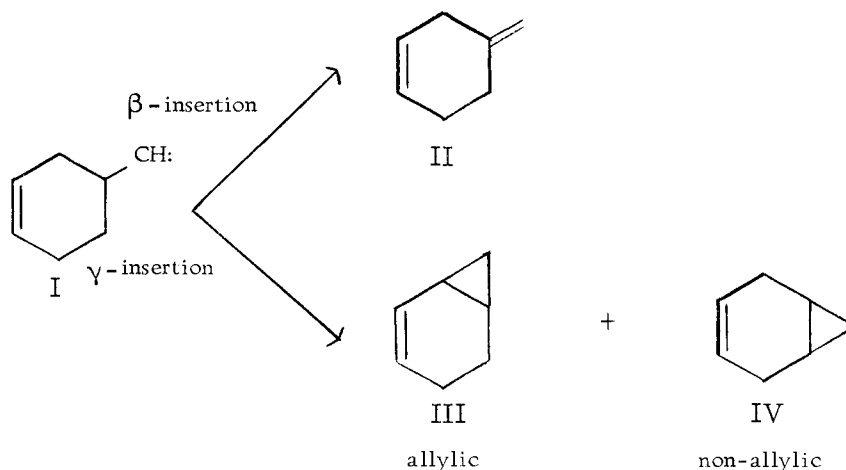
Dihalocarbene electrophilic strength can be measured by trapping with various olefins of differing nucleophilic strength. Trapping of dialkylcarbenes is rare and is usually observed only with carbenes formed by  $\alpha$ -elimination. If dialkylcarbenes could be trapped, then their relative stability could be measured.

## RESULTS AND DISCUSSION

In order to study the formation of carbenes and to understand how reaction conditions influence the product composition, the 3-cyclohexenyl carbinyl system, I, was chosen for investigation.



Preliminary studies by Dr. Judson P. McClure (126) indicated that the predominant pathway for decomposition involved  $\beta$ -insertion, but that both  $\gamma$ -insertion products were formed in small amounts.



The products were identified by their spectral (IR, NMR) properties; and, in the case of the cyclopropane derivatives, by synthesis via Simmons-Smith treatment of the appropriate cyclohexadiene. The

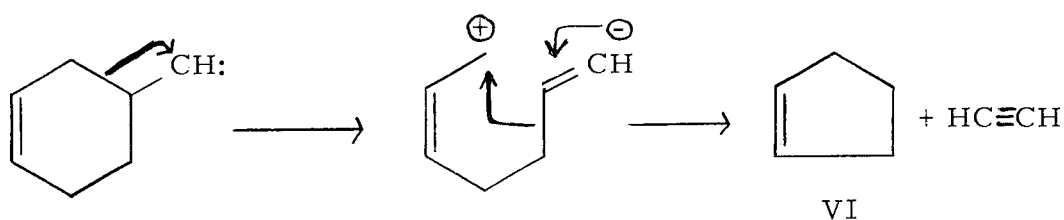
yield and nature of the hydrocarbon products appeared to fluctuate randomly. As many as twelve additional compounds could be detected by gas chromatographic analysis. Thus, carbene I seemed to offer the advantage of a system in which other types of carbene reactions might be observed.

### Rearrangement

Migration (ring expansion)

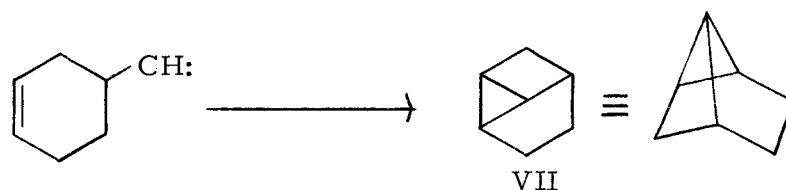


### Fragmentation

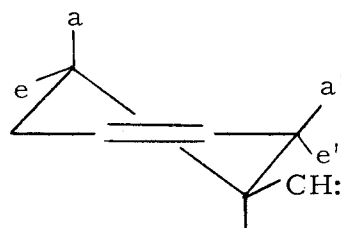


### Addition

## Intramolecular

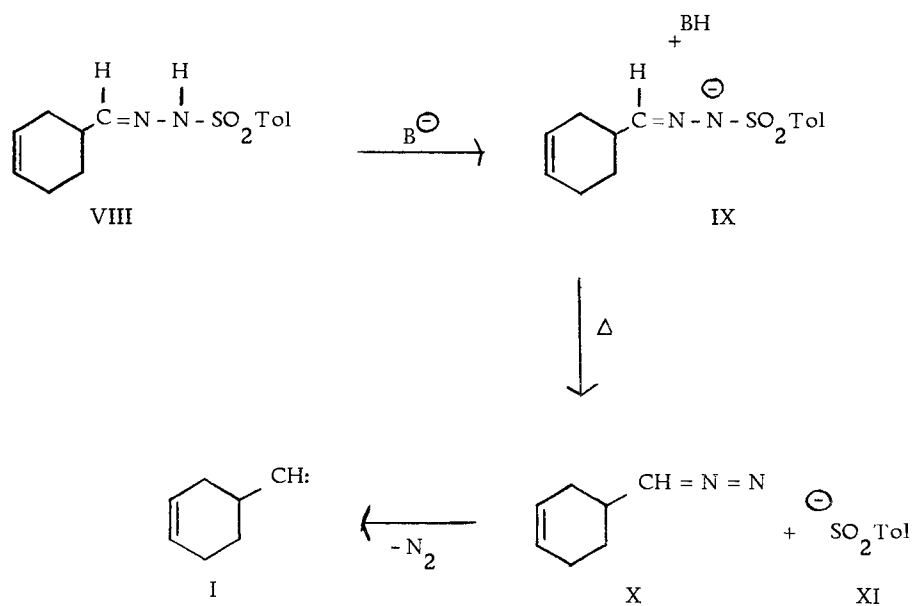


Conformational factors influencing these reactions could also be investigated.



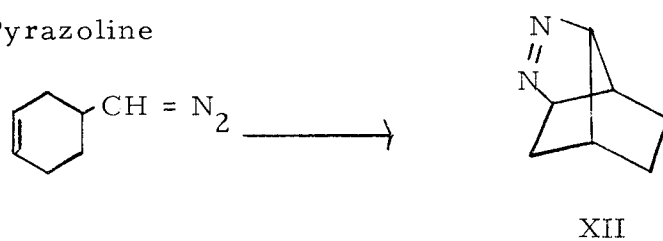
If the cyclohexene ring exists in the half-chair conformation and the carbene carbon is in an equatorial position then the dihedral angle between the carbene and the allylic hydrogen ( $\text{a}'$ ) will be about  $30^\circ$  and the non-allylic hydrogen ( $\text{a}$ ) will be about  $60^\circ$ .  $\gamma$ -Insertion into the allylic carbon-hydrogen bond would be preferred since the angle is smaller. This insertion might also be preferred since the allylic hydrogen is more acidic.

Initial efforts were centered around the p-toluenesulfonylhydrazone (tosylhydrazone) route to carbene I.

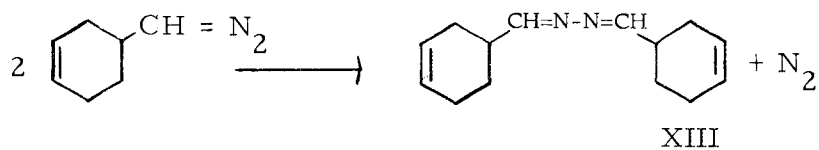


In these reactions the intermediacy of the diazocompound X raises the possibility of other reactions, including pyrazoline and azine formation.

Pyrazoline



Azine



Using the carbene system I also permitted investigation of the effects of such variables as base, temperature, solvent, rate of decomposition, and mode of generation.

#### Tosylhydrazone Route to 3-Cyclohexenyl Carbinyl Carbene

In the tosylhydrazone investigations it was considered desirable to remove the products at the lowest possible temperature because of their potentially unstable nature. Preliminary studies showed that the solvent free decomposition of the dry salt IX was achieved at approximately 80<sup>o</sup>. This procedure also eliminated the possibility of the intermediate reacting with the ether solvent. At the same time it was recognized that such a technique increased the possibility of intermolecular reactions.

