

CHAPTER - I

REVIEW ON CARBENE REACTIONS

1.1 Carbene - its nomenclature and history

Divalent carbon compounds were suggested as intermediate in certain chemical reactions such as alkaline hydrolysis of chloroform¹, in the decomposition of diazoalkanes and diazoketones but only from the middle of this century the carbenes and their reactions were being considered for a close study.

The name carbene was given by Doering, Winstein and Woodward² in 1951, to describe the reactive class of compounds where the carbon is linked to two adjacent groups by covalent bonds, and posses two non-bonding electrons which may have antiparallel spins (singlet state) or parallel spins (triplet state). The formal relationship of carbenes to other simple intermediate are presented in table I.

Table I

Simple intermediates in Chemistry of carbon compounds

Intermediates		No. of covalent bonds	No. of valence electrons
Carbanious	$\rightarrow\text{C}^{\ominus}$	3	8
Radicals	$\rightarrow\text{C}$	3	7
Carbonium ions	$\rightarrow\text{C}^{\oplus}$	3	6
Carbenes	>C:	2	6

The first attempt to prepare methylene were made at a time when the quadrivalency of carbon was not established. Dumas³ and Regnault tried to dehydrate methanol by phosphorus pentoxide or concentrated sulphuric acid. Perrot⁴ tried to eliminate hydrogen chloride from methylene chloride when Butlerov⁵ attempted with methylene iodide and copper powder to obtain methylene but all attempts were in vain. Though Nef⁶ could not prepare methylene, he thought it to be a stable compound. Staudinger⁷ and associates contributed much to the recognition of carbenes as transient species.

Recently two approaches to carbene chemistry were taken, firstly the insertion of methylene or other carbenes into C-H bonds^{8,9} and adequately interpreted that carbenes were unique type of intermediate, giving characteristic reactions not encountered with radicals. Secondly, the studies of Hine¹⁰ et al, on haloform solvolysis. Actually, Hine, in 1950, reactivated the current interest in carbene chemistry by proposing α -elimination in the haloform solvolysis as a potential route to carbenes. In 1954, Doering, Hofmann showed that dihalocarbenes from the haloforms could be trapped by olefins to give cyclopropane derivative, cyclohexene also acts as trap in presence of chloroform (or bromoform) and potassium tert-butoxide giving 7,7-dichloronorcarane¹¹.

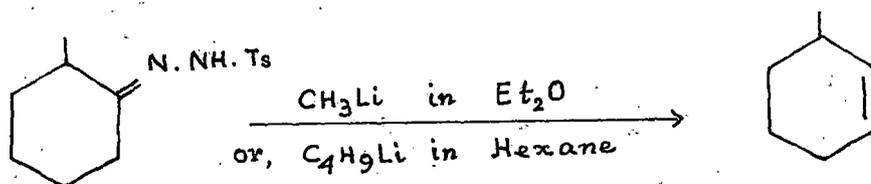
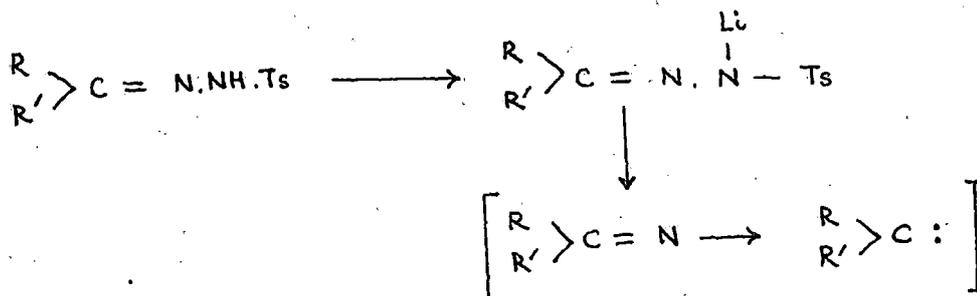


1.2 General procedure for carbene generation

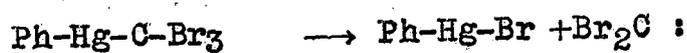
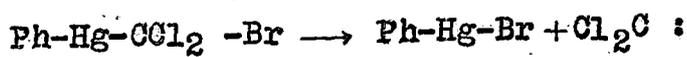
Carbenes are generated in numerous ways but for synthetic purposes they are usually generated by thermal¹²⁻¹⁴ or photolytic^{2,15-29} decomposition of diazoalkanes or by α -elimination^{10,30-34} of hydrogen halide from a haloform or of halogen from a gem-dihalide³⁵ by the action of a base or a metal. It seems more likely that in these reactions the carbene is complexed with a metal or held in a solvent cage with a salt or that the reactive intermediate is in fact an organometallic compound and not a carbene. Such organometallic or complexed intermediates which while not free carbenes, give rise to products expected to carbenes are usually called Simmons-Smith reactant.

Thermal decomposition of diazoalkanes³⁶ often produces a less energetic and more selective carbene particularly in presence of copper powder or copper salts, copper-carbene complexes are probably involved in these reactions. With these C-H insertion and rearrangement products with olefins are also known.

Another convenient and widely used route to alkyl carbenes is thermal or photolytic decomposition of lithium or sodium salts of p-toluene sulphonyl hydrazones³⁷. The diazoalkane is formed and decomposed under the reaction conditions.

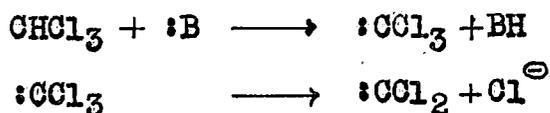


The reaction of esters of trichloroacetic acid with alkoxide produces dichlorocarbene. One of the most convenient methods for generating halogeno-carbene in the thermal decomposition of organometallic precursors^{38,39}.

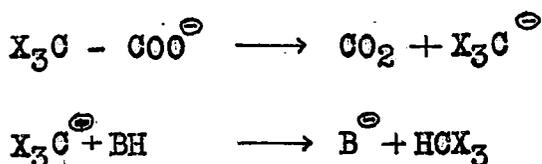


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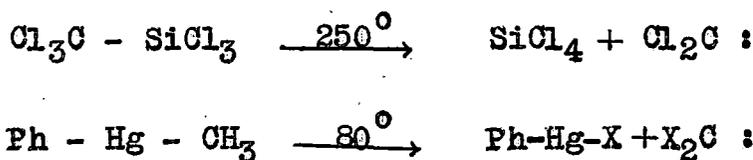
Basic hydrolysis of haloform results in the generation of dialkyl carbenes via the intermediate carbanion⁴⁰.



Decarboxylation of trihaloacetic acid gave dihalo-
carbene⁴¹



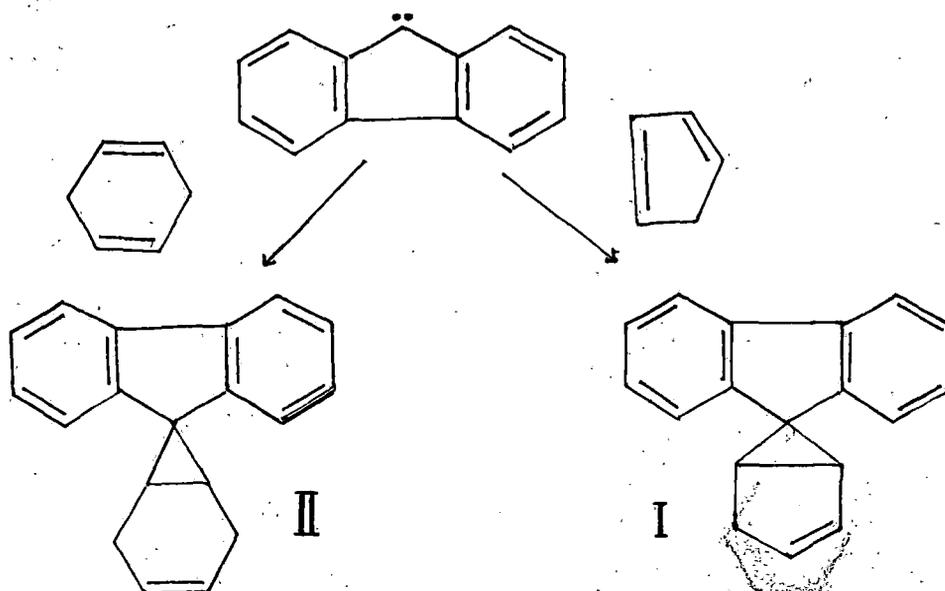
Thermal and photochemical reactions are also the
generating source of dihalocarbene which are shown by the
following reactions^{42,43}



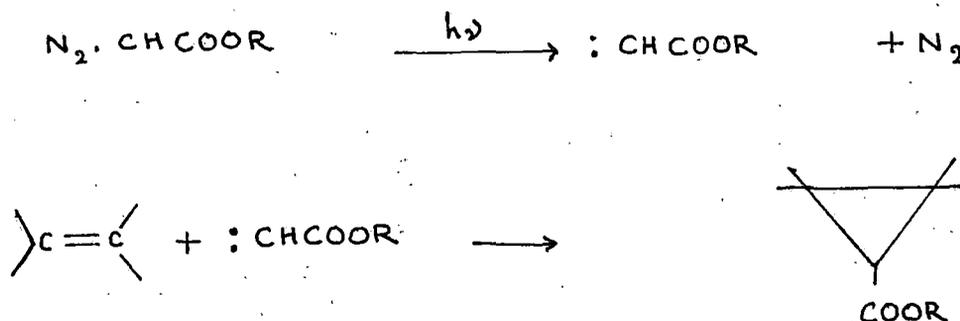
Phenyl carbene is generated by photolysis of phenyl diazo-
methane and added with trans-2-butene and cis-2-butene
non stereospecifically⁴⁴. to

Fluorenylidene, generated by photolysis from 9-
diazofluorenes, unlike diphenylcarbene, adds to π -systems
without the complications of large amount of hydrogen
abstraction. Fluorenylidene adds easily to a variety of

olefins⁴⁵. Fluorenylidene was found to add to cyclopentadiene to give only I and to add to cyclohexadiene to give II

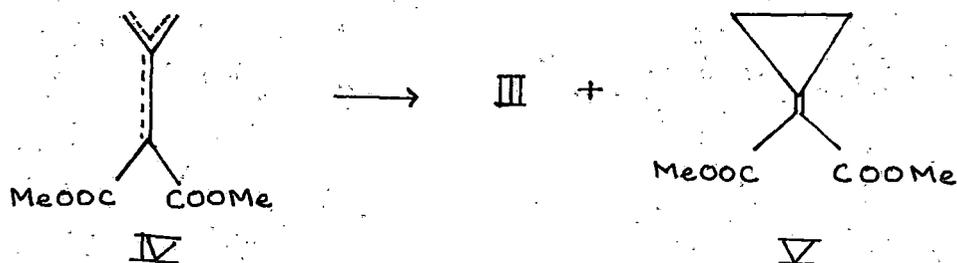
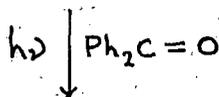
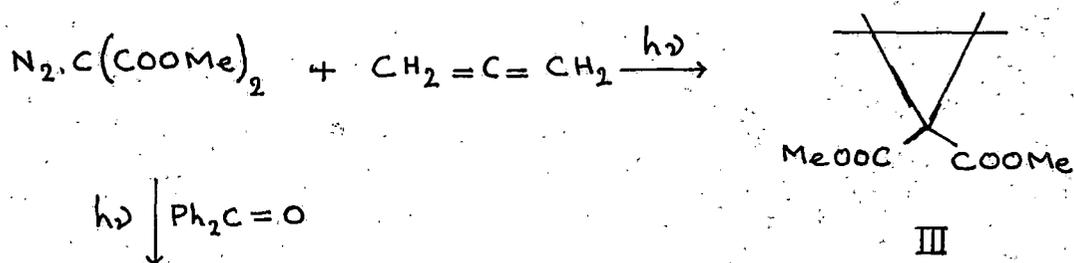


Diazo esters react with olefins by two distinct paths to produce cyclopropanes. Diazoacetic esters might lose nitrogen under the influence of heat or light to produce a carboalkoxycarbene which adds to the olefin or to acetylene giving a cyclopropane or cyclopropane carboxylate⁴⁶.



