CHAPTER - I

A general introduction to Carbene Chemistry.

Section A : Historical Background

The possibility that divalent carbon compounds might be intermediates in certain chemical reactions was suggested more than hundred years ago to account for the products of the alkaline hydrolysis of chloroform (1). Divalent carbon intermediates were also involved from time to time during the first half of the present century, particularly as intermediates in the decompositions of diazoalkanes and of ketenes, but it was not until last decade that the 'carbenes' and their reactions were subjected to close scrutiny.

The generic name "carbene" was 'collaborately conceived by Doering, Winstein and Woodward (2), to be descriptive methylene (CH_2), in analogy with the derivation of "carbinols" methanol.

One of the major problems of carbene chemistry has been the determination of the configuration of the non-bonding electrons on the divalent carbon atom. It has now been established that in most, but not all divalent carbon intermediates which have been identified, these electrons are paired, i.e. their spin quantum numbers have opposite signs. It has been suggested that the term carbene should be reserved for those species, while those with unpaired electrons, and which exibit the reactions characteristic of free radicals, should be termed methylenes(3).

The current interest in the divalent carbon species seems to date from 1950, when Hine published his first paper on a reinvestigation of the alkaline hydrolysis of chloroform, and concluded that dichloro carbene (: CCl_2) was probably an intermediate in this reaction (4).

It was not until 1954 that Doering and Hofmann showed that dihalo carbenes from the haloforms could be trapped by addition to olifins to give cyclopropane derivatives (5).

Thus cyclohexene, chloroform (or bromoform) and Potassium t-butoxide gave 7,7-dihalo nor carane - (equation 1).

.. (1)

While α-elimination reactions have furnished a route to the dihalocarbenes, and more recently, to variety of other substituted carbenes, a second route to divalent carbon intermediates involves the thermal, photo chemical or catalytic decomposition of diazo alkanes and ketenes. Dyakanov ( ) made an extensive study on the decomposition of diazomethane, and more particularly of ethyl diazoacetate, catalysed by copper or copper salts in the presence of olefin which resulted in cyclopropane derivatives.

The interest in divalent carbon may, perhaps, be divided into three main categories. Two of these are of a physiochemical nature; namely, the study of the energetics of methylene production and of its reactions, and the configuration of the non-bonding electrons.

The third major aspect of carbene chemistry concerns the synthetic utility of divalent carbon intermediates with olifins. A further synthetic application makes use of the "insertion reaction", in which methylene itself, and more reactive carbenes can directly insert into a carbon hydrogen bond (Equation-2).

.. (2)

Now attention is drawn to the electrophilic and nucleophilic character of divalent carbon species. Singlet carbenes are electron deficient species, comparable to carbonium ions; on the other hand they possess a non-bonding pair of electrons, comparable to that of carbanions.

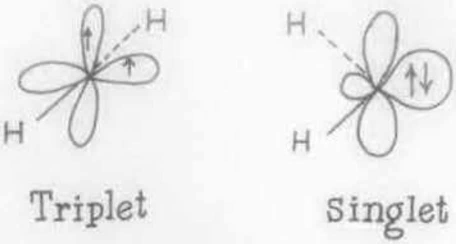
The electrophilic and nucleophilic character of singlet carbenes depends, therefore, largely on the ability of adjacent groups to withdraw electrons from or supply electrons to, the carbene carbon. Triplet carbenes may be considered as diradical. The formal relationship of carbenes to other simple intermediates is presented in table-1.

Table - 1

Name of the intermediates	Number of covalent bond	Nos. of valence Electrons.
Carbanions $\geqslant C :^{(-)}$	3	8
Radical $\geqslant C \cdot$	3	7
Carbonicumion $\geqslant C^{(+)}$	3	6
Carbene $> C:^{\ominus}$	2	6

Section B: Singlet and triplet state of Carbene.