When the reactions were conducted under high vacuum, the red-orange diazocompound X was distilled. It was characterized by a 2040 cm.<sup>-1</sup> absorption band in the infrared region. The diazocompound, if allowed to decompose at room temperature (30 hours), forms mostly the azine XIII (see #1, Table XVI). The azine was identified by comparison of its spectral properties (IR, NMR, UV) with an authentic sample prepared by the addition of hydrazine hydrate to excess aldehyde.

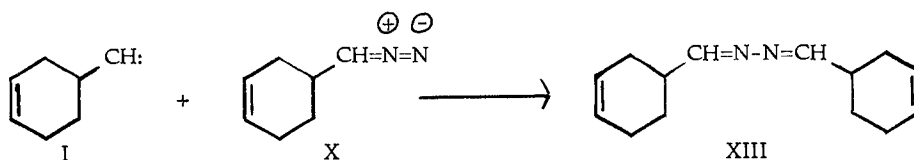
Table XVI. Stoichiometry of Tosylhydrazone Decompositions

Decomposition Number	Description	Temperature and Pressure	Yield of Volatiles	Total Yield <sup>(d)</sup>	
				Hydrocarbons	Azine XIII
1	Diazo 25 <sup>o(a, e)</sup>	84 <sup>o</sup> 1 mm.	66%	0.5%	86%
2	Diazo 25 <sup>o(a, e)</sup>	84 <sup>o</sup> 1 mm.	60%	0.9%	81%
3	Diazo 55 <sup>o(b, e)</sup>	84 <sup>o</sup> 1 mm.	63%	28 %	51%
4	no added diethylene glycol <sup>(c, e)</sup>	108 <sup>o</sup> 25 mm.	33%	33 %	39%
5	1 equivalents diethylene glycol	128 <sup>o</sup> 25 mm.	27%	27 %	48%
6	2 equivalents diethylene glycol	134 <sup>o</sup> 25 mm.	31%	31 %	38%
7	Bamford and Stevens conditions	130 <sup>o</sup> 25 mm.	28%	28 %	25%
8	Temperature 90 <sup>o(d)</sup>	90 <sup>o</sup> 25 mm.	32%		
9	Temperature 130 <sup>o</sup>	130 <sup>o</sup> 25 mm.	35%		
10	Temperature 160 <sup>o</sup>	160 <sup>o</sup> 25 mm.	49%		

(a) collected diazocompound (X) decomposed at 25<sup>o</sup>/760 mm. (b) collected diazocompound (X) decomposed at 55<sup>o</sup>/760 mm. (c) In #4, #5 and #6 three portions of the same salt were used. (d) In #8, #9, #10 three portions of the same salt were used. (e) also found as sulfur containing product.



In the presence of the high concentration of diazocompound the carbene I was trapped when formed.








When the temperature was raised to  $55^\circ$ , approximately one-half the diazocompound formed hydrocarbons. The volatiles were analyzed by gas chromatography, and the results are reported in Table XVII. The major product was from  $\beta$ -insertion, and both minor  $\gamma$ -insertion products were observed. The ratio of  $\beta$ - to  $\gamma$ -insertion was 19.8 showing the carbene species' large preference for  $\beta$ -insertion into a tertiary carbon-hydrogen bond. The ratio of allylic to non-allylic  $\gamma$ -insertion was 8.4 which is slightly larger than would be expected for the large angle difference. Apparently the allylic character of the hydrogen is not too significant.

Some minor hydrocarbon products in the above reactions were traced to the presence of methanol. Methanol was extremely

difficult to remove from the salt IX. After heating the salt IX for 5 hours at 50° (1 mm.) the methanol still remained.

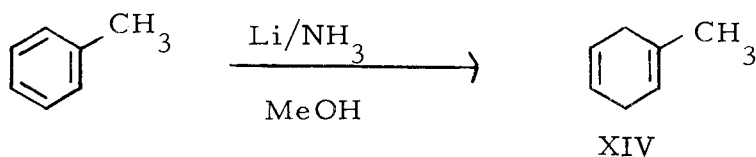
Table XVII. Hydrocarbon Composition Under Tosylhydrazide "Carbene" Conditions

					XVII Other Products
93.0%	4.2%	0.5%	2.2%	trace	0.1% none

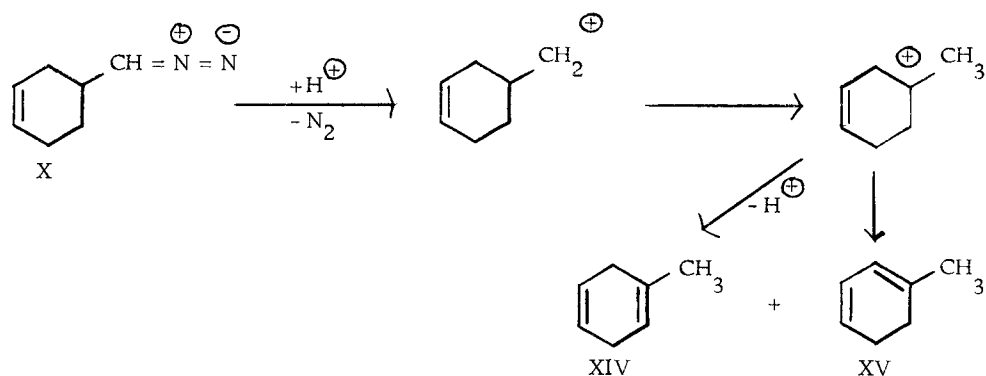
The more usual conditions for the formation of I involved decomposition at ca. 25 mm. Here the diazocompound X was distilled in varying amounts depending on the temperature of decomposition. Its presence was shown by the red-orange color, but its significance was not fully appreciated at first. Having methanol and diazocompound together in varying amounts led to volatile compositions which were unreproducible. To eliminate one variable high vacuum was used which gave the diazocompound without hydrocarbons in approximately 65% yield. As mentioned previously, the diazocompound when decomposed gave mostly azine and for the first time the product composition could be completely reproduced (see #1, #2 in Table XVI).

Since the second variable, methanol, was difficult to eliminate, further investigation of the hydrocarbons formed in the presence of

methanol was initiated. In the diazo decomposition at 55° (see #3, Table XVI) the presence of 1-methyl-1,4-cyclohexadiene (XIV) was confirmed by collection and comparison of its physical properties (IR, NMR) with an authentic sample prepared by Birch reduction of toluene.

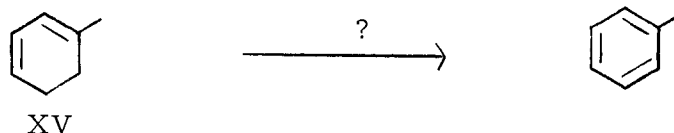


The origin of this compound is somewhat dubious. It could be formed from the carbonium ion pathway shown below.



If this pathway is correct, one would expect the conjugated diene XV to also be present although it was not detected. Fleischacker and Wood (195) found toluene in attempting to prepare 1-methyl-1,3-cyclohexadiene (XV) by cyclization of the appropriate conjugated

heptatriene. Possibly the diene XV was converted to toluene under the conditions for decomposing the diazocompound X.



The presence of toluene (XVI) was confirmed by coinjection and by collection and comparison of its properties with an authentic sample.

One other compound (XVII) which was not identified was observed in the above reaction. It was also present in the Bamford and Stevens reaction which will be discussed later. Since compound XVII had a short retention time, it may have been a fragmentation product but was shown not to be cyclopentene (VI).

A proton source was necessary if the carbonium ion pathway shown previously was to be operative. Apparently the methanol present was a strong enough acid to protonate the diazocompound. An alcohol was deliberately added to the salt IX to observe its effects on the hydrocarbon products. Figure I shows a striking change in volatile composition between no added alcohol, two equivalents of added diethylene glycol, and using diethylene glycol as the solvent (Bamford and Stevens conditions). The percentage composition of the volatiles for these reactions is reported in Table XVIII (#4, #5, #6, and #7).