Alternatively, the diazoacetic ester might react with the olefin to form a pyrazoline which loses N_2 to produce cyclopropane carboxylate.

Unsensitised decomposition of dimethyl diazomalonate in allene gives (III) as only isolable product⁴⁷

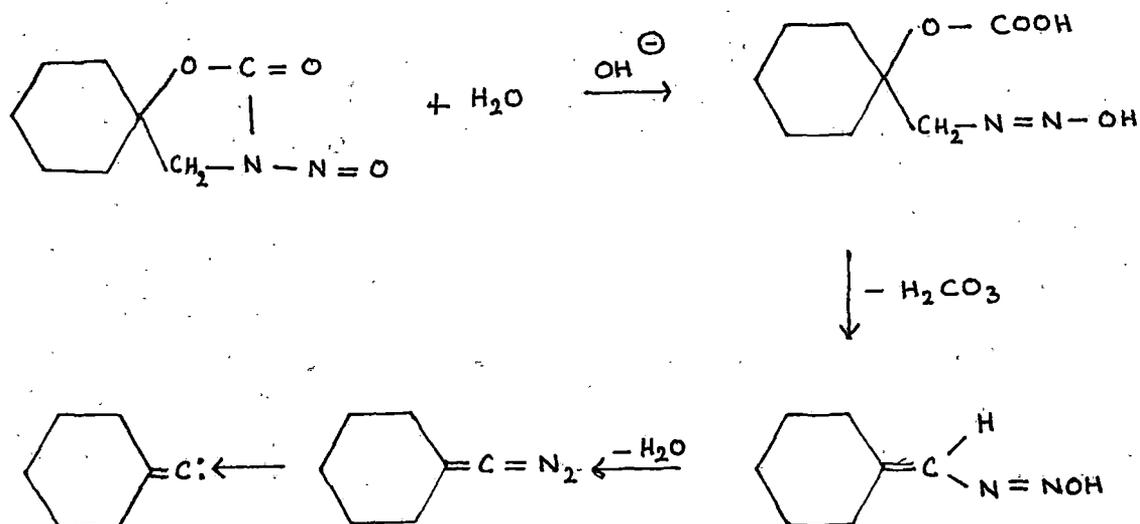


One might speculate that the sensitised reaction, proceeding through a triplet, would lead to a trimethylenemethane (IV) and then to III and V.

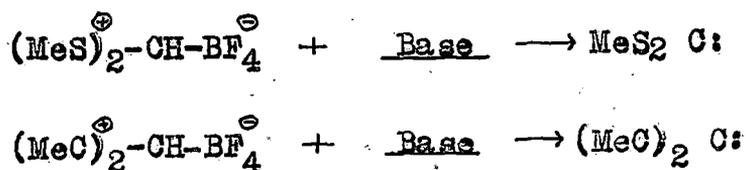
Photolysis of ethyl bromo-, iodo- and chloro-diazoacetates afford the bromo, iodo and chloroethoxycarbenes which add cis-stereospecifically to olefins and insert to C-H bonds of alkanes, though less readily than the unsubstituted carboethoxy carbene⁴⁸.

Photolysis of dicyanodiazomethane gave dicyano carbene which adds to olefins largely stereospecifically.

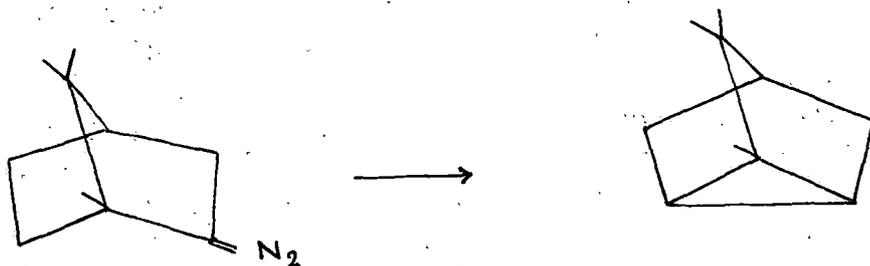
Vinyl carbenes can be generated in various ways. The initial work by Newman which involves the reaction of bases with nitro oxazolidinones^{49,50}.



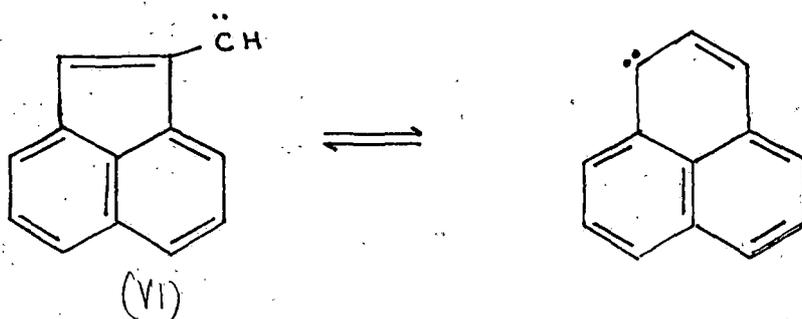
Olofson et al have reported interesting synthesis of carbene by treatment of stable cations viz. $(\text{MeS})_2^{\oplus}\text{CH}-\text{BF}_4^{\ominus}$ with base⁵¹



Methylene insertion via carbene generation takes place intramolecularly as diazocamphane gives tricyclene⁵².



Carbene to carbene type rearrangements e.g. acenaphthyl carbene (VI) to phenylidene carbene have been reported⁵³.

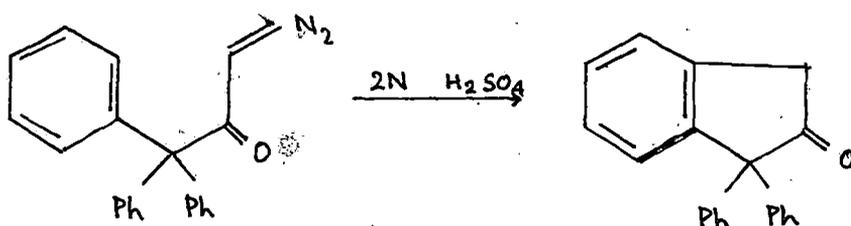


Works of Arndt, Eistert and co-workers⁵⁴ and of Bradley and Robinson⁵⁵ contributed significantly for a ready access to the diazoketones from diazomethane and acid chlorides. The first review on preparative significance of diazoketones was published by Eistert⁵⁶ and Huisgen⁵⁷.

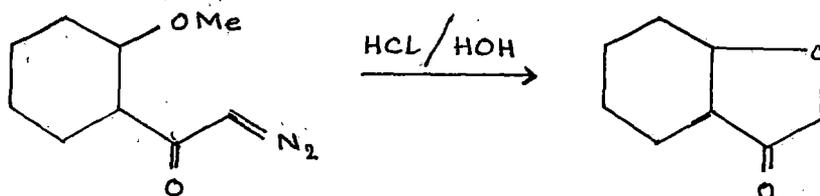
Diazoketones are decomposed by light, heat and various catalysts. The relationship between structure and quantum yield in photolysis has been studied with a variety of diazoketones⁵⁸.

When a diazoketone loses nitrogen a sextet of electron remains on the carbon atom which was linked to the diazo group. The α -keto carbene thus formed is capable of undergoing the most diverse reactions, depending on the condition under which nitrogen elimination occurs (thermal, photolytic, or metal catalysed).

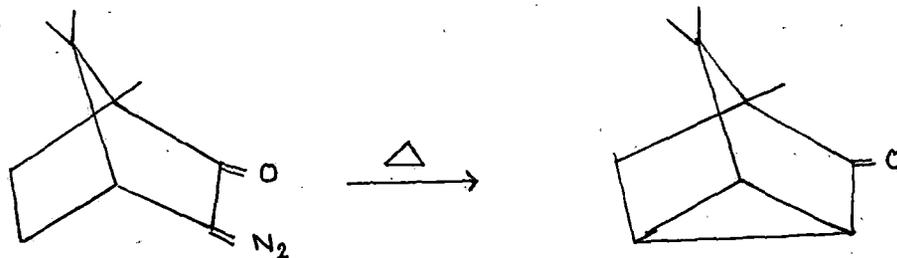
The decomposition of diazoketone by strong acids can lead to cyclisation⁵⁹.



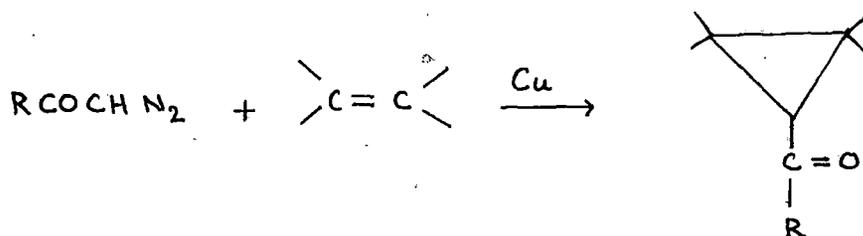
Intramolecular carbene insertion reaction occurs when diazoketone acts with the acid catalyst, very good yield of coumarones can be realised⁶⁰.



Pyrolysis of diazocamphor, leads to intramolecular insertion of the divalent carbon neighbouring C-H bond⁶¹.

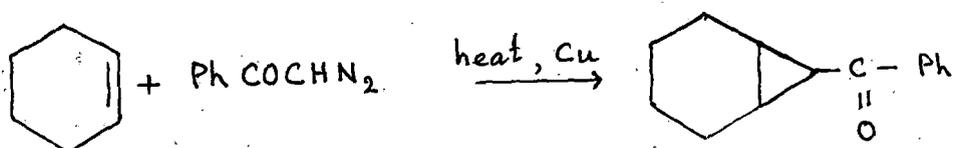


Acetyl carbene, generated by copper catalysed decomposition of diazoacetone, added easily to olefins such as styrene, cyclohexene, cyclopentene⁶². The presence of acetoxy group did not interfere with this reaction.