Thus there are two chemically accessible kinds of carbene, singlet ($^1CH_2$) and triplet ($^3CH_2$). As constructed with carbon 2s and 2p and the orbitals of hydrogen, halogen etc., the triplet methylene is linear or near-linear species (X-C-X angle close to 180°) singlet methylene is a bent species (X-C-X) angle nearer 120° actually 103°. Triplet carbene has two unpaired electrons in mutually perpendicular p orbitals and singlet carbene has none (127). Studies by Hertzberg and associates demonstrated a linear triplet ground state for carbenes which, in the gas phase, is rapidly



Triplet Singlet

Fig- 1

formed by collisional quenching of the initial short lived bent or singlet carbene.([illegible], [illegible], 5).

Studies of carbenes have shown singlet ground state for halogeno and mixed halogenocarbene derivatives and triplet ground state for arylcarbenes. The latter are probably generated as singlets but trapped in a solid host at a very low temperature, they decay to their triplet ground state more rapidly than reacting with neighbouring molecules.

Studies at very low temperatures, verify singlet ground states for halogeno carbenes. The reaction of a triplet carbene gives dimeric product. Several aspect of carbene chemistry have fascinated a large number of chemists during the past quarter of a century. First, their reactions are novel insertions into σ bonds addition to π bonds, and the various carbene rearrangements are all sufficiently distinctive from the reactions of other species to excite curiosity about their scope, mechanisms and synthetic possibilities. Second, the electronic structures of carbenes are unusual in that most carbenes have two low-lying electronic states near enough to each other in energy both may participate in the chemistry of the intermediate. Third, many carbenes are small enough to be treated by a variety of quantum mechanical calculations that provide insight into carbene structure and reactivity.

Carbenes are, among the few simple molecules (O_2 is another) that have more than one accessible low-energy state. If we exclude the carbon 1s atomic orbital, which is not strongly involved in chemical bonding, there are four valence atomic orbitals of carbon, the 2s and the three 2p orbitals, that contribute to bonding in carbenes. Two combinations or 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 two valence shell non-bonding molecular orbitals has been an important theoretical problem. The distribution depends on a play off between the orbital energies and electron-electron repulsion. Three possibilities are displayed in Fig. 2.

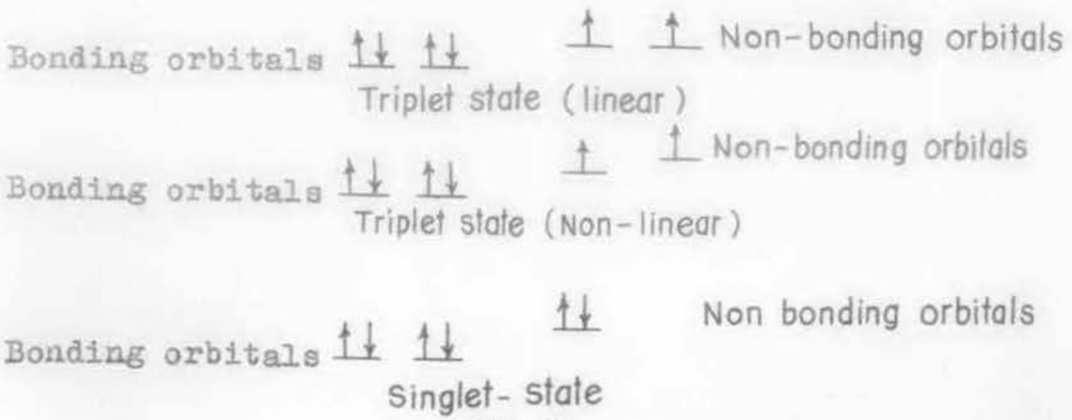
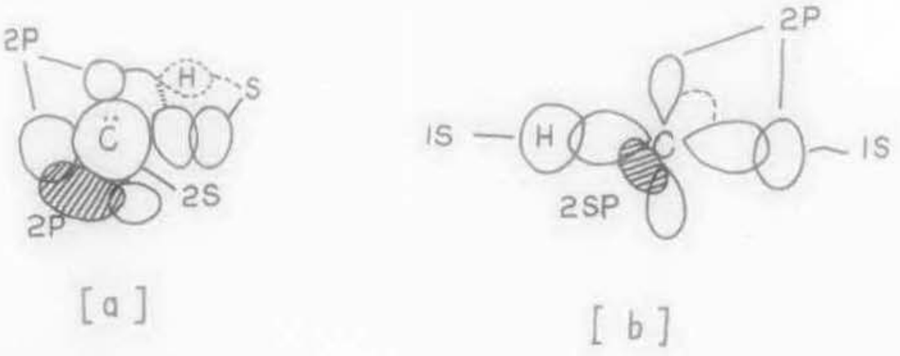