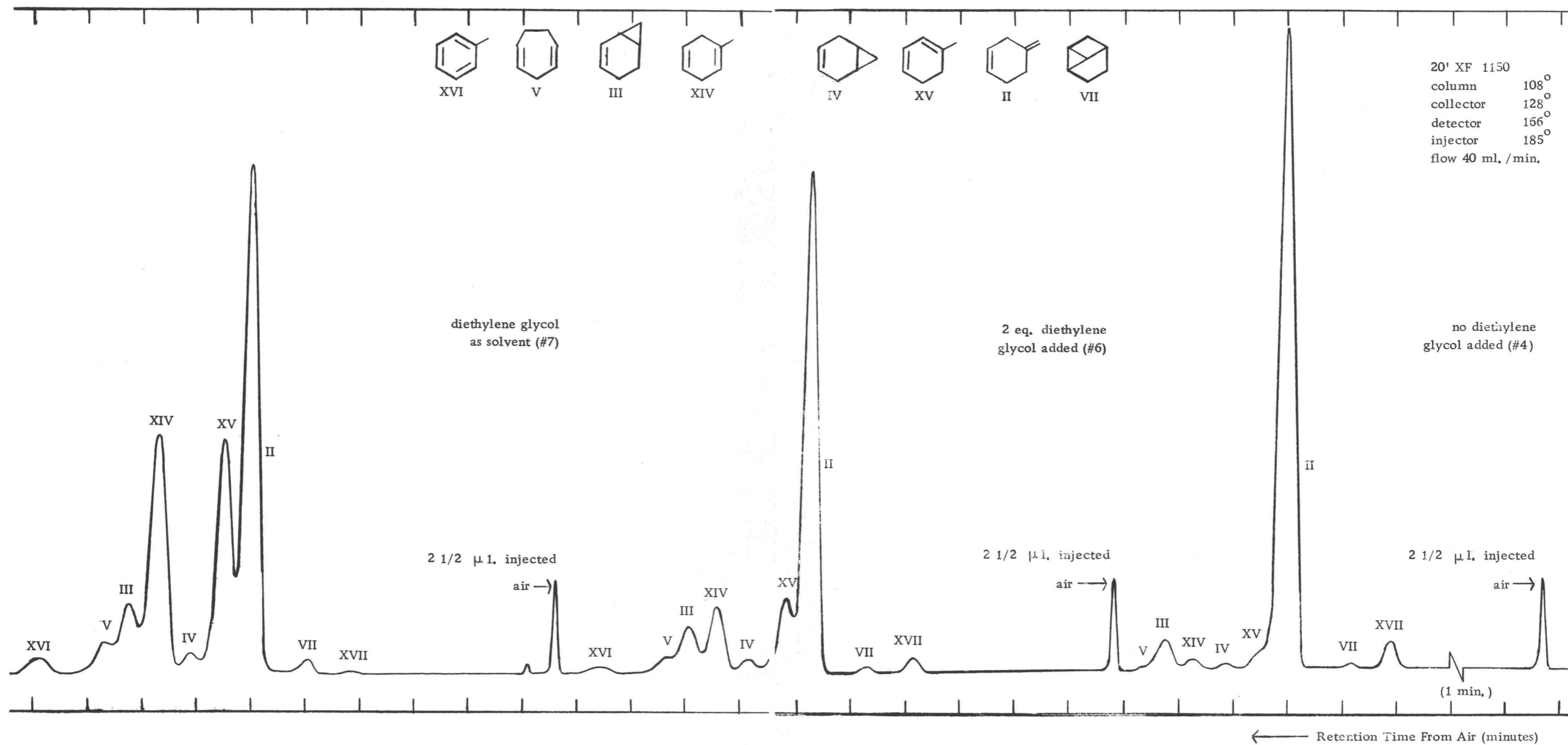










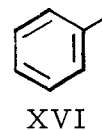
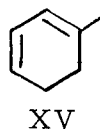
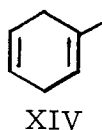
Figure 1. Gas Chromatogram of the Effect of Alcohol on the Tosylhydrazone Decomposition

Table XVIII. Tosylhydrazone Hydrocarbon Composition

Decomposition Number	Description	XVII	VII 	II 	XV 	IV 	XIV 	III 	V 	XVI 	other products
3	Diazo 55°	0.1%		93.0%		0.5%	2.2%	4.2%		trace	
4	no alcohol added	4.5%	0.5%	73.5%	7.6%	1.9%	4.2%	6.0%	1.4%	0.5%	3 trace
5	1 eq. alcohol	1.0%	1.0%	57.5%	13.6%	2.7%	12.4%	8.0%	2.4%	1.2%	3 trace
6	2 eq. alcohol	2.0%	1.3%	54.6%	12.6%	3.0%	13.4%	8.5%	3.2%	1.7%	3 trace
7	Bamford and Stevens	0.4%	1.7%	39.0%	17.9%	2.4%	22.8%	10.0%	3.8%	2.4%	1 trace
8	Temperature 90°	0.5%		92.6%	trace	0.8%	1.3%	4.2%			2 trace
9	Temperature 130°	0.8%		91.5%	trace	1.4%	1.0%	4.8%			2 trace
10	Temperature 160°	1.8%		89.4%	trace	1.4%	1.0%	6.2%			2 trace

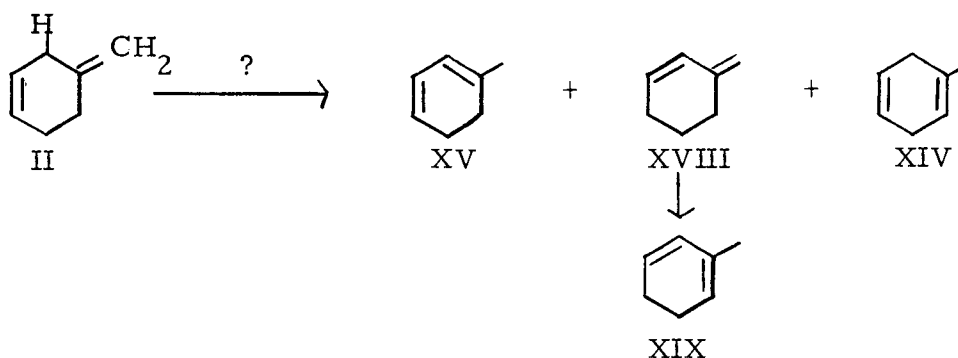
Before discussing the products in these experiments the method of obtaining the results in Figure 1 will be elaborated. The gas chromatogram was obtained by using a 20 ft. 1/4 in. nitrile silicone column. After trying several columns this was found to be best. The conditions shown in Figure 1 were optimum.

The four products shown below increased as the system became more protic while methylenecyclohexene II decreased.



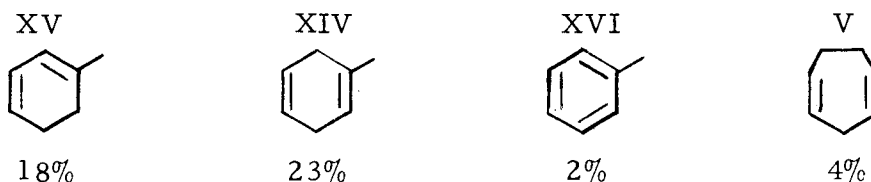
1,4-Cycloheptadiene (V) was identified by collection and comparison of its infrared spectrum with one in the literature (45, #8010). The n.m.r. spectrum shows four vinyl hydrogens, four allylic hydrogens, and two doubly allylic hydrogens.

Compound XV was collected and showed spectral properties (IR, UV, NMR) consistent with the structure 1-methyl-1,3-cyclohexadiene. Compound XV has an ultraviolet absorption at  $\lambda = 260 \text{ m}\mu$  ( $\epsilon \approx 5,000$ ) and an n.m.r. spectrum with three vinyl hydrogens, four allylic hydrogens, and a methyl on a double bond. With these properties one cannot eliminate the isomeric structure XIX formed by the thermal, acid, or base rearrangement of the major product II.



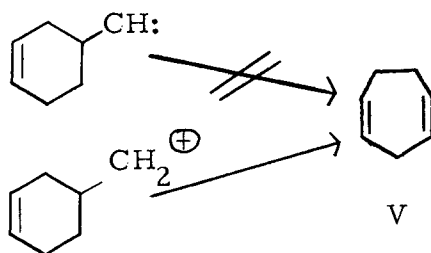
Neither compound XVIII nor XIX were observed, however. Attempts to synthesize the dienes by other routes were ambiguous.