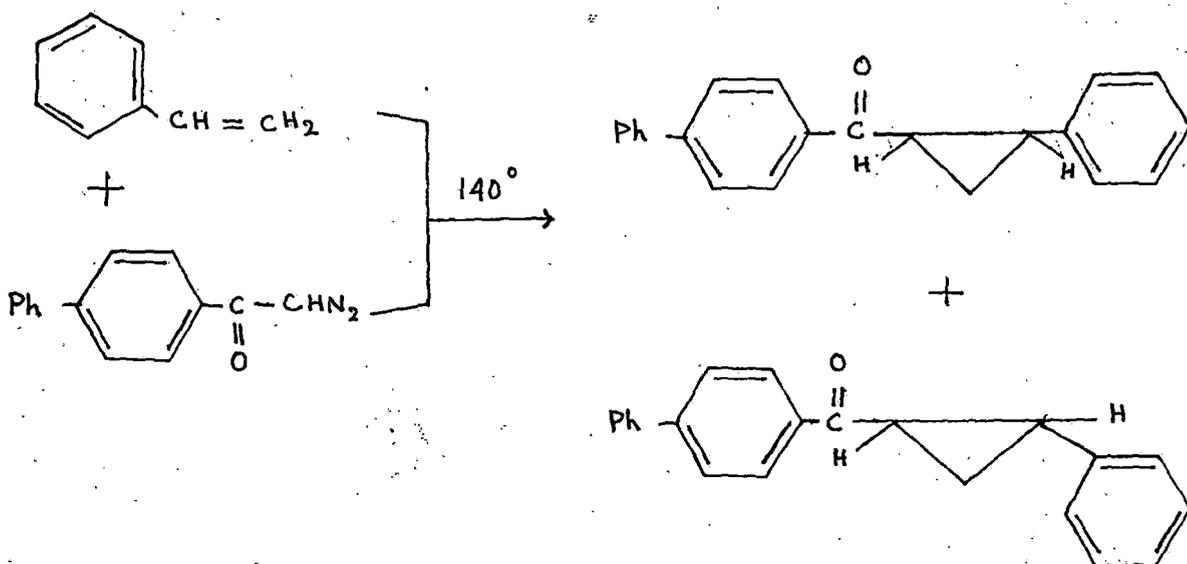
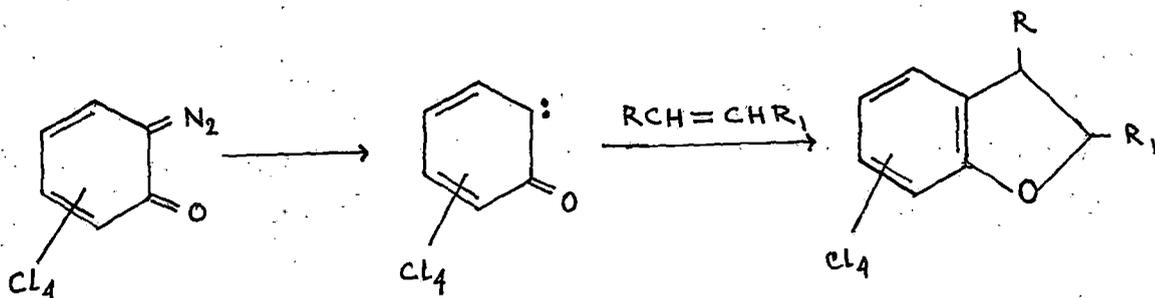


Benzoyl carbene⁶³ and p-phenyl benzoyl carbene⁶⁴ were found to react with olefins even in the uncatalysed pyrolysis of the related diazoketones, but the yields are considerably

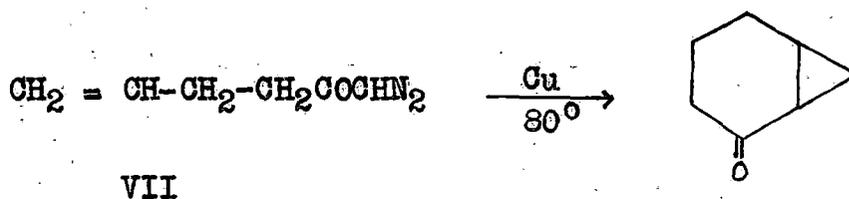
improved by the presence of copper powder⁶⁵.



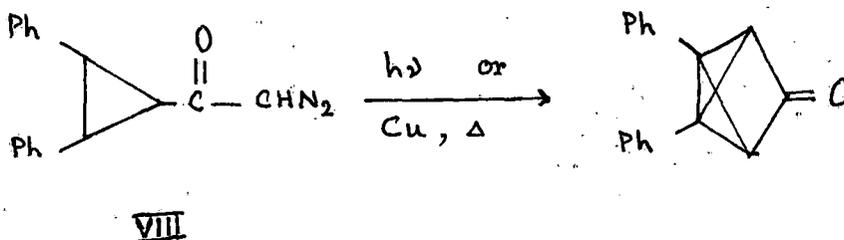
Cyclic diazoketo carbene of the following type has been found to be trapped by the olefin in the following fashion⁶⁶.



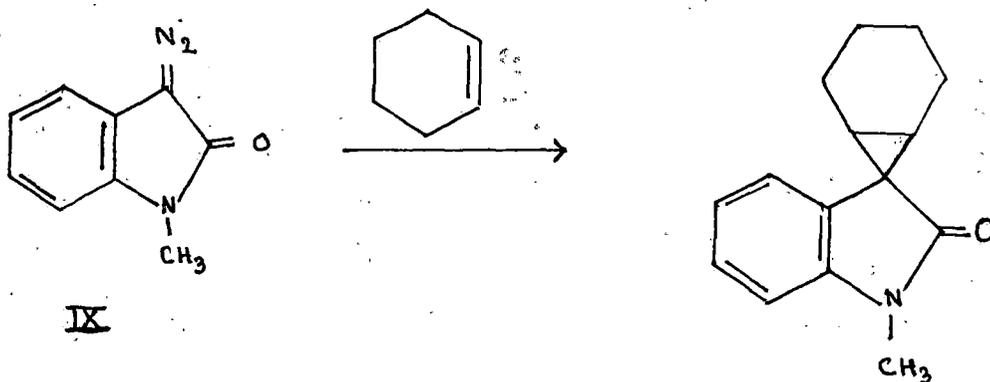
Ketocarbenes derived from unsaturated diazoketones may undergo intramolecular addition rather than Wolff rearrangement. Thus (VII) affords bicyclo (4,1,0) heptanone which was identified by independent synthesis⁶⁷.



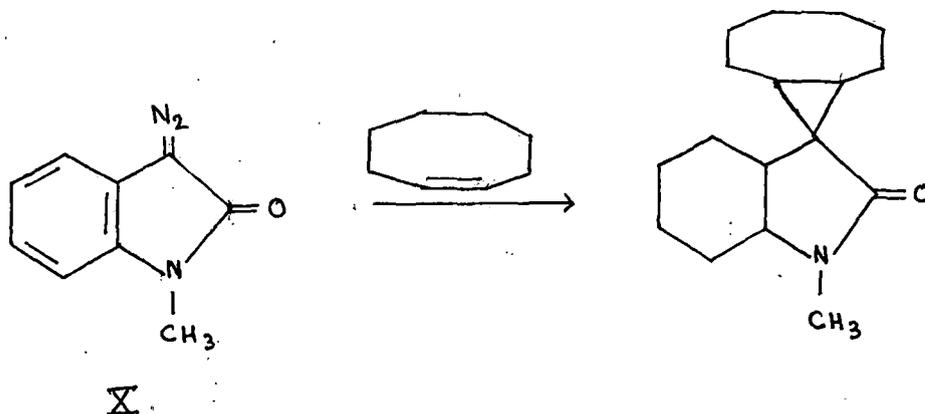
The tricyclic ketone is formed from (VIII) on photolysis⁶⁸ or on heating with copper⁶⁹.



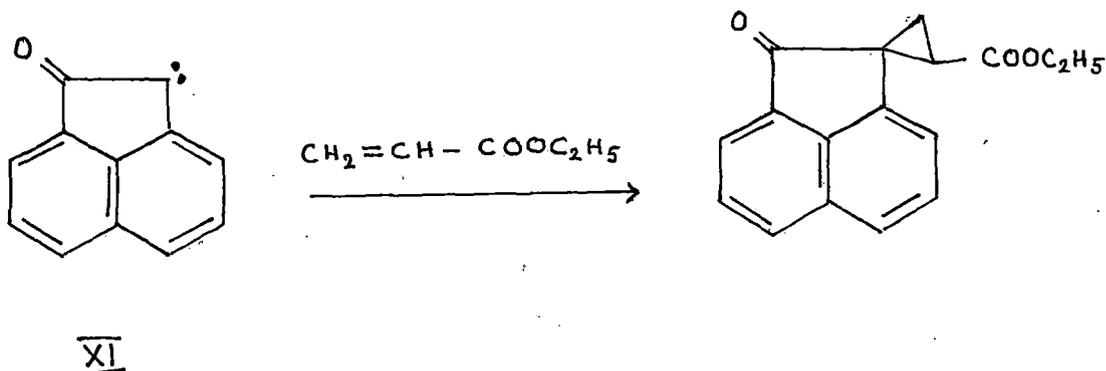
Photolysis of diazoketone (IX) in cyclohexene or 1,1-diphenyl ethylene gives adducts presumably because mobility of the amide in the Wolff rearrangement is low⁷⁰,



and imine (X) gives a carbene which also adds to cyclo-octene⁷¹

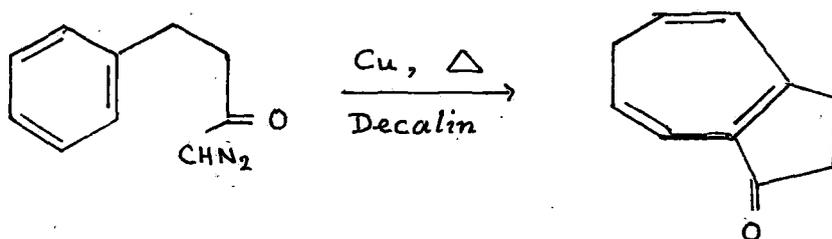


Addition is easier when copper catalyst is employed but occasionally uncatalysed additions are successful. These are often doubtful, however and do not give the total picture. Additions of (XI) to olefins was reported on thermal decomposition of diazoacenaphthenone⁷².



Olefin not bearing electron withdrawing groups do not form cyclopropanes. However, the intermediary of pyrazolines seem quite possible.

Addition of keto carbene to aromatic systems have generally failed, even when copper catalysed. But it has recently been demonstrated that both intramolecular and ^{or}intermolecular reactions are possible⁷³.

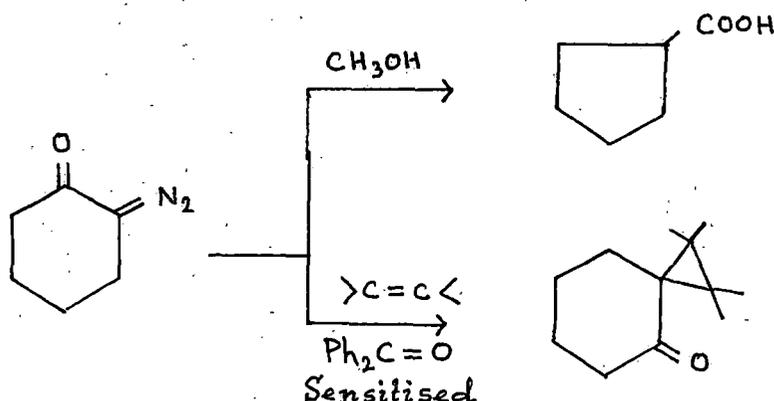


Wolff rearrangement may be arrested and cyclopropanation may occur by applying sensitizers but without sensitizers rearrangement occurs⁷⁴.