Fig- 2

If the difference between the energies of the non bonding molecular orbitals 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 orbital energies is less than the increase in electron-electron repulsion energy for the non-bonding electrons when they are brought together in the same special orbital, then the non-bonding electrons will occupy different orbitals. Hund's rule tells us that two electrons occupying different orbitals achieve minimum energy when their spin functions are the same, and thus a triplet electronic state results.

In this description we have used a simple picture of molecular structure which assumes that an acceptably accurate description of a molecule can be given in terms of the unique allocation of electrons to molecular orbitals (7). Even in this simple picture we should add that the energies of the four bonding electrons are affected by the non-bonding electrons. Therefore, we should be comparing the sum of all the orbital energies, bonding and non bonding, with the sum of all electron-electron repulsion energies, bonding and non bonding, to obtain estimates of the total energy for each allocation of electrons to carbene molecular orbitals.

Two extremes of carbene molecular structure are more easily described than the intermediate structures that belong to most real carbenes. 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 two 2p orbitals which comprise the non bonding orbitals of the linear molecule takes on S character and is lowered in energy (8). At the other extreme, in perpendicular methylene one bonding orbital is a nearly pure 2s carbon orbital (plus some hydrogen 1s), and the other is pure P. The very large splitting between S and P would certainly lead to a double occupation of the S orbital, making the state a singlet.



(a) p^2-methylene (Perpendicular); (b) SP Methylene (linear).

Fig. 3

Walsh was the first to correlate the molecular orbitals of linear methylene (designated by the σ and π Symmetry classifications of the D_{2h} point group) with the molecular orbitals (designated by the a_1, a_2, b_1, b_2 irreducible representations of the C 2 point group) of the bent molecule. Such correlation diagrams are now called Walsh diagrams. Walsh presented qualitative arguments about the energy change for each orbital, with change in bond angle for AH_2 molecules. Comparison of Walsh's original diagram of 1953 Fig. 4 with one based on an *ab initio* calculation for CH_2 made in 1969 Fig. 5 shows considerable similarity. The b_2 (σ) orbital is antibonding between the hydrogens but bonding between carbon and hydrogen. Therefore an increase in H-C-H angle decreases repulsion between the bonding electrons and decreases the b_2 molecular orbital energy. The a_1 (σ) molecular orbital increases in S character as the bond angle increases, and this factor was believed by Walsh to lead to a decrease in energy, that is, a stronger σ bond.

The molecular orbital energies vary in derivatives of methylene (:CRR') depending on the groups attached to the divalent carbon atom (9). Therefore, the determination of the electronic structures of the lowest energy and first excited states of carbenes has been a problem requiring sophisticated theoretical calculations and elaborate spectroscopic experiments.