The Bamford and Stevens reaction (Table XVI, #7) in which diethylene glycol was used as a solvent showed the "protic" products in very high concentration.

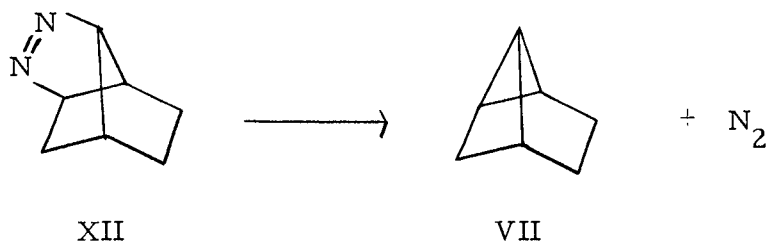


One would expect more XV than XIV since XV is conjugated. The unexpected results could reflect the very unstable, non-selective character of the intermediate. That the carbonium ion in the Bamford Stevens reaction would be so non-discriminating is quite surprising since solvation stabilization is possible in diethylene glycol. An alternate possibility is the loss of the diene XV by some further reaction. The presence of 1,4-cycloheptadiene (V) under

these "carbonium ion" conditions and not under "carbene" conditions (Table XVII) was also surprising.



In all the decompositions with added alcohol a product with g.l.c. properties similar to tricyclo[4,1,0,<sup>3,7</sup>0]heptane (VII) was observed. A sample of this compound was obtained for comparison purposes from James H. Kawakami of Purdue University. It was not further identified. The probable precursor of VII, the pyrazoline XII, was not detected.



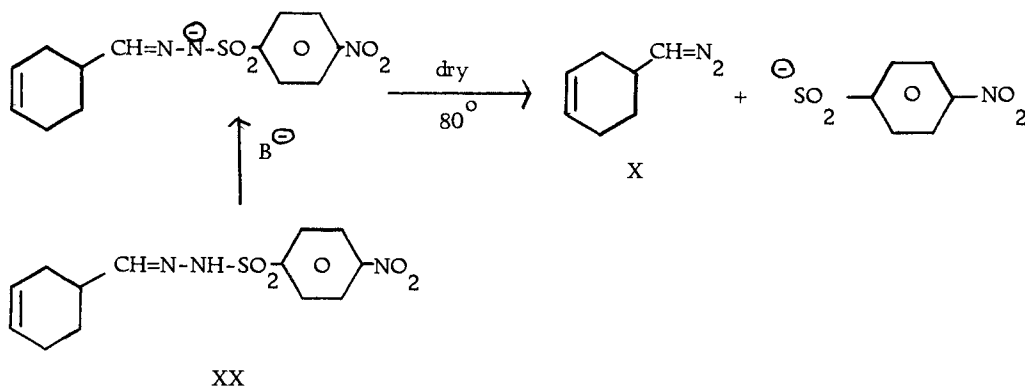
The effect temperature had on the decomposition of salt IX was investigated. A method for lowering the temperature of decomposition was required before this investigation could be conducted. The results of decomposing the salt both dry and in solvent are reported in Table XIX. The volatiles were collected from both decompositions

before the oil bath was raised to the next temperature. When the salt was decomposed dry, most of the hydrocarbon products were produced at  $80^{\circ}$  (95%), whereas most were found at  $148^{\circ}$  (77%) when the salt was decomposed in solvent. The hydrocarbon products were similar except for minor solvent decomposition products. Therefore, for a lower temperature of decomposition, the dry conditions were superior.

Table XIX. Effect of Solvent Versus No Solvent in Tosylhydrazone Decompositions

	% Volatiles Collected		
	$80^{\circ}$	$108^{\circ}$	$148^{\circ}$
Tetraglyme	none	23%	77%
Dry	95%	5%	none

An attempt to lower the temperature even further by changing the leaving group was unsuccessful. The dry salt of the nosylhydrazone XX again decomposed at  $80^{\circ}$ . The temperature of decomposition appears to depend more on the diazocompound being formed than on the leaving group, as discussed in the Introduction.



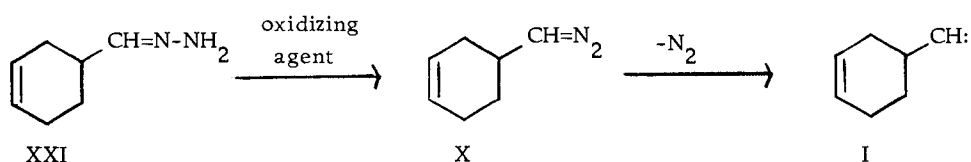
In these effect of temperature studies (XVIII, #8, #9, #10) one salt was used and divided into three parts in order to limit other variables. Each portion was placed in an oil bath preset to the desired temperature. An increase in volatile yield was observed with an increase in temperature. The volatile composition was about the same. The increase in volatiles reflects the more efficient conditions for distilling the diazocompound. Since the same salt was used, the amount of methanol was the same in these three reactions. Therefore, side reactions forming hydrocarbon products occurred to approximately the same extent.

In summary, the aprotic decomposition of the diazocompound (#1, Table XVIII) at  $25^{\circ}$  required 30 hours. The reason for the stability of the diazocompound in the absence of a proton source is not known. As the diazocompound decomposed, it formed mostly the azine XIII. When an alcohol was present, the characteristic

red-orange color of X disappeared in less than 30 minutes. When the proton source was present, the stability of the diazocompound was lost with concomitant formation of hydrocarbon products. Most of these hydrocarbon products were not present under aprotic conditions. The increase in the amount of hydrocarbon products as the system became protic was the opposite of what was expected from the results of other systems (Table IX, XI, and XII).

#### Hydrazone Route to 3-Cyclohexenyl Carbinyl Carbene

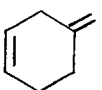
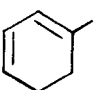
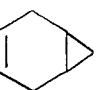
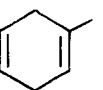


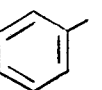
The products of oxidation of the hydrazone XXI were investigated as a different route to the carbene I.



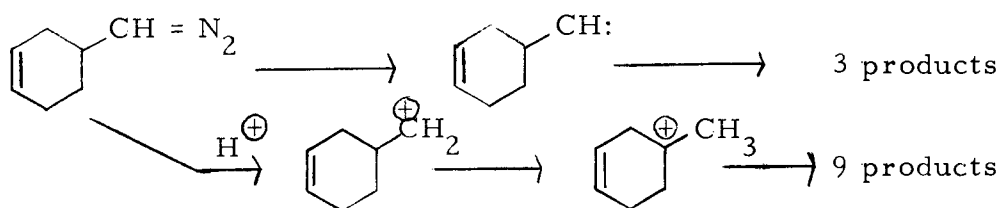
The most informative oxidation was one containing ethanol as an impurity in the undistilled hydrazone. The first trap contained the diazocompound X (IR band at  $2040\text{ cm}^{-1}$ ) and ethanol. After the diazocompound decomposed at room temperature, the hydrocarbon products were analyzed by g.l.c. These products will be referred to as "protic." After carefully filtering the residue, the red-orange filtrate was heated at  $90^\circ$  for 9 hours and then extracted with

pentane. The hydrocarbons in this pentane fraction will be designated "aprotic" since they were formed in the absence of any detectable proton source. The "protic" and "aprotic" hydrocarbon products are reported in Table XX.

Table XX. "Protic" versus "Aprotic" Hydrazone Hydrocarbon Composition

	XVII								other
"Protic"	3.7%	65.4%	trace	2.1%	9.6%	14.7%	trace	4.0%	1 other
"Aprotic"		90.5%		1.1%		8.4%			none

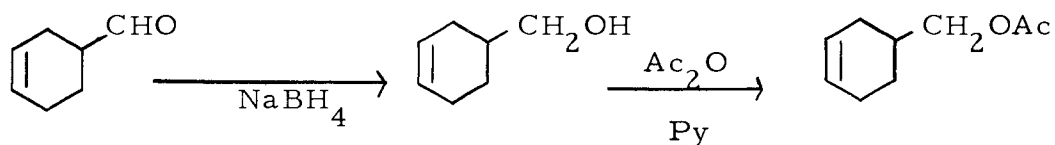
The appearance of six new products by merely having a proton source available was extraordinary. Presumably hydrogen shift in the carbonium ion is responsible.