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1.3 Mechanism of Ketocarbene addition to olefins

Copper catalysts facilitate keto carbene addition to double bonds probably via the formation of an olefin-carbene-complex. Takebayashi et al⁶⁵ found that when α -diazoacetophenone reacts with olefins such as vinyl acetate, cyclohexene and cis and trans-stilbenes, several products were formed in presence of $\text{bis}(\text{acac})_2\text{Cu}$. The products are not only the keto carbene addition products but also 1,2-trans dibenzoyl ethylene, 1,2-dibenzoyl ethane and dilactone. To explain these products they assumed a copper carbenoid intermediate. They also concluded that since no addition product to benzene was obtained, the

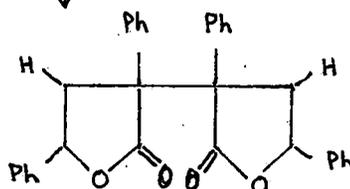
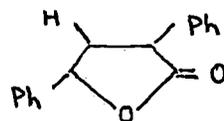
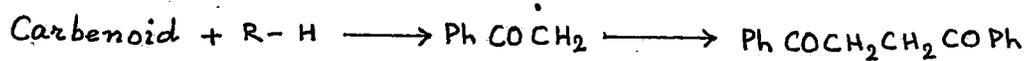
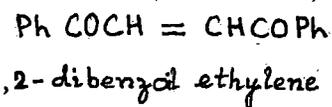
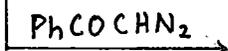
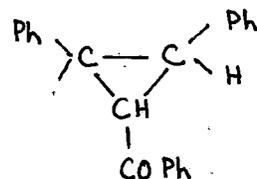
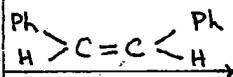
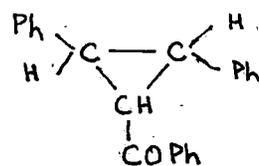
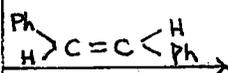
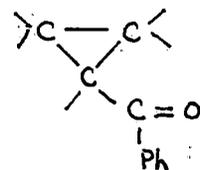
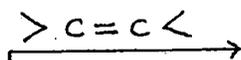
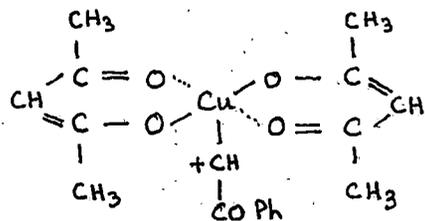
reactivity of this carbenoid perhaps minimum.

The cis and trans 1,2-dibenzoyl ethylenes may be formed by the reaction of α -diazoketones with carbenoid species. In the case of 'mixed method' when no substrate having enough reactivity to the carbenoid is present except α -diazoacetophenone in the reaction system. Groundmann and Trischmann⁷⁵ have reported that the copper powder catalysed decomposition of α -diazoacetophenone in various solvents give trans-1,2-dibenzoyl ethylene.

On the other hand, dilactone was observed in the reaction of α -diazoacetophenone with cis and trans-stilbenes, which have much reduced reactivity towards carbenoid. In this case, the concentration of substrate reaction with the carbenoid is so small that a part of carbenoid releases benzoyl carbene, which leads to phenyl ketene by concerted phenyl migration. Phenyl ketene reacts with diazoacetophenone and finally affords dilactone.

The formation 1,2-dibenzoyl ethane is explained by the dimerisation of relatively stable phenacyl radical.

These are summarised below.



Concerning the first step in the scheme it is quite reasonable that the co-ordinately satisfied tetrameric^{78,79} copper complex $\square A$ is cleaved by diazoalkane to form 3 moles of co-ordinately unsaturated monomer, and 1 mole of mono saturated carbene-metal-complex. Since the reactive monomer $\square B$ is formed in huge excess of cyclohexene and Cu^I forms strong olefin complexes, the most reasonable step is to co-ordinate with either 1 or 2 mole of cyclohexene to form intermediate complex $\square C$. This complex cannot form the product directly, therefore, it is obvious that it reacts further with ethyl diazoacetate to form the final intermediate $\square D$, before product formation. This intermediate $\square D$ depicted in scheme is tetrahedral and co-ordinately satisfied.

Since the central metal atom Cu^I is 4 co-ordinated and tetrahedral⁸⁰, in this complex $\square D$, the olefin as well as the carbene could be co-ordinated back donation type bonding. This requires donation of 2-electrons in sp^2 orbital from a singlet carbene and back donation of electrons from a d_{xz} orbital of the metal into vacant p_z orbital of the carbene carbon atom. Stable carbene complex of this type with various metals as the central metal atom have been reported⁸¹ and the

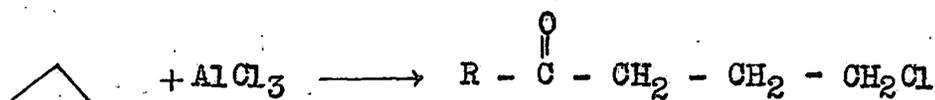
X-ray study indicates sp^2 hybridisation of the carbene carbon and $d_{\pi} - p_{\pi}$ bonding⁸². Certain transition metal complexes also give stable metal carbene complexes upon treatment with diazoketones^{82a}.

Mechanism of decomposition of diazoketones in presence of catalysts must be different from the photolytic processes. Cowan et al¹⁴⁰ showed that catalytic decomposition of

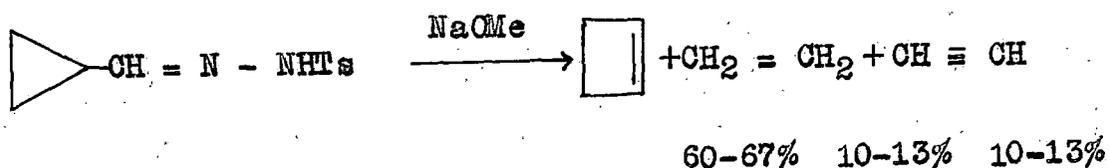
α -diazacetophenone in presence of cyclohexene leads to formation of norcaryl phenyl ketone, usually in much larger yield than that obtained by either direct or sensitised photolysis. Catalytic decomposition of diazoketones in presence of butenes also gave higher yields of cyclopropane derivative than were obtained in the photochemical experiments. It has also been observed that the addition of keto-carbenes to the trans-butene was stereospecific but not in the case of cis-butene.

1.4 Cleavage and rearrangement of cyclopropane ring

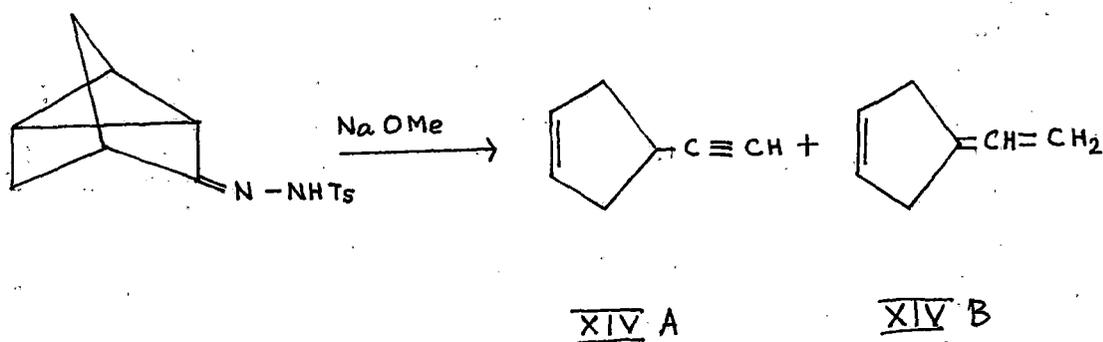
Ring cleavage of cyclopropane occurs when it is acted upon by anhydrous aluminium chloride⁸³.



The tosylhydrazones of cyclopropane carboxaldehyde and cyclopropyl methyl ketone yield mainly cyclobutenes if heated with sodium methoxide in an aprotic solvent⁸⁴.

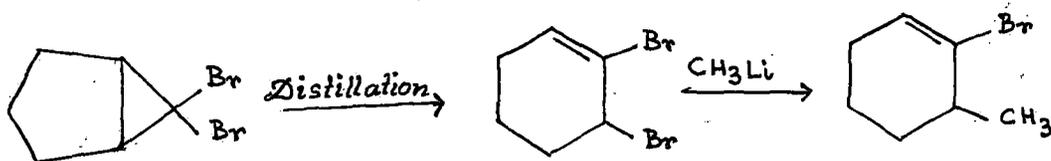


Intramolecular fragmentation to olefin and acetylene has been observed with the tricyclic carbene derived from nortricyclenone tosylhydrazone⁸⁵.



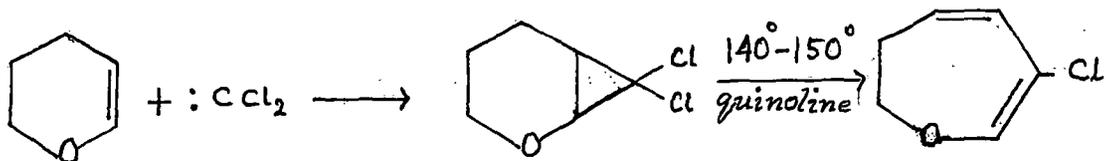
XIV B
The allene ■ is probably formed by base catalysed isomerisation of acetylene ■ XIV A.

The cyclopentene —dibromocarbene adduct isolable at a low temperature, rearranges on distillation with the formation of 2,3-dibromocyclohexene which on reaction with methyl lithium gives 2-bromo-3-methyl cyclohexene⁸⁶.

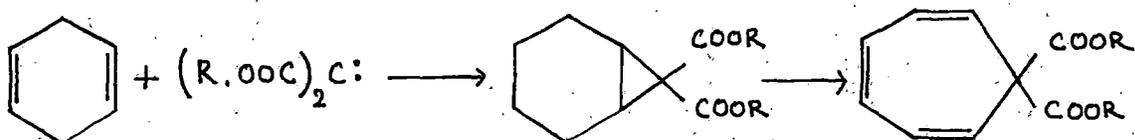


Similar other rearrangements occur with aqueous silver nitrate.

Chloro-dihydrooxepine has been synthesised⁸⁷ from dihydropyran via addition of dichlorocarbene but the analogous synthesis of benzo oxepines failed.

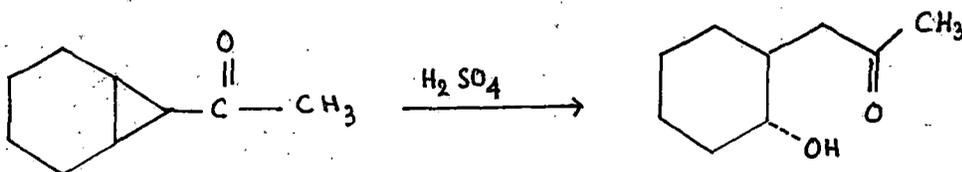
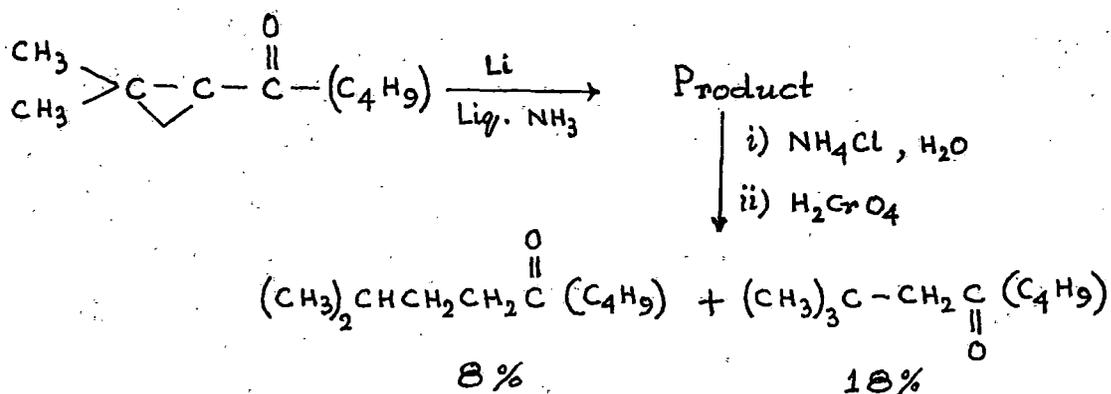