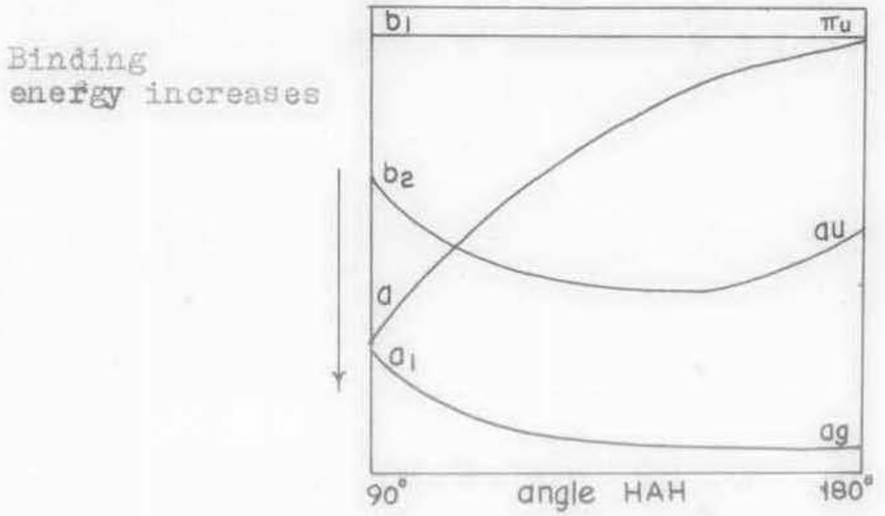


Fig-

Intuitively inferred orbital energies in methylene as a function of bond angle (A.D).

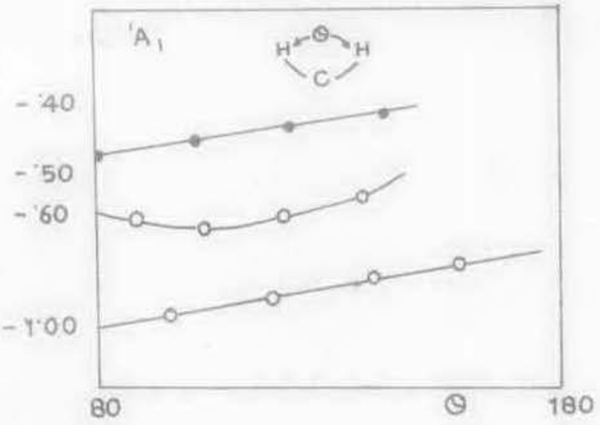


Fig- 5

Calculated variation of orbital energies with bond angle in 1_A, state of methylene.

According to the Frontier orbital theory if the carbene approaches the olefin in a straight line the HOMO/LUMO interactions would be antibonding. But as the reaction is common the anomaly is explained by the probability of a sideways approach at the initial stage when overlap begins to develop (12).

A lot of mechanistic work has been done which centres on correlation of reactivity and stereochemistry with spin multiplicity and excess energy of the divalent carbon unit. ( ). Moreover it is known that methylene produced in the phase photolyses 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 intersystem crossing to the triplet state occurs (30).

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.

SPECTROSCOPIC EVIDENCE

Observation and analysis of the spectra of a species as simple as methylene should give very detailed information concerning both ground and excited states of the molecule.

Assignment of a group lines at 4050 A^{o} in the spectra of comets to methylene (10) gave a great deal of useful guidance in early discussions of methylene even though it later turned out the lines were due to C_3 rather than CH_2 (11). In 1959 Herzberg (12,13) finished a 17 years hunt for the elusive methylene and 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.

Attempts to preserve CH_2 for spectroscopic observation by matrix isolation (14,15) have let to ambiguous results. Pimental and his co-workers (14,16) irradiated diazomethane in argon and nitrogen matrices at 20°K. Under various conditions. They observed infrared absorption bands at 4182, 3968 possible methylene absorption bands.

A new band system spread from 5500 - 9500 A° was observed when higher ratios of CH_2N_2 / N_2 were used. Apparently the first product of photolysis has long wave length absorption but decays rapidly to the triplet absorbing at 1415 A°. The rotational fine structure of the three bands indicated the absorbing species is bent with a bond angle of about 103° (C-H) distance = 1.12 A°) and a linear upper state. No triplet splitting of spectral lines could be found.

It is interestingthat Herzberg also saw faint bands in the 3000 - 3500 A° region. **Appearance** of the lines was not favoured by condition which maximize the triplet absorption at 1415 Å. Consequently Herzberg feels species must be $^1A_1$. If the absorption is to be associated with the sharp lines found by Robinson and McCanly, and attributed to CH_2, a problem arises since the species seen at 4.2°K, was obviously long lived. Shortly before Harrison's paper was submitted for publication once again one of the periodic revolutions in the experimental view of the geometry of ground state methylene occurred. Schaefer has described ESR spectroscopic evidence for the structure of methylene as "an experimental break through" (17).