The ratio of allylic to non-allylic  $\gamma$ -insertion was 7.6 under "aprotic" conditions, lower than that found in aprotic tosylhydrazone runs. The preference for insertion into the allylic carbon-hydrogen bond may again be partially attributed to its more favorable dihedral

angle with the carbene carbon. The importance of this effect of geometry on insertion ratios has been shown in two laboratories, Kirmse's (114) and these at Oregon State University (14). The preference for the allylic carbon-hydrogen bond remains about the same under "protic" conditions (7.0).

Several other hydrazone oxidations were carried out to investigate various oxidizing agents. The results are reported in Tables XXI and XXII. In these oxidations the hydrazone was distilled immediately before use. The  $\text{MnO}_2$  and  $\text{Pb}(\text{OAc})_4$  oxidations were instantaneous; the ethanol,  $\text{HgO}$  oxidation (#1) was heated for two hours; and the tetraglyme,  $\text{HgO}$  oxidation (#15) took 18 hours. The ethanol,  $\text{HgO}$  oxidation was conducted according to the procedure of Reusch et al. (146). The  $\text{MnO}_2$  and  $\text{Pb}(\text{OAc})_4$  oxidations were run under standard conditions without the calcium hydride added. The alcohol and acetate were identified by comparison of their spectral properties (IR, NMR) with authentic samples prepared from the aldehyde by standard methods.



The products in the oxidations appeared to depend on the receptor of the hydrazone protons. With  $\text{Pb}(\text{OAc})_4$  acetic acid was formed while  $\text{HgO}$  and  $\text{MnO}_2$  produced water.

Table XXI. Stoichiometry of Hydrazone Oxidations


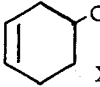



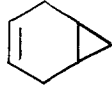



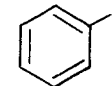
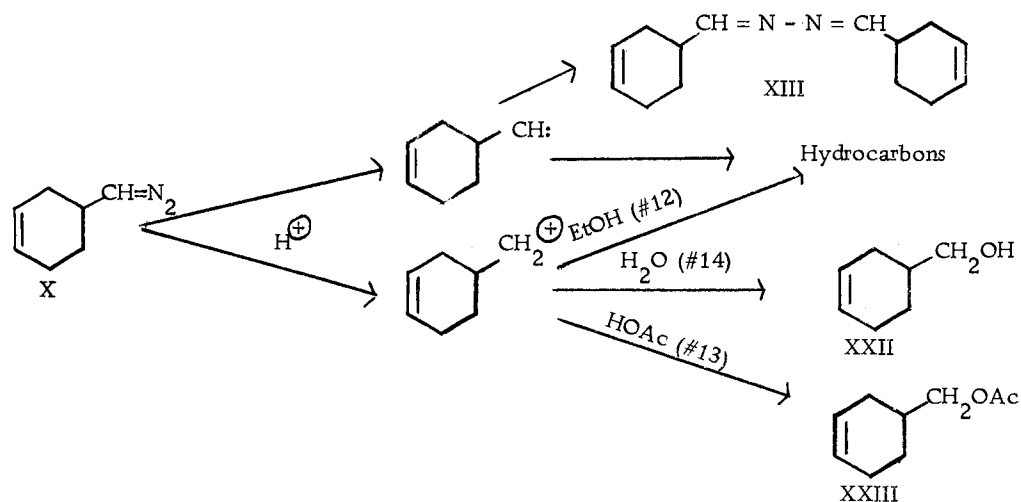
Oxidation Number	Solvent	Oxidizing Agent	Temperature and Pressure	Hydrocarbons	Azine XIII	 CH <sub>2</sub> OH XXII	 CH <sub>2</sub> OAc XXIII
11	EtOH	HgO	82° 760 mm.	37%	62%	0	0
12	EtOH	HgO	85° 760 mm.	46%	54%	0	0
13	Tetraglyme	Pb(OAc) <sub>4</sub>	25° 760 mm.	0	0	0	96%
14	Tetraglyme	MnO <sub>2</sub>	25° 760 mm.	6%	51%	43%	0
15	Tetraglyme	HgO	24° 26 mm.	2%	93%	0	0
16	dry	HgO	25° 1 mm.	21%	77%		

Table XXII. Hydrazone Hydrocarbon Composition

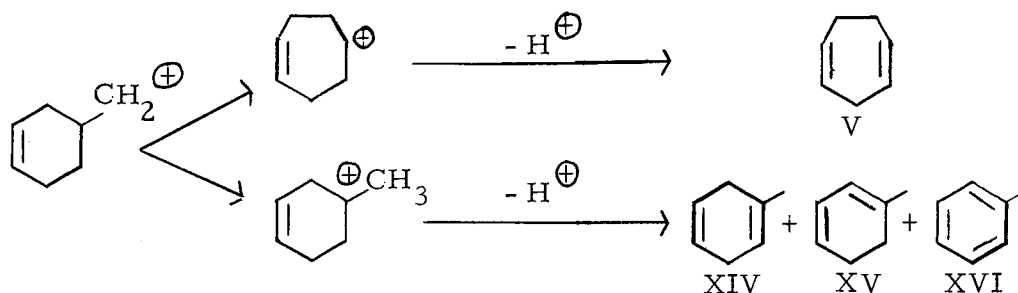
Oxidation Number	Oxidizing Agent and Solvent	XVII	VII 	II 	XV 	IV 	XIV 	III 	V 	XVI 	other products
11	HgO EtOH	0.8%		74.3%		1.7%		13.0%	9.8%		2 trace
12	HgO EtOH	1.9%		73.3%		1.8%		13.4%	9.7%		2 trace
14	MnO <sub>2</sub> T. G.	3.1%		68.7%	10.2%	0.8%	9.1%	4.2%		2.2%	2 trace
15	HgO T. G.	4.4%		65.6%		0.6%		6.4%		23.2%	
16	HgO dry	6.4%		84.0%	trace	2.1%	trace	7.5%	trace	trace	3 trace



Acetic acid, water, and ethanol were the proton sources in forming the carbonium ion in #13, #14, and #12 respectively (Table XXI).

For  $\text{HgO}$  and  $\text{MnO}_2$  (#12 and #14) the  $\text{C}_7$  product yield was approximately the same, although less than for the  $\text{Pb}(\text{OAc})_4$  case. In #14 water acts as a nucleophile for trapping the intermediate carbonium ion.

The hydrocarbon products of the ethanol oxidations had several peculiarities. The formation of 1,4-cycloheptadiene (V) and the absence of the cyclohexadienes XIV and XV and toluene was quite unusual.

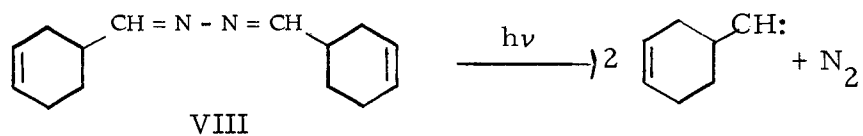


The formation of a secondary carbonium ion rather than a tertiary one has confusing implications. Furthermore, it will be recalled that the Bamford and Stevens reaction in diethylene glycol (#7, Table XVIII) gave all four products. One cannot explain this interesting effect with the available information.

Oxidation with HgO in tetraglyme (#15, #16, Table XXI) and with HgO dry were nearly aprotic since calcium hydride was used to stop water formation in #15, and anhydrous magnesium sulfate was used as a drying agent in #16. The aprotic hydrazone oxidation gave a very low yield of hydrocarbons (2%) like the aprotic tosyl-hydrazone decomposition (1%). The hydrocarbon yield was raised by lowering the pressure and using no solvent.

#### Azine Route to 3-Cyclohexenyl Carbinyl Carbene

The azine XIII was irradiated in an attempt to generate carbene I by a third route.



After irradiating for 26 hours nearly all the azine was recovered.

Careful efforts to detect any hydrocarbon products were unsuccessful. Considering these results and others discussed in the Introduction the formation of the carbene species from the azine is unsatisfactory, if it is even possible.