One particular cycloaddition of biscarbomethoxy carbene which seems worthy of mention is the route to 7,7-disubstituted cycloheptatrienes used by Bersen et al⁸⁸

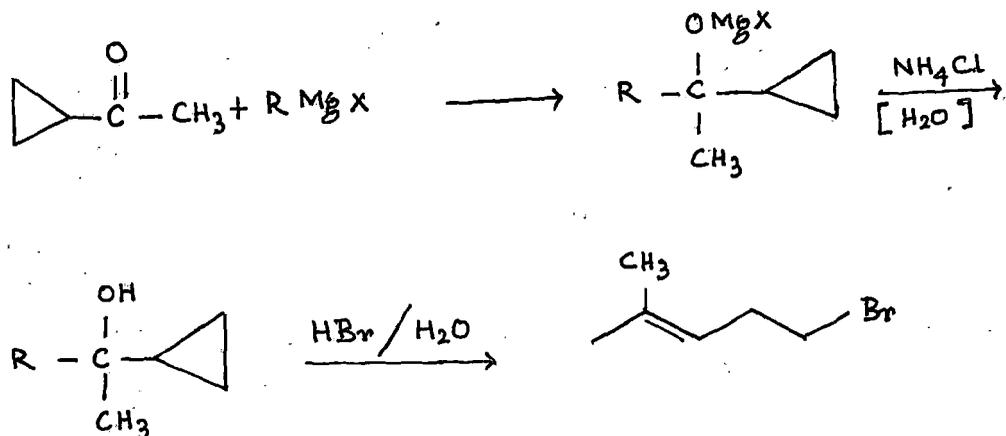


Reductive cleavage of cyclopropyl ketones and cyclopropane derivatives using different metal have been reported. A simple reductive cleavage of cyclopropyl ketone has been effected by irradiating a methanolic solution of cyclopropyl ketone and tri-n-butyl-hydride with ultra-violet light⁸⁹.

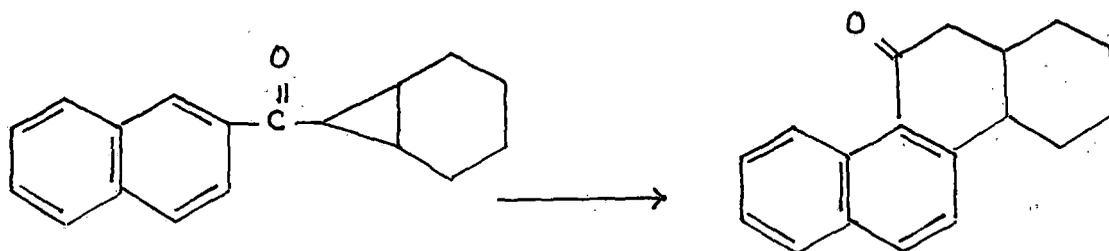
When a cyclopropyl ketone was subjected to lithium in liquid ammonia it broke into two parts in the following way⁹⁰.



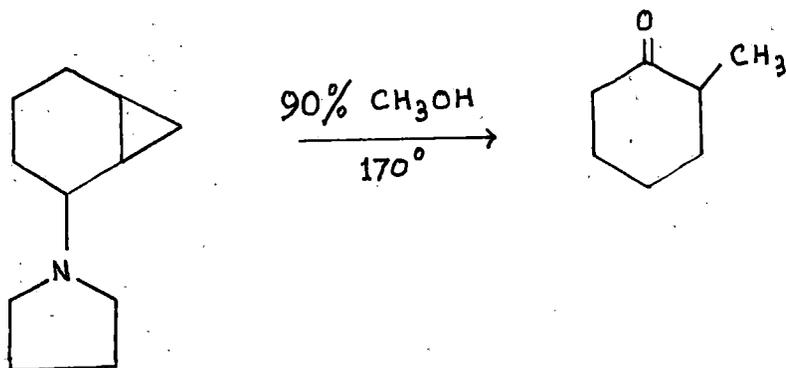
Cyclopropyl methyl ketones give homoallylic bromides and iodides with Grignard reagents followed by hydrolysis with HBr or HI⁹¹.



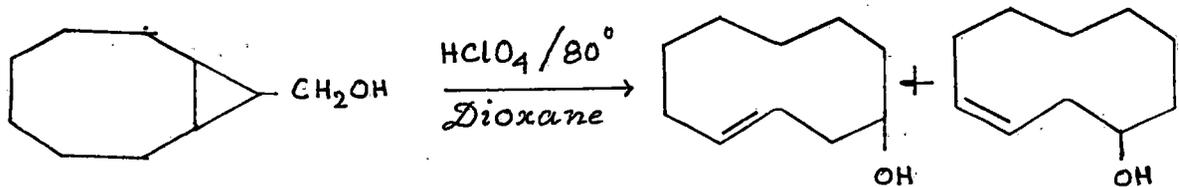
High boiling solvents sometimes favour ring cleavage as in the following reaction where ring opens with simultaneous rearrangement.



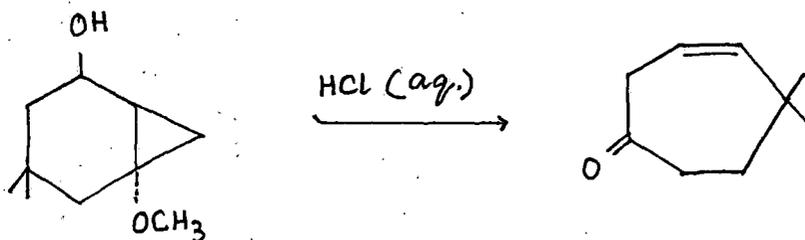
Cyclopropane ring rearranges⁹² in presence of 90% methanol



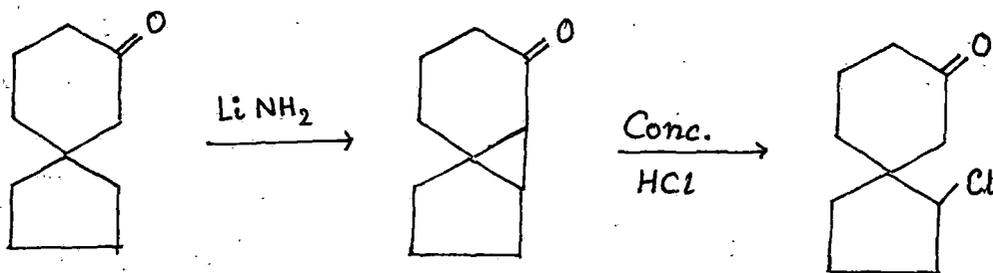
Perchloric acid rearranges cyclopropane when refluxed at 90° in dioxane⁹³.



Wenkart⁹⁴ found that cyclopropane derivative rearranges in presence of aqueous hydrochloric acid. Le



Concentrated hydrochloric acid also affects cyclopropane ring. Lithium amide, p-toluene sulphonic acid in methanol also acts to rearrange cyclopropane derivatives⁹⁵.



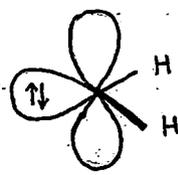
1.5 The spin states of carbenes

A. The Singlet and Triplet States.

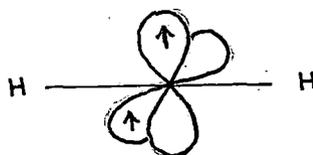
Theoretical chemists have referred for many years, to 'singlet' and 'triplet' methylene and organic chemists have referred to 'carbenes' without much regard for ambiguities arising from spin multiplicity. Electron deficient carbon species, comparable to carbonium ions are designated as 'singlet' carbenes but on the other hand they possess a non-bonding pair of electrons, comparable to that of carbanions. The electrophillic and nucleophillic character of singlet carbenes depend, therefore, largely on the ability of adjacent group to withdraw electrons from or supply of electrons to, the carbene carbon. The carbon species with unpaired spins would therefore be 'triplet carbenes'. Triplet carbenes may be considered as a diradical.

Thus there are two chemically accessible kinds of carbenes, singlet ($^1\text{CH}_2$) and Triplet ($^3\text{CH}_2$). Structurally singlet methylene is a bent species, (X - C - X angle nearer to 120° actually 103°) and the triplet methylene is linear or non-linear species (X - C - X angle close to 180°). Triplet carbenes have two unpaired electrons in mutually perpendicular p-orbitals and singlet carbenes has none⁹⁶. Studies of Herzberg et al demonstrated a linear triplet ground state for carbenes which in the gas phase (flash

photolysis of CH_2N_2 , CHDN_2 , CD_2N_2) is rapidly formed by collisional quenching of the initial short-lived bent or singlet carbene⁹⁷⁻⁹⁹. Singlet ground state for halogeno and mixed halogeno carbene derivatives and triplet ground state for aryl carbenes have been shown.



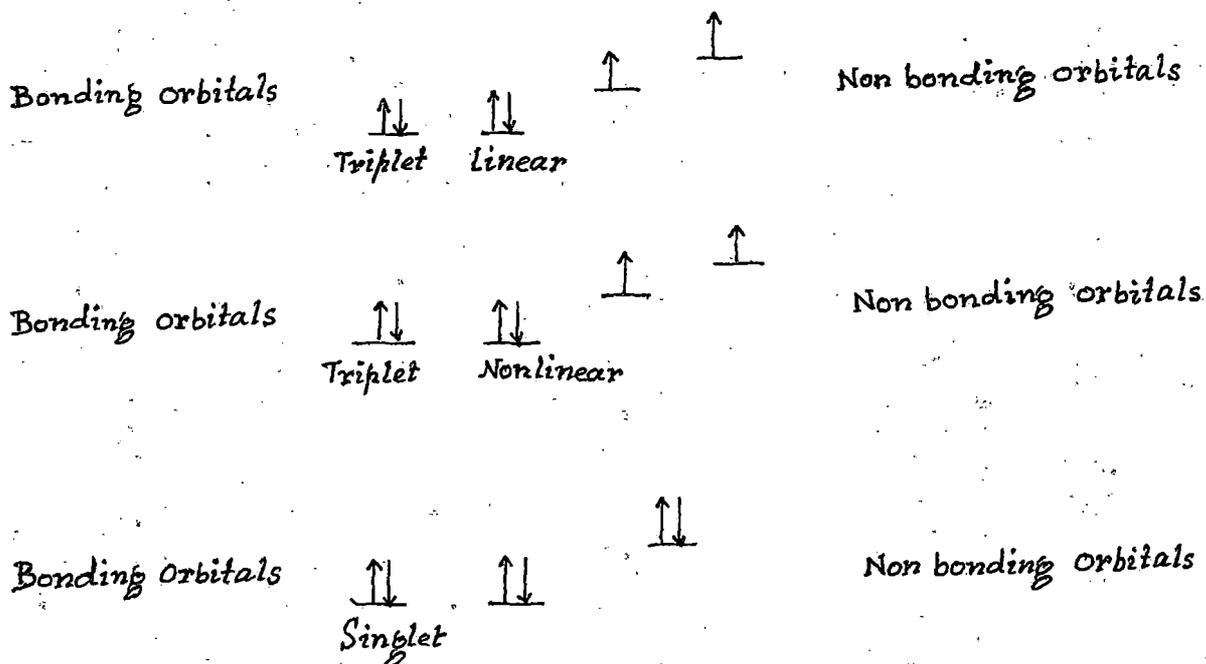
Singlet



Triplet

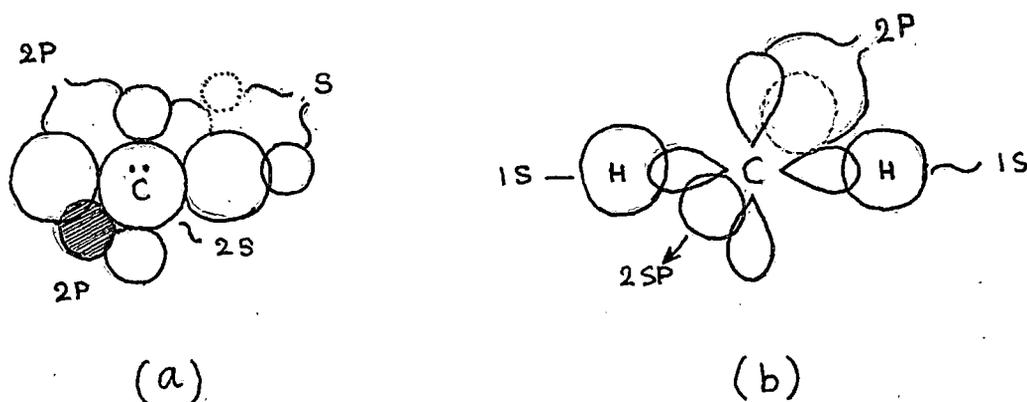
Singlet ground state for halogeno carbene were verified at a very low temperature while triplet carbene gives dimeric product. Carbenes are among the few simple molecules (O_2 is another) that have more than one accessible low energy state. There are four valence atomic orbitals of carbon neglecting the weak 1s atomic orbital for carbon, the 2s and 2p orbitals which contribute to bonding in carbene. Two hybrids of the valence atomic orbitals contribute to the bonds to the central carbon atom, whereas two other combinations of the valence orbitals accommodate the unshared electrons on the central carbon atom.