In the August 1, 1970, issue of the Journal of chemical physics Berrheim, Bernaard, Wang, Wood and Skell reported the detection of the ESR spectrum of triplet methylene observed from the photolysis of diazirine in solid Xenon at liquid helium (4.2°K) temperature (18). The D and E Zerofield parameters that measure the dipolar interaction of the unpaired electrons and their deviation from cylindrical symmetry, respectively, were deduced from the spectra. Since E was found to be non zero, ground state triplet methylene was certainly bent at least slightly in the xenon environment. Shortly thereafter in November 1970 Wasserman, Yager and Kuck also reported the ESR spectrum of triplet methylene from the photolysis of diazomethane and diazirine in xenon at 4.2°K. These workers deduced on H-C-H angle of 128-143° from the zerofield splitting parameters, with the most probable value. 136°, in splendid agreement with latest theoretical predictions. It should be pointed out that the bond angle is related in a quite complicate manner to the magnitude of E for a stationary unperturbed methylene molecule. Very soon Bernheim, Bernard, Wang, Wood and Skell deduced and even more precise bond angle, 137.7°, from the ^{13}C hyperfine interaction in CD_2 (20). It was noted that the isotopic shift in the zerofield splitting parameters observed in going from CH_2 to CD_2 might be due to either rotational motion or a matrix interaction.

In 1971 Herzberg and Johns cited the recent ESR work and also the theoretical studies of Harrison and Allen and Bender and Schaefer as indicating that the ground triplet is bent (21). On the assumption that the molecule is bent, reanalysis of the spectroscopic data gave a bond angle of 136° and bond length of 1.078A°, in splendid agreement with latest theoretical and ESR spectroscopic conclusion.

Such measurement has been used to characterize triplet states substituted carbenes also (21, 23, 24). These indicate that diphenyl carbene, phenyl carbene and fluorenylidene have triplet ground states. The magnitude of the triplet splitting at zerofield and the hyperfine interactions with protons indicate that in diphenyl carbene, the two phenyl groups lie close to, but not exactly, perpendicular planes. Surprisingly, the extent to which the unpaired electrons are constrained to stay at the central carbon atom is about the same in diphenyl carbene and in fluorenylidene despite their different geometry. Fig. 6.

Diphenyl methylene

Fluorenylidene

Fig. 6

CHEMICAL EVIDENCE

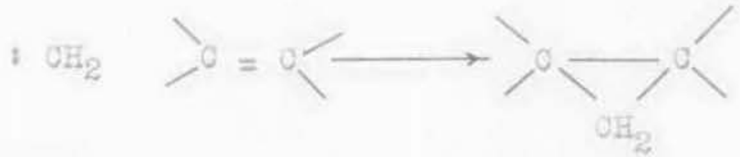
Carbenes of all sorts have been detected by a variety of spectroscopic techniques, and valuable structural information has been obtained. The spectroscopic results have been reviewed recently (25).

Now attempts to draw inference concerning the spin state of methylene from chemical reactivity, and vice-versa, have a long and some times undistinguished history. Early attempts to characterize methylene in gas streams involved removal of tellurium, selenium, aresnic and antimony mirrors, and the tellurium-method (26) was favourite for detection until it was shown (27) that mirror removal was due largely to reaction with other species, at least when methylene was produced by photolysis of ketene. Methylene and its derivatives would probably react with many other materials if given the chance, since in either the singlet or triplet state, it is a highly reactive species. It is doubtful that any but the most detailed study of randomly chosen reactions would yield much information concerning the characteristic chemical properties of singlets and triplets. In retrospect, assumptions such as low reactivity of singlet methylene (28) or clearly "radical like reactivity" of the triplet seem either wrong or harmfully oversimplified.