## SUMMARY

In summary, the hydrazone and tosylhydrazone methods gave the same products in about the same yield under aprotic conditions. The ratio of  $\beta$ - to  $\gamma$ -insertion decreased as the systems became protic. The tosylhydrazone system showed the larger effect (Table XXIII). This stronger preference in both systems for greater cyclopropane formation in protic media is in agreement with the results of Smith, Shechter, Bayless, and Friedman (163) abstracted in Table XIV.

Table XXIII. Hydrocarbon  $\beta/\gamma$  Insertion Ratios

	Hydrazone	Tosylhydrazone
"Aprotic"	9.5	19.8
"Protic"	3.9	3.1

The disadvantages of the hydrazone method are twofold. First the hydrazone disproportionates to the azine. This disproportionation can be slowed by storing the hydrazone under  $N_2$  in a freezer. One such sample showed no azine after 20 days. Using freshly distilled hydrazone eliminates this problem.

The second disadvantage is inherent in the system. Removing the hydrazone protons without rendering the system protic is very

difficult. The formation of carbenes in protic media is dubious.

It appears possible to generate the diazocompound at lower temperatures in the hydrazone system than in the tosylhydrazone system. On the other hand, tosylhydrazones are easier to prepare in high yield and are more stable. The difficulties with the tosylhydrazone method are also twofold. It is difficult to form the tosylhydrazone salt without excess base or starting material. This problem can be solved, however, by repeated recrystallizations of the tosylhydrazone and then using the preformed salt in the decompositions.

The more difficult problem to solve is removal of all the methanol. The salt appears to have a methanol of crystallization which is difficult to remove from salts that decompose at a low temperature.

In conclusion, the 3-cyclohexenyl carbinyl carbene I was formed from several routes in order to investigate methods for formation of alkyl- and dialkylcarbenes. The carbene species was generated via the diazocompound X intermediate which was unusually stable though very sensitive to reaction conditions. The diazocompound decomposition was investigated in the presence of an alcohol and at various temperatures. It was found that the formation of the carbene species was slow and extreme precaution had to be taken to avoid competing pathways.

## EXPERIMENTAL

All melting points were recorded on a Büchi melting point apparatus and are uncorrected. Proton n.m.r. spectra were run in carbon tetrachloride or deuteriochloroform and are reported as parts per million from the internal standard tetramethylsilane. Infrared absorption spectra were determined using a Beckman IR-8 spectrometer. Ultraviolet absorption spectra were measured with a Beckman Model DB recording spectrometer. The gas chromatograms were taken on the Aerograph A-90P using helium as the carrier gas. A 20 foot, 1/4 inch nitrile silicone column, XF1150, was used. Unless otherwise specified the column, detector, and injector temperatures were 108°, 166°, and 185° respectively, and the flow rate was 40 ml./minute. Activated MnO<sub>2</sub> from Lehn and Fink Products, Cambridge, Massachusetts, and purified HgO red powder were used for the oxidations. Tetraglyme, tetraethylene glycol dimethyl ether, was distilled from sodium and then from LiAlH<sub>4</sub> in vacuo behind a safety shield. Diethylene glycol and 3-cyclohexenecarboxaldehyde were distilled before use.

3-Cyclohexenecarboxaldehyde p-Toluenesulfonylhydrazone (VIII)

To a solution of 186 g.(1.0 mole) of p-toluenesulfonylhydrazine in 1 l. of dry methanol was added 110 g.(1.0 mole) of distilled

3-cyclohexenecarboxaldehyde. The mixture was stirred for 2 hours at room temperature, poured into 5 l. of ice and placed in the refrigerator overnight. The resulting white precipitate was collected and recrystallized from methanol-water to give 229 g. (83%) of product, m.p.  $89-91^{\circ}$  (dec.) (lit. 126,  $99-100^{\circ}$ ).

The infrared spectrum in nujol exhibits major bands at  $3230\text{ cm.}^{-1}$  (N-H),  $3060\text{ cm.}^{-1}$  and  $3030\text{ cm.}^{-1}$  (vinyl-H),  $1625\text{ cm.}^{-1}$  (C = N),  $1600$  and  $1500\text{ cm.}^{-1}$  (phenyl),  $1330$  and  $1160\text{ cm.}^{-1}$  ( $\text{SO}_2$ )  $810\text{ cm.}^{-1}$  (p-substituted aromatic), and  $655\text{ cm.}^{-1}$  (cis olefin).

Sodium Salt of 3-Cyclohexenecarboxaldehyde  
p-Toluenesulfonylhydrazone (IX)

Into a dry 200 ml. round bottom flask containing 15.000 g. (0.0540 mole) of 3-cyclohexenecarboxaldehyde p-toluenesulfonylhydrazone was added 120 ml. of 0.452 N sodium methoxide solution (0.0541 mole). The mixture was stirred until a clear solution formed. The methanol was removed in vacuo and the salt dried overnight at 0.5 mm. The salt was heated at  $50^{\circ}$  (0.5 mm.) for 3 hours to remove traces of methanol to give 16.2 g. (100%) of a light yellow, flakey solid, m.p.  $80-81^{\circ}$  (dec.). The infrared spectrum in nujol shows no N-H stretching.

Thermal Decomposition of 3-Cyclohexenecarboxaldehyde  
p-Toluenesulfonylhydrazone Sodium Salt

Aprotic Conditions

The dry sodium salt (0.054 mole) was connected over a short path to a trap. After evacuating to 1 mm. the apparatus was flame dried and the trap was immersed into a dry-ice acetone bath. The salt was then lowered into a preheated oil bath at 84°. Within ten minutes decomposition took place. After ten hours the pot with the remaining yellow-white solid was removed from the oil bath, while the trap containing a dark red-orange liquid was transferred from the dry-ice acetone bath to an ice bath. Dry nitrogen was bled into the system. The red-orange liquid in the trap slowly decomposed at 0° and after four hours was brought to room temperature.

When the red-orange color had vanished completely (24 hours), the yellow liquid was distilled over a short path for four hours at 60° (25 mm.), collecting the volatiles with a dry-ice acetone trap to give a hydrocarbon yield of 25.7 mg. (0.5%). The yellow residue was identified as the pure azine (XIII) by comparison of the infrared spectrum and the thin layer chromatography  $R_f$  value (benzene-ethylacetate 4:1) with an authentic sample for a yield of 3.8132 g. (65.0%).

The solid was extracted three times with purified pentane

(200 ml.) and the solvent removed in vacuo to give 1.8152 g. of crude product. Gas chromatography on a 5 ft., 15% nitrile silicone column at 180° showed two products. The major product (67%) was identified as the azine (XIII) by coinjection. The minor product, which contained sulfur, was not identified. The solid residue, from the pentane extraction, was identified by comparison of the infrared spectrum with an authentic sample as p-toluenesulfinic acid sodium salt (XI). The combined yield of the azine (XIII) from the trap (65.0%) and the pot (20.9%) was 85.9%.

#### Bamford and Stevens Conditions

Into 50 ml. of dry diethylene glycol was added 1.0 g. (0.0435 g-atom) of sodium metal. After complete reaction, 10.0 g. (0.0360 mole) of 3-cyclohexenecarboxaldehyde-p-toluenesulfonylhydrazone was added and stirred for one hour. The flask containing the reactants was connected by a short path to a trap immersed in a dry-ice acetone bath. The solution was stirred two hours at 130° (25 mm.). The trap contained 930 mg. (27.5%) of hydrocarbons. Continuing the collection overnight at 100° (25 mm.) gave no more product. The glycol phase was poured into 50 ml. of water and extracted three times with pentane (120 ml.) and back extracted with water. After drying the pentane layer with anhydrous magnesium sulfate and filtering, the solvent was removed in vacuo to give

1.215 g. (25%) of the azine (XIII).

The hydrocarbon fraction showed twelve compounds by gas chromatographic analysis. Products with retention times of 0.6, 0.9, and 3.1 minutes were in trace quantities. The peak at 4.1 minutes (0.4%) (XVII) was not identified. The infrared spectrum exhibited major bands at 3070, 3040, 3000-2800, 1650, 1440, 890, and 652  $\text{cm}^{-1}$ . The n.m.r. spectrum shows peaks at  $\delta = 5.59$  (1), 4.53 (1), 2.05 (4), 1.53 (4), 0.97 (2).