The two non-bonding molecular orbitals of a carbene are identical only if the H-C-H bond angle is 180° . For all other angles the non-bonding orbitals are non degenerate. The distribution of the non-bonding electrons of the carbene between the valence shell depends on a play off between the orbital energies and the electron-electron repulsion. Three possibilities are illustrated below.



If the difference between the energies of the non-bonding molecular orbitals ^{is} ~~is~~ greater than the energy required to bring a pair of electrons together in a single molecular orbital then both electrons will occupy the lower energy non-bonding molecular electronic state. If, however, the difference in molecular energies is less than the increase in electron-electron repulsion for the non-bonding electrons will occupy different orbitals and then according to Hund's rule a triplet electronic state results.

As shown in fig. 3 if CH_2 were linear, symmetry arguments demand that the two non-bonding molecular orbitals must be degenerate, pure p-atomic orbitals. Hence, the lowest energy linear form of methylene must be a triplet state. However, as Walsh pointed out in 1953, this degeneracy is removed on bonding. As the H-C-H angle is decreased from 180° , one of the two 2p orbitals which comprises the non-bonding orbitals of the linear molecule takes on s character and is lowered in energy³⁶. Again in perpendicular methylene one bonding orbital is a nearly pure 2s carbon orbital (plus some hydrogen 1s), and the other is pure p-orbital. The very large splitting between s and p-orbital would certainly lead to a double occupation of the s-orbital, making the state a singlet.



A lot of mechanistic work have been done which centres on correlation of reactivity and stereochemistry with spin multiplicity and excess energy of the divalent carbon unit ($^1\text{CH}_2$). Moreover, it is known that methylene produced in the flash photolysis of diazomethane adds stereospecifically to olefins and it has been shown to be in the singlet state. Under high pressure and in presence of inert gas inter system crossing to the triplet state occurs ($^3\text{CH}_2$).

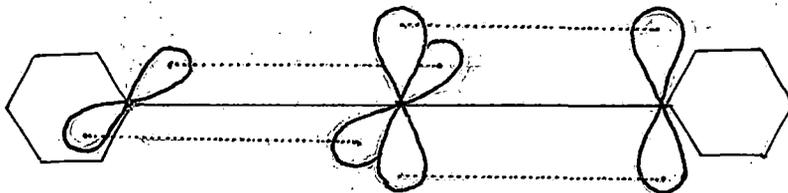
Thus the nature of substituents, nature of medium, presence of catalysts and reaction conditions easily influence the course of reactions of these divalent carbon species.

B. Spectroscopic evidences

Observation and analysis of the spectra of methylene should give very detailed information concerning both ground and excited states of the molecules. In 1950, Herzberg^{97,98} after a 17 years hunt for the elusive methylene obtained spectra of both the lowest singlet and triplet states. Straight forward observations show that since the singlet state decays to the triplet, the latter must have the lower energy content.

E.s.r. spectra of methylene trapped in a xenon matrix at 4.2 K have been one of the most recent achievements in this field^{100,101}. The e.s.r. signal survived warming to 20 K but disappeared upon warming to 77K. Analysis of the results demonstrated the production of a linear or near linear species with the C-H bond length of 1.03\AA which absorbed U.V radiation at about 1414\AA , and a bent species, bond angle $102-103^\circ$, C-H bond length 1.12\AA , which absorbed radiation in the $5500-9500\text{\AA}$ region. Moreover, in the presence of a large excess of nitrogen, the absorption of the short wavelength, linear CH_2 increased at the expense of the long wavelength, bent CH_2 . This experiment pointed to triplet CH_2 as ground state.

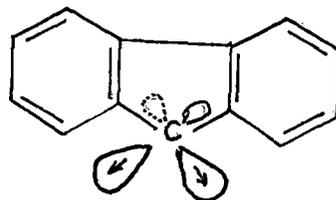
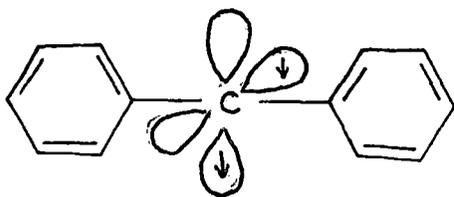
The short lived singlet CH_2 was being degraded through collisions with the moderator, nitrogen and dropping to the more stable species. Wasserman and co-workers¹⁰¹ observed two species with $D = 0.6636 \text{ cm}^{-1}$, $E = 0.002 \text{ cm}^{-1}$ and $D = 0.6844 \text{ cm}^{-1}$, $E = 0.00347 \text{ cm}^{-1}$ respectively. The value of D is related to the average $1/r^3$ where r is the distance between the two spins, so that a high value of D implies a large spin-spin interaction and a close proximity of the two spins. The value of E indicates qualitatively, the magnitude of the deviation of the spin-spin interaction from cylindrical symmetry. The site with the lower D and E values in methylene is believed to allow greater motional freedom, a bent molecule which rotates freely about the long axis will have $E = 0$. Wasserman et al arrived at a H-C-H angle of 136° in good agreement with most theoretical calculations. Angles of $150-155^\circ$ have been estimated for phenyl - and diphenyl carbenes. It was found that for diphenyl carbenes the magnitude $D = 0.4055 \text{ cm}^{-1}$ and $E = 0.0194 \text{ cm}^{-1}$ shows a small dependence on the nature of the host matrix.



The higher D values of diphenyl carbene shows that two unpaired electrons are largely localised on the divalent carbon atom¹⁰².

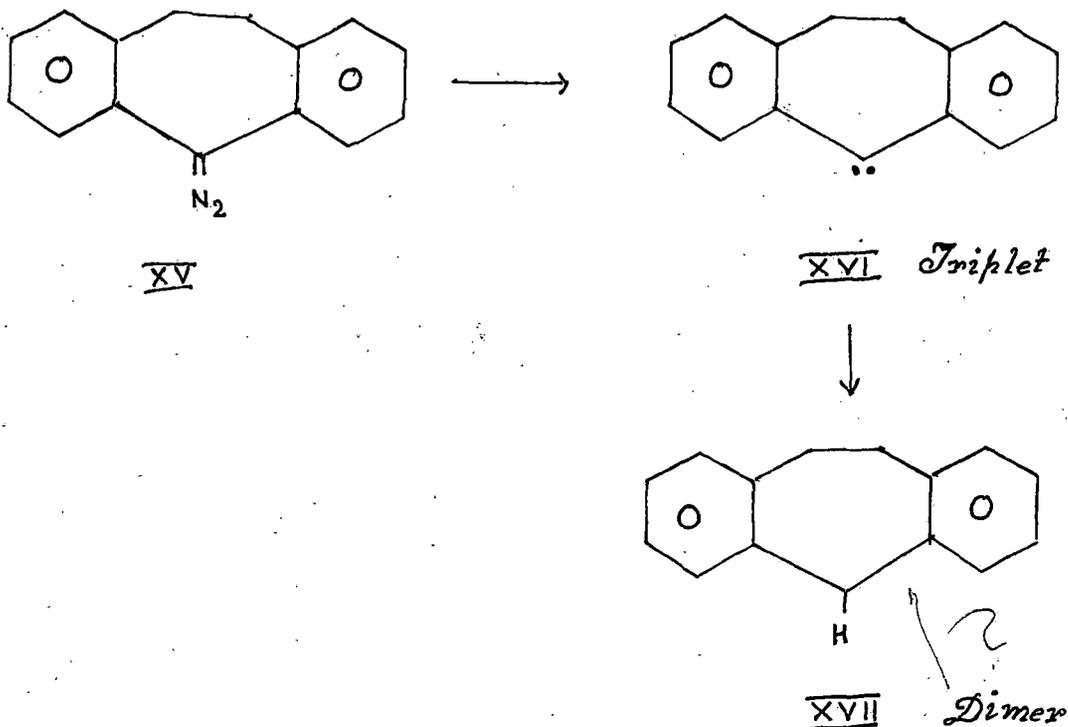
Closs and co-workers reported the long wavelength absorption band of diphenyl carbene oriented in single crystals of 1,1-diphenylethylene¹⁰³. Moritani et al found two new absorption bands in photolysed solution of diphenyldiazomethane, by correlating e.s.r studies, fluorescence, fluorescence excitation and absorption spectroscopy¹⁰⁴.

Gibbons, Trozzolo reported the luminescence, excitation and absorption spectra of diphenyl carbene¹⁰⁵. The same spectrum was obtained for all excitation wavelengths in the range 230-470 nm. The emission was identified as the fluorescence or triplet ground state diphenyl carbene^{106,107}.

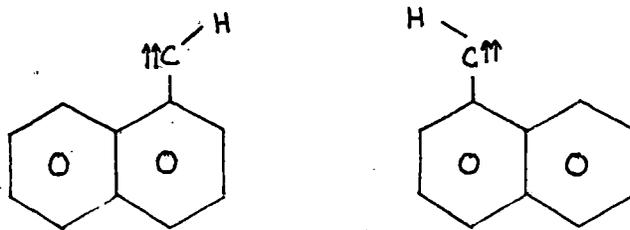


The photolysis of other diaryl diazomethanes gave almost exclusively the corresponding substituted diphenylmethylene which e.s.r studies have shown to be ground state triplet molecules in each case.

The absorptions were considered to involve transitions. Moritani et al^{104,108} have obtained the electronic spectrum of (XVI) ($\lambda_{\max} = 510 \text{ nm}$) by photolysis of the corresponding diazo compound (XV) in a variety of rigid matrices at 77K and also in liquid paraffin at room temperature. The final product is the free radical dimer, and the decay of (I) was assigned to the doublet free radical (XVII).

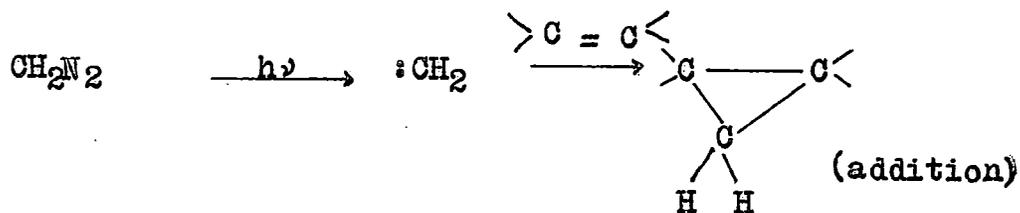
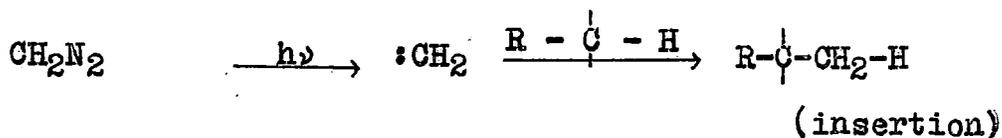


E.S.r experiments also show that at 4K or 77K such triplet as α -naphthylcarbene can exist in two non-interconverting isomeric forms, which are possible since the triplet is not linear¹⁰⁹.



C. Chemical evidences

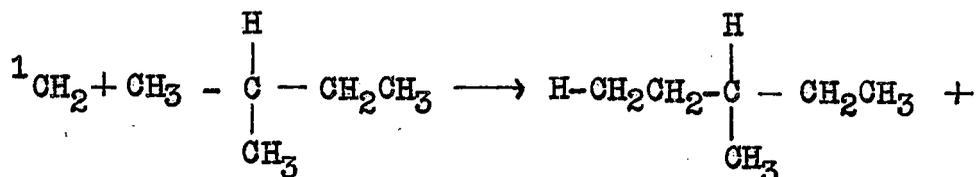
A principal aim in the structural studies of carbenes is to correlate the observed chemistry with the multiplicity, singlet or triplet, of the carbenes formed. Two typical reactions are observed : the insertion into a C-H bond and addition to an unsaturated bond.

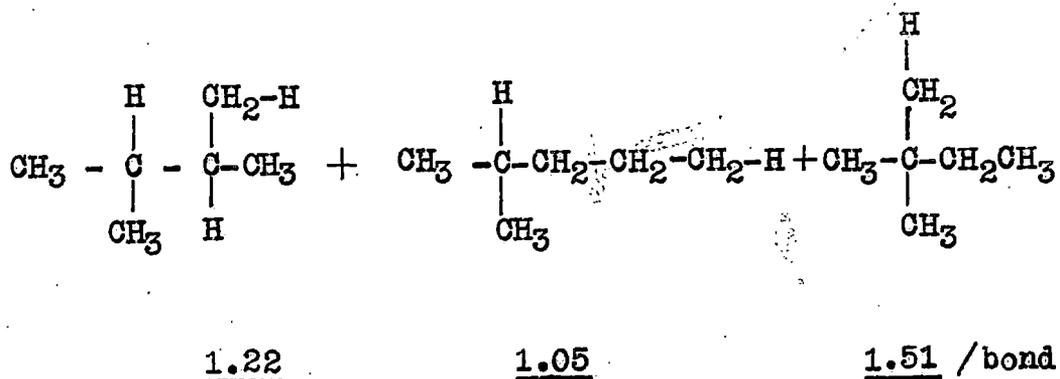


These reactions have been studied in great detail. Singlet and triplet methylene show significantly different behaviour and that study of insertion and addition reactions can distinguish between the two species. However, an opposite view was advanced by Demore & Bensen¹¹⁰. Meerwein, Rathjen and Werner reported in 1942, the C-H insertion products from irradiation of diazomethane in diethyl ether, tetrahydrofuran and isopropanol⁸. Doering, Buttery, Laughlin and Chaudhuri in 1956, recognised the real nature of the photolysis of diazomethane in presence of alkanes⁹. The addition of dichloromethylene to cyclohexene was the first authenticated example of cyclopropanation via carbene, reported in 1954.

The C-H insertion reaction

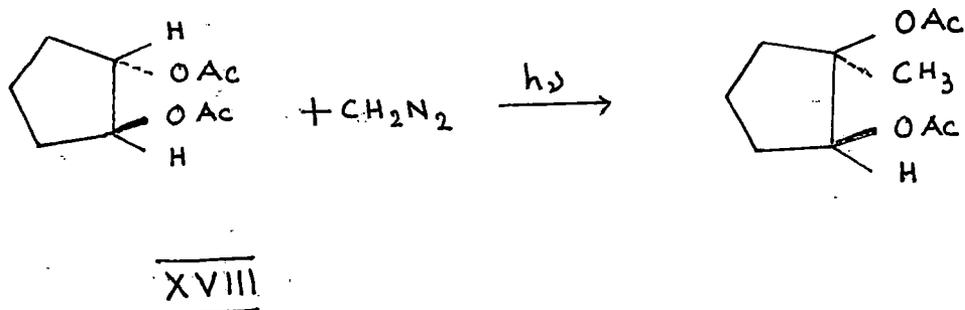
An example of singlet methylene insertion provided by the liquid phase photolysis of diazomethane in 2-methyl butane¹¹¹.





Only slight preference for the tertiary hydrogen (1.51) and secondary hydrogen (1.22) appear.

Studying the configurational relationship between substrate and insertion product, Frauzen reported that methylene reacted with the tertiary C-H bonds in the trans diacetate (XVIII) with inversion^{112,113}.



However, generally the insertion of the carbene has been shown to proceed with retention of configuration¹¹⁴. Optical activity is maintained in the reaction with the methoxy-carbonylcarbene¹¹⁵ and methyl (-)(S)-2-methoxy propionate and silicon-hydrogen bond^{115,116}.

Doering and Prinzbach demonstrated that direct insertion is the major pathway in the photolysis of diazomethane in the absence of moderators and sensitizers¹¹⁷.

Recent nmr experiments have reinforced the view that singlet methylene undergoes direct insertion into C-H bond and that triplet methylene abstracts hydrogen atoms even in the solution.

Ho and Noyes had shown that the reaction of triplet methylene with propane involved abstraction¹¹⁸, since dimeric products, hexane and 2,3-dimethyl butane, were isolated.



Average values for the relative values of abstraction by triplet carbene are primary/secondary/tertiary = 1/2/7.

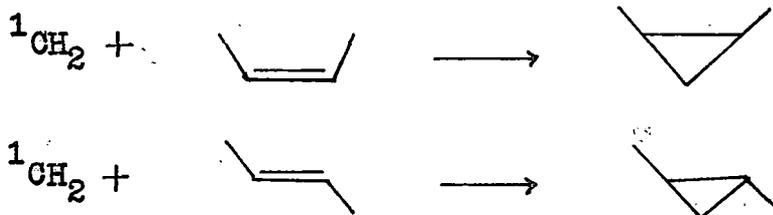
Study of the nmr benzylic proton signal from an irradiated solution of diphenyldiazomethane in toluence and chemically induced dynamic nuclear polarisation (CIDNP)

were very important for the verification of hydrogen abstraction by triplet carbenes¹¹⁹.

Carbon-Carbon double bond addition reactions

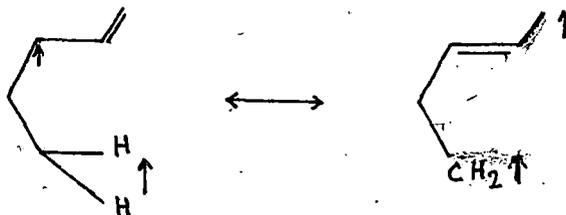
Incisive information concerning the chemical characteristics of singlet and triplet carbenes comes from study of addition reactions involving C-C double bonds^{40,120-122}.

As in C-H insertion, singlet methylene adds stereospecifically in a concerted step: both bonds of the cyclopropane are formed simultaneously since such a step may occur with spin conservation. The addition of ¹CH₂ (from photolysis of diazomethane in liquid phase) to cis-2-butene and trans-2-butene yield only ^{cis}-1,2-dimethylcyclopropane and trans-1,2-dimethylcyclopropane, respectively. These additions are stereospecific, the geometrical relationship of the olefinic substituents is preserved in the products.



This behaviour has been taken as evidence that the addition of ¹CH₂ to an olefin is a direct reaction and no diradical intermediate intervenes. Triplet methylene generated in the

gas phase by the mercury photosensitised decomposition of ketene adds to olefins with greater discrimination e.g. its addition to butadiene is 6.6 times faster than isobutene; the corresponding ratio with singlet methylene is 3.2. The increased preference of $^3\text{CH}_2$ for butadiene can be attributed to the radical character of this addition, which presumably involves a diradical intermediate somewhat stabilised by allylic resonance.

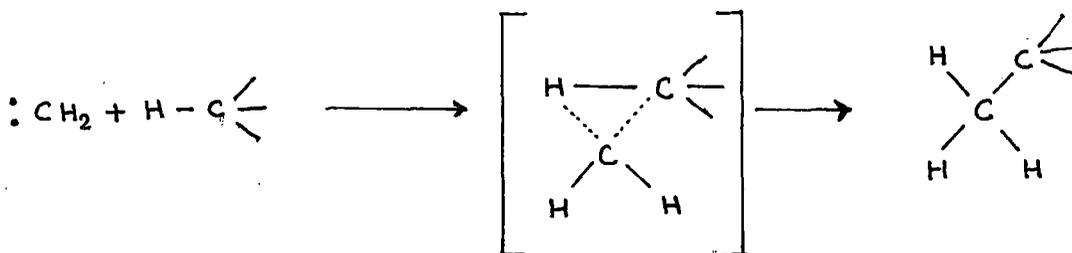


The addition of triplet methylene to cis- and trans-2-butenes is an indirect, two step reaction and takes place non-stereospecifically. This phenomenon is most readily understood in terms of Skell-Woodworth hypothesis.

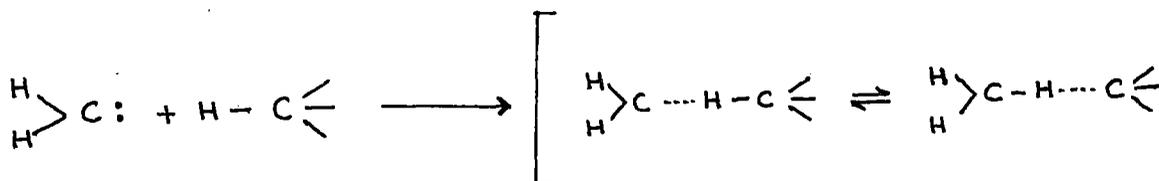
A number of factors can influence the stereospecificity of the addition, notably solvent cage effects or unusual rapid intersystem crossing. In spite of some difficulties, Skell's criterion appears to work well in practice in distinguishing between singlet and triplet carbene species.

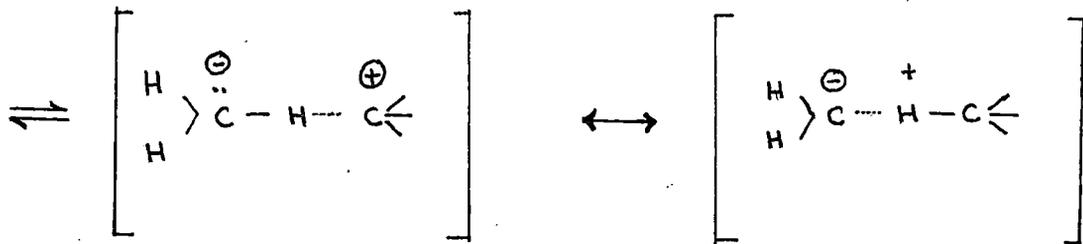
Nature of transition state in the C-H insertion and C = C addition.