The peak at 5.5 minutes (1.3%) was tentatively identified as tricyclo[4,1,0,0<sup>3,7</sup>]heptane (VII) by g.l.c. retention time and coinjection of an authentic sample.

The peak at 6.2 minutes (39.0%) was 3-methylenecyclohexene (II), at 7.5 minutes (2.4%) was  $\Delta^3$ -norcarene (IV), and at 8.7 minutes (10.0%) was  $\Delta^2$ -norcarene (III).

The peak at 6.7 minutes (17.9%) was collected with some (II) as an impurity. The ultraviolet spectrum gave  $\lambda_{\text{Max.}}^{\text{EtOH}} = 260 \text{ m}\mu$ . The infrared spectrum of the impure sample shows new strong bands at 952 and 685  $\text{cm}^{-1}$ . The n.m.r. of the impure material shows new peaks at  $\delta = 5.61$  (3), 2.08 (4), and 1.78 (3). The compound was assigned the structure 1-methyl-1,3-cyclohexadiene (XV).

The peak at 8.7 minutes (22.8%) was identified as 1-methyl-1,4-cyclohexadiene (XIV). The spectral properties (IR, NMR) were identical with the sample synthesized by Birch reduction of toluene.

The compound has no ultraviolet absorptions.

The peak at 9.1 minutes (3.8%) was identified as 1,4-cycloheptadiene (V). Its infrared spectrum shows bands at 3030, 2980-2800, 1650, 830, and 682  $\text{cm.}^{-1}$ . Its slightly impure n.m.r. spectrum shows peaks at  $\delta = 5.77$  (2), 2.9 (1) and 2.3 (2). The compound has no ultraviolet absorption.

Toluene (2.4%) with a retention time of 10.6 minutes was identified by coinjection and finally by collection and comparison of the infrared spectra with an authentic sample.

#### Standard Conditions at 25 mm.

Into an oil bath preset at  $130^{\circ}$  was placed 8.4 g. (0.0273 mole) of 3-cyclohexenecarboxaldehydetosylhydrazone sodium salt. After 11 hours at 25 mm., 1.28 g. of a crude red-orange product was collected in a trap cooled by a dry-ice acetone bath. This product contained 0.40 g. of methanol identified by comparison of its infrared spectrum and g.l.c. retention time with an authentic sample. After loss of the red-orange color the remaining 0.88 g. (35.3%) were hydrocarbons. The hydrocarbon yield was corrected for methanol in the starting material. The composition of the volatiles is reported as #9 in Table XVIII of the text. The reaction mixture was extracted three times with purified pentane (75 ml.), and the solvent removed in vacuo to give 1.03 g. (36%, corrected)

of the azine XIII. The azine was identified by comparison of its infrared spectrum with an authentic sample.

1-Methyl-1,4-Cyclohexadiene (XIV)

A 1 l. three-necked flask, fitted with dry-ice reflux condenser, 500 ml. dropping funnel, and gas inlet tube was filled two-thirds full with liquid ammonia. While keeping at  $-78^{\circ}$  and with good stirring, 14 g. (2 g-atoms) of lithium metal was added. To this blue solution was added dropwise with good stirring, 46 g. (0.5 mole) of toluene dissolved in 64 g. (2.0 moles) of dry methanol (30 minutes). After stirring for 5 hours during which the solution turned white, 50 ml. of methanol was added to quench the reaction. The ammonia was evaporated overnight at room temperature. The residue was diluted to 500 ml. with ice water, the organic layer separated and dried over anhydrous magnesium sulfate, and filtered to give 25.1 g. (55%) of crude product.

Gas chromatography on a 20 ft. nitrile silicone column at  $100^{\circ}$  showed three components. The minor components were collected and shown to be toluene (11.3%) and 1-methylcyclohexene (1.9%) by comparison of their infrared spectra, neat, with those in the literature (45, #1015 and #4218 respectively).

The major component (86.6%) was collected and identified as 1-methyl-1,4-cyclohexadiene,  $n_D^{28} = 1.4670$  (lit. 94,  $n_D^{20} = 1.4682$ ).

The infrared spectrum, neat, shows major bands at  $3040\text{ cm.}^{-1}$  (vinyl C-H),  $2980\text{-}2800$  and  $1450, 1430\text{ cm.}^{-1}$  (aliphatic),  $955\text{ cm.}^{-1}$  (trisubstituted olefin), and  $655\text{ cm.}^{-1}$  (cis olefin). The n.m.r. spectrum in carbontetrachloride show broad absorptions at  $\delta = 5.63$  (2),  $5.35$  (1),  $1.67$  (3) and a doublet at  $\delta = 2.56$  (4) with 2 c.p.s. coupling. The diene had only end absorption in the ultraviolet region.

### 3-Cyclohexenecarboxaldazine (XIII)

A solution of 50% hydrazine hydrate was prepared by adding 7.7 ml. (0.159 mole) of 99-100% hydrazine hydrate to 100 ml. of absolute ethanol containing 20 drops of glacial acetic acid. This solution was added dropwise to 35.0 g. (0.318 mole) of 3-cyclohexenecarboxaldehyde. The stirred solution was held at  $80\text{-}90^{\circ}$  and flushed with dry nitrogen during the reaction. After heating under reflux for two hours the solution was dried over anhydrous magnesium sulfate and the solvent removed in vacuo. Distillation of the yellow oil through a Claisen head yielded 34.5 g. (99%) of the azine, b.p.  $123^{\circ}$  (0.4 mm.),  $n_D^{25} = 1.5325$ .

Anal. Calcd. for  $C_{14}H_{20}N_2$ : C, 77.73; H, 9.32; N, 12.95

Found: C, 77.40; H, 9.50; N, 12.76

The ultraviolet spectrum of the product shows  $\lambda_{\text{Max.}}^{\text{EtOH}} = 206\text{ m}\mu$  ( $\epsilon = 20,000$ ). The n.m.r. spectrum exhibits a doublet at  $\delta = 7.71$  (1),

broad absorption at  $\delta = 5.67$  (2) and a broad peak from  $\delta = 3.0$  to 1.5 (7). The infrared spectrum, neat, shows strong bands at  $3030 \text{ cm.}^{-1}$ ,  $3000\text{-}2800 \text{ cm.}^{-1}$ ,  $1650 \text{ cm.}^{-1}$ , and  $654 \text{ cm.}^{-1}$

### 3-Cyclohexenecarboxaldehydrazone (XXI)

Into a 1 l. flask containing a solution of 150 ml. of 99-100% hydrazine hydrate and 350 ml. of triethylamine in 200 ml. of absolute ethanol was added dropwise 40 ml. (0.363 mole) of 3-cyclohexene-carboxaldehyde. After heating under reflux for 1 hour, the solvent was removed in vacuo. The crude solution was poured into 100 ml. of ice water and extracted four times with ether (100 ml.). The combined extracts were dried with anhydrous magnesium sulfate, filtered, and the solvent removed in vacuo. Distillation through a 10 inch glass helix packed column yielded 20.6 g. (45%) of colorless product, b.p.  $58\text{-}60^{\circ}$  (0.45 mm.),  $n_D^{27} = 1.5232$ . The hydrazone, if not used immediately, should be stored at  $0^{\circ}$  under dry  $N_2$ .

The ultraviolet spectrum of the product exhibits  $\lambda_{\text{Max}}^{\text{EtOH}} = 215 \text{ m}\mu$  ( $\epsilon = 4800$ ). The infrared spectrum, neat, shows major bands at  $3380$ ,  $3220$ ,  $3030$ ,  $3000\text{-}2800$ ,  $1645$ ,  $1610$ ,  $1450$ ,  $1430$ , and  $655 \text{ cm.}^{-1}$ . The n.m.r. spectrum exhibits a doublet at 6.94 (1), multiplet at 5.63 (2), and broad  $\delta = 5.00$  (2) and 2.5 to 1.3 (7).

Oxidation of 3-Cyclohexenecarboxaldehydhydrazone  
with Mercuric Oxide in Tetraglyme

Standard Conditions

Into a three-necked flask fitted with dropping funnel, thermometer, and short path column connected to a trap immersed in a dry-ice acetone bath, was placed 50 ml. of dry tetraglyme, 1.92 g. (0.0455 mole) of commercial calcium hydride, and 24.0 g. (0.111 mole) of mercuric oxide. To this was slowly added with stirring 5.6662 g. (0.0455 mole) of 3-cyclohexenecarboxaldehydhydrazone in 500 ml. of dry tetraglyme at 50° (25 mm.). After six hours the trap was empty.