Two hypothesis concerning transition state for C-H direct insertion have been presented. Doering & Skell proposed that methylene being a vigorous electrophile a triangular transition state occurs for direct C-H insertion^{40,117,122,123}. The triangular transition state accommodate the one step nature of singlet methylene insertion.



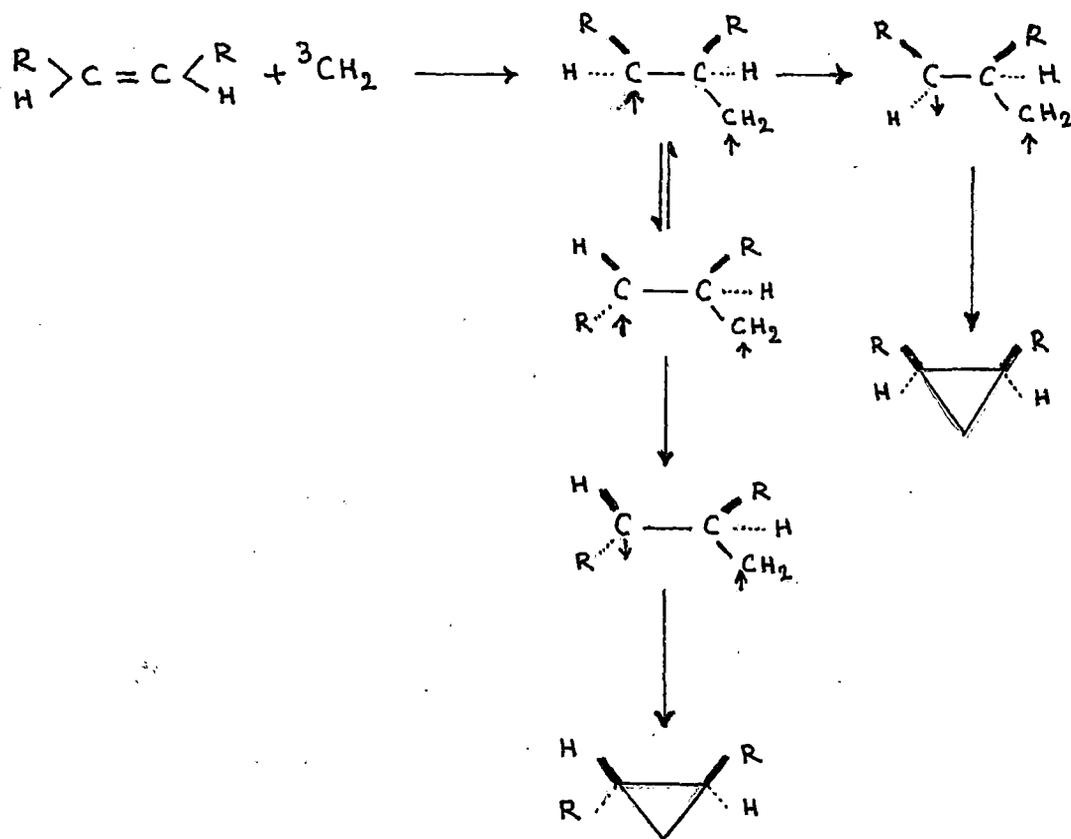
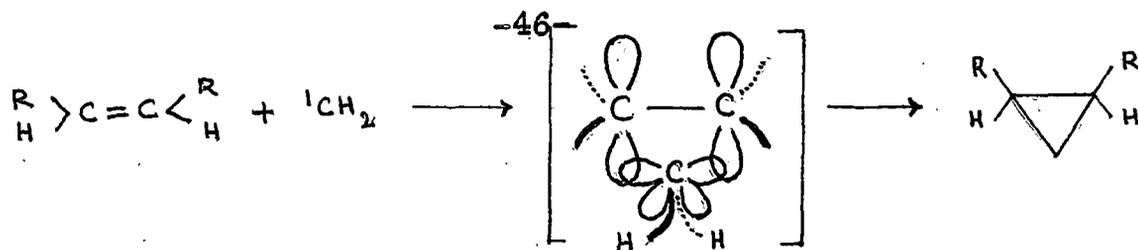
Demore and Benson proposed, on the other hand, transition state with diradical character is probably intended, with stabilisation due to contribution by ionic terms to the wave function¹²⁴.





Evidences support one step, three centre, direct insertion mechanism for singlet ($^1\text{CH}_2$) carbene and two step abstraction recombination mechanism for triplet ($^3\text{CH}_2$) carbene.

However, Skell argued that the addition of a triplet carbene to an olefin would generate a triplet trimethylene intermediate, in which rotation about the single C-C bonds would be at least as rapid as the spin inversion needed before formation of the final cyclopropane C-C bond could occur. The addition of a triplet carbene to cis-or- trans-2-butene should then yield both cis- and trans-1,2-dimethyl cyclopropanes. On the other hand addition of a singlet carbene could be stereospecific, since there would be non spin restriction on the simultaneous formation of both cyclopropane C-C bonds.



Factors influencing the reactivity of Carbenes

Various factors influence the relative reactivities of carbene reactions¹²⁵. Mainly these are of two types such as

- i) Steric effects
- ii) Electronic effects

To discuss the (i) steric effect the reaction of dichlorocarbene is a good example of steric hindrance to carbene addition. A 1-cyclohexyl substituent is 7.4 times less effective than 1-methyl substituent at promoting the addition of dichlorocarbene to cyclohexene. Even phenyl, which should help electronically, is less effective than methyl, and a 1-naphthyl substitution retards the addition¹²⁶. Similarly $:\text{CBr}_2$ experiences greater steric hindrance to addition than $:\text{CCl}_2$ ¹²⁷. Relative to cyclohexene, styrene and 2,4,6-trimethyl styrene are equally reactive toward $:\text{CCl}_2$. Toward $:\text{CBr}_2$, styrene is more than 3 times as reactive. The hindrance arises at the ortho substituents.

The photolysis of methyl diazo acetate in trimethylsilane gave three major products¹²⁸. The rates show that an α -secondary C-H bond (2.5) is more reactive than a primary α -C-H bond (1.0), which in turn is less reactive than a primary β -C-H bond (1.2). The difference was explained by steric hindrance to carbene insertion. The reaction of 1,1,3,3-tetramethyl-1,3-disilacyclobutane gave carbene insertion into the Si-C bond, as has been observed with dichlorocarbene¹²⁹, as well as insertion into primary and secondary C-H bonds in comparable rates.

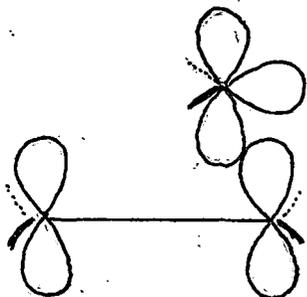
Photolytically generated aryl carbenes¹³⁰ do not exhibit characteristic steric effect with simple alkanes. These appear to be a substantial selectivity difference between photolytically¹³¹ and thermally¹³² generated carboethoxy carbene. The former does not discriminate between cis-and trans-butene; the latter prefer cis-butene by a factor of 2.8. The role of steric effect here is not yet defined.

(ii) Electronic effects

Electronic effects may be initiated due to factors discussed below.

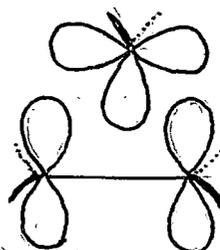
(A) Olefinic substitution

Carbene addition to an olefin has been considered as an electrophilic process. A theoretical analysis of the addition of $^1\text{CH}_2$ to ethylene suggests initiation of the reaction as in (XIX), a ' π -approach' in which the vacant p-orbital of the carbene begins to overlap with the π -system. As reactants move along the reaction co-ordinate towards product geometry, the ' π -approach' goes over to a ' σ -approach'¹³³. Transfer of electron density from the olefins' π -system to the carbene's p-orbital occurs; this is an electrophilic addition^{40,125,130,134}.



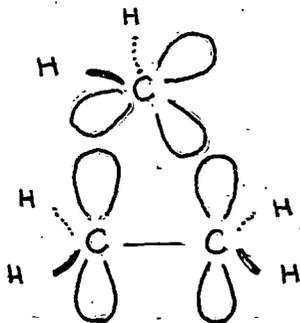
π - approach

XIX

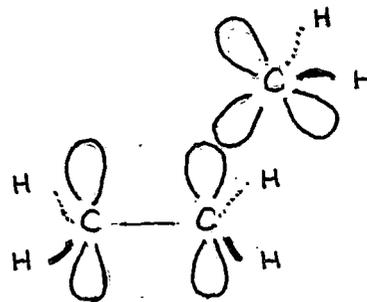


σ - approach

More recent calculations suggest that ' π -approach' (XXa) is energetically preferable to a ' σ -approach' (XXb) in the addition of singlet methylene. Addition of CF_2 is calculated to follow a similar course, with less charge transfer from olefin to carbene in the transition state¹³⁵,



XX a



XX b

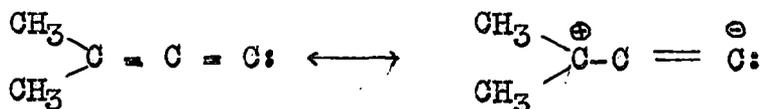
Related calculations for additions of CH_2 and CF_2 to isobutene again suggest that Va is preferred to Vb, but only by a small energy difference. The intramolecular reactions of thermally generated carboethoxy carbene with benzene derivatives are correlated by Hammett treatment $\rho = 0.38$ ($\delta\rho$)¹³⁶. Here, too, the carbene acts as an electrophile, impinging on the aromatic π -system.

Some carbenes like thio-xanthenylidene⁷⁷ are nucleophilic also M.O calculations show nucleophilic character and triplet ground state for these carbenes¹³⁷.

(B) Carbenic substituents

Substituted carbenes develop variations of reactivity toward simple alkenes with the exception of butadiene.

2,2-diphenyl cyclopropylidene¹³⁸ and dimethyl ethylidene carbene show for more selectivity than $:\text{CH}_2$ due to steric effect. The selectivity of dimethylvinylidene carbene¹³⁰ is independent of precursor; it appears to lie between that of $:\text{CCl}_2$ and $:\text{CBr}_2$. Resonance stabilisation of the carbene (XXI) is suggested to account for its selectivity, the vacant carbenic p-orbital is part of an allylic cation



XXI

system.

The substituted phenyl carbenes also show only modest ability to distinguish between simple alkenes⁷². The isobutene/trans-butene reactivity ratio varies with carbenic aryl substituent in the order $m\text{-Cl} > p\text{-Cl} > \text{H} > p\text{-CH}_3 > o\text{-CH}_3$ which parallels the expected order of increasing carbene stability.

(C) Highly stabilized carbenes

If a carbene can be made less electrophilic by overlap of its vacant p-orbital with electron-donating substituents, then ^{with} continued increase of the donating power of such groups to lead ultimately toward olefins. Alternatively, the carbenic centre could be incorporated in an aromatic π -system such as cyclopropylidene. X

(D) Triplet carbenes

It is suggested that the triplet carbene should show a 'radical like' selectivity toward olefins. Such addition should be a two-step procedure, involving a triplet 1,3-biradical intermediate, triplet carbenes are expected to show exalted reactivity toward such substrates as 1,3-dienes, styrenes and 1,1-diphenylethylene. Here the intermediate is resonance stabilised. Singlet carbenes, which add to olefins in one step, are not expected to show unusual

reactivity towards these substrates.

(E) Carbenoids

There are 'intermediates' which exhibit reactions qualitatively similar to those of carbenes without necessary being free divalent carbon species¹³⁰.