The solution was filtered and the red-orange filtrate was again distilled at 50° (25 mm.). After ten hours the trap was again empty. The filtrate had turned yellow and a black solid had separated.

The yellow filtrate was poured into 1 l. of water and extracted five times with pentane (300 ml.). The pentane solution was distilled at 20° (25 mm.) over a short path collecting the volatiles in a dry-ice acetone trap. The residue was identified as pure azine (XIII) by comparison of the infrared spectrum and thin layer chromatography  $R_f$  value (in benzene-ethylacetate 4:1) with an authentic sample, yield 4.582 g. (93%). The distillate was

carefully distilled through a 10 inch glass helix packed column leaving a residue of 5.17 g. The yield of hydrocarbons determined by gas chromatography was 0.083 g. (2%). The composition of the volatiles is reported in Table XXII of the text.

#### Trace of Ethanol Conditions

Into 70 ml. of dry tetraglyme containing 2.50 g. (0.060 mole) of calcium hydride and 31.0 g. (0.14 mole) of mercuric oxide was added 7.34 g. (0.059 mole) of 3-cyclohexenecarboxaldehydehydrazone. The solution was heated at 50° (25 mm.) and the volatiles collected in a trap immersed in a dry-ice acetone bath. After 12 hours the trap contained 1.31 g. of crude product. The bottom layer, 1.13 g., was identified as ethanol by comparison of its infrared spectrum and gas chromatography retention time with an authentic sample. The top red-orange layer was identified as the diazocompound (X) by the band at 2040 cm.<sup>-1</sup> in the infrared region. Upon decomposition the diazocompound yielded 179 mg. (3.8%) of hydrocarbon products. The yield was corrected for ethanol in the starting material.

After inserting a dry trap the reaction mixture was distilled for an additional 1 1/2 hours at 90° (25 mm.) to give only trace amounts of volatiles. After filtration under a nitrogen blanket the red-orange reaction mixture was heated at 90° for 9 hours. The resulting yellow colored liquid was poured into 400 ml. of saturated

salt solution and extracted five times with pentane (100 ml.). The combined pentane extracts were back extracted with water, dried over anhydrous magnesium sulfate, filtered, and distilled in vacuo. The volatiles were collected in a trap cooled by a dry-ice acetone bath. The residue 4.1042 g. (76%) was identified as the azine XIII by its infrared spectrum. The pentane volatiles were carefully distilled to give 0.376 g. (7.8%) of hydrocarbon products. The volatile compositions are reported in Table XX of the text.

### 3-Cyclohexene-1-Methanol (XXII)

Into 100 ml. of water kept at 0° and containing 6.0 g. of sodium borohydride was added 34.8 g. (0.316 mole) of 3-cyclohexenecarboxaldehyde with stirring. After 2 hours at room temperature the solution was extracted three times with ether and the combined ether extracts (100 ml.) dried with anhydrous magnesium sulfate. The ether was removed in vacuo, and further distillation through a Claisen head yielded 13.2 g. (38%) of product, b.p. 99-100° (20 mm.),  $n_D^{27} = 1.4820$  (lit. 178, b.p. 102° (19 mm.),  $n_D^{25} = 1.4828$ ).

The infrared spectrum, neat, shows a broad band at 3360 cm.<sup>-1</sup> and an intense band at 1020 cm.<sup>-1</sup> (primary alcohol). Other major bands were at 3030, 1640, 652 cm.<sup>-1</sup> (cis olefin) and 2980-2800 cm.<sup>-1</sup> (aliphatic). The n.m.r. spectrum shows absorption at  $\delta = 5.62$  (2),

doublet 3.90 (2), broad peak  $\delta = 2.3$  to 1.1, and  $\delta = 3.71$  (alcohol).

### 3-Cyclohexene-1-Methanol Acetate (XXIII)

Into a 50 ml. Erlenmeyer flask containing 15 ml. of pyridine and 10 ml. of acetic anhydride was added 4.0 g. (0.0356 mole) of 3-cyclohexene-1-methanol. The solution was stirred overnight. After adding 150 ml. of water, the solution was extracted four times with ether (60 ml.). The combined ether extracts were washed with 5% hydrochloric acid until acidic, then with 5% sodium bicarbonate, and again with water. After drying the ether layer with anhydrous magnesium sulfate, the solvent was removed in vacuo. Distillation through a Claisen head yielded 4.24 g. (77%) of the ester, b. p.  $103^{\circ}$  (25 mm.),  $n_D^{25} = 1.4578$ .

The infrared spectrum, neat, exhibits major bands at 3030, 1640, 655  $\text{cm.}^{-1}$  (cis olefin) and 1735, 1240, 1030  $\text{cm.}^{-1}$  (ester). The n. m. r. spectrum shows absorption at  $\delta = 5.62$ , 3.90 doublet, 1.98 singlet, and 2.5-1.5 broad.

### Azine Decomposition by Ultraviolet Light

A solution of 33.29 g. (0.153 mole) of 3-cyclohexenecarboxaldazine in 1.2 l. of 95% ethanol was irradiated for 26 hours with a Hanovia 450 watt mercury pressure lamp. One-fourth of the irradiated material was poured into 300 ml. of distilled water and

extracted 4 times with carefully purified pentane (250 ml.). The combined pentane extracts were dried with anhydrous magnesium sulfate, filtered, and distilled on an Oldershaw column until head temperature rose above  $36^{\circ}$ .

The residue (ca. 10 ml.) was distilled at 25 mm. pressure over a short path leaving a yellow residue identified by infrared and ultraviolet spectroscopy and thin-layer chromatography as starting material, 6.80 g. (80%).

The volatile fraction, collected in a dry-ice acetone trap, had the solvent carefully removed through a 10 inch glass helices packed column. The residue (2.5 g.) was shown by gas chromatography on 20' XF 1150 at  $110^{\circ}$  to contain only pentane, no  $C_7H_{10}$  hydrocarbons. The infrared spectrum also showed only pentane.

The aqueous portion from the pentane extraction was then extracted four times with ether (100 ml.). The combined ether extracts were washed with saturated salt solution and then water. After the ether layer was dried with anhydrous magnesium sulfate, the solvent was removed in vacuo at  $40^{\circ}$  to give 220 mg. of product. This product was not fully characterized but the infrared spectrum, neat, shows bands at 3400 (broad), 3030, 1640, 1040, 878, and 653  $cm.^{-1}$

3-Cyclohexenecarboxaldehyde p-Nitrobenzenesulfonylhydrazone (XX)

To a solution of 19.7 g. (0.091 mole) of p-nitrobenzenesulfonylhydrazine in 250 ml. of tetrahydrofuran was added 10.0 g. (0.091 mole) of 3-cyclohexenecarboxaldehyde and 1 drop of concentrated hydrochloric acid. After stirring 14 hours the solvent was removed in vacuo. The yellow solid was collected, yield 29.8 g. (88%), m. p. 131-132°(d).

Anal. Calcd. for  $C_{13}H_{15}N_3SO_4$ :

C, 50.49; H, 4.89; N, 13.59; S, 10.34; O, 20.68

Found: C, 50.20; H, 4.96; N, 13.29

The infrared spectrum in nujol shows major bands at 3240, 3040, 1640, 1610, 1530, 1370, 1350, 1180, 1170, 855, 755, 745, and 660  $\text{cm.}^{-1}$ .

Thermal Decomposition of the p-Nitrobenzenesulfonylhydrazone Sodium Salt

A sample of 2.2 g. (0.0066 mole) of p-nitrobenzenesulfonylhydrazone sodium salt was placed in an oil bath and the temperature raised slowly. At 80° decomposition commenced and after 4 hours in vacuo 0.232 g. (37%) of hydrocarbon products were collected in a trap cooled by a dry-ice acetone bath. Raising the temperature to 113° and continuing collection for another 12 hours yielded 0.046 g.

(7%) of hydrocarbon products. The residue contained the azine XIII by comparison of its infrared spectrum with an authentic sample. The volatiles had a similar product composition to the tosylhydrazone decompositions.

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