Reactions which have been most studied insertion reactions (eqn. 3)

$$
\begin{array}{l}
:CH_2 + H_2 \longrightarrow CH_4 \\
:CH_2 + RH \longrightarrow RCH_3
\end{array}
\quad \ldots (3)
$$

and addition to carbon-carbon double bonds. (eqn. 4)



... (4)

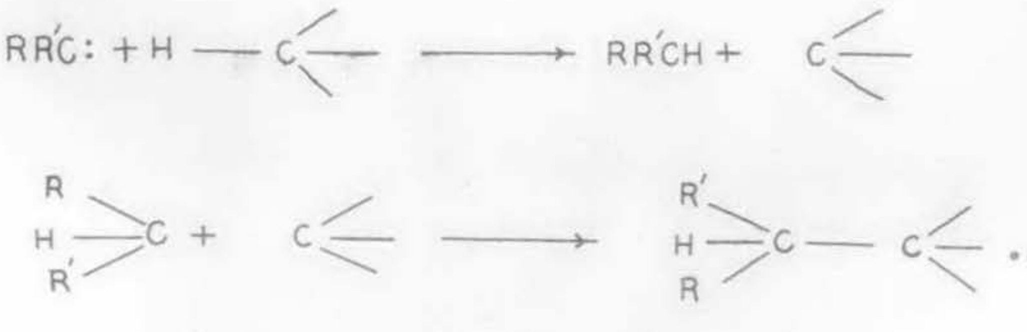
These reactions have been studied in great detail and much of the related discussions relate to chemistry of singlets and triplets. Singlet and triplet methylene show significantly different behaviour and that study of insertion and addition reactions can distinguish between the species. An opposite view was given by Demore and Benson (29).

Meerwein, Rathjen, and Werner reported in 1942 C-H insertion products from irradiation of diazomethane in diethyl ether, tetrahydrofuran, and isopropanol (31). It was not until 1956, however, when Doering, Buttery, Laughlin and Chaudhuri investigated the photolysis of diazomethane in the presence of alkanes, that the real nature was recognized (32). The addition of dichloro methylene to cyclohexane, reported in 1954, was the first authenticated cyclopropanation via carbene or carbenoid species (33). The addition of methylene to olefins was established in 1956 (34,35).

THE INSERTION REACTIONS

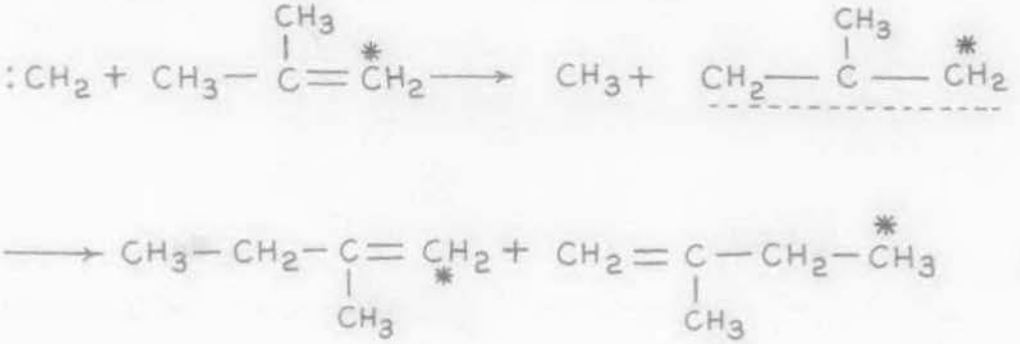
Stoichiometrically the C-H insertion reaction takes the form:

A mechanistic ambiguity in description of the reaction was recognised quite early (36,37). Abstraction of a hydrogen atom followed by coupling of the radical pair could give rise to the same products as concerted insertion. (eqn. 5).



..(5)

Doering and Prinzbach demonstrated that direct insertion is the major path was in the photolysis of diazomethane in the absence of moderators and sensitizers (37). Reaction of methylene with labeled isobutene gives the rearranged product expected from the radical path was in only 8% yield in the gas phase and 2% yield in the liquid phase. This means that a maximum of 16% of the methylenes follow the radical mechanism in the gas phase and 4% in the liquid phase. (eqn. 6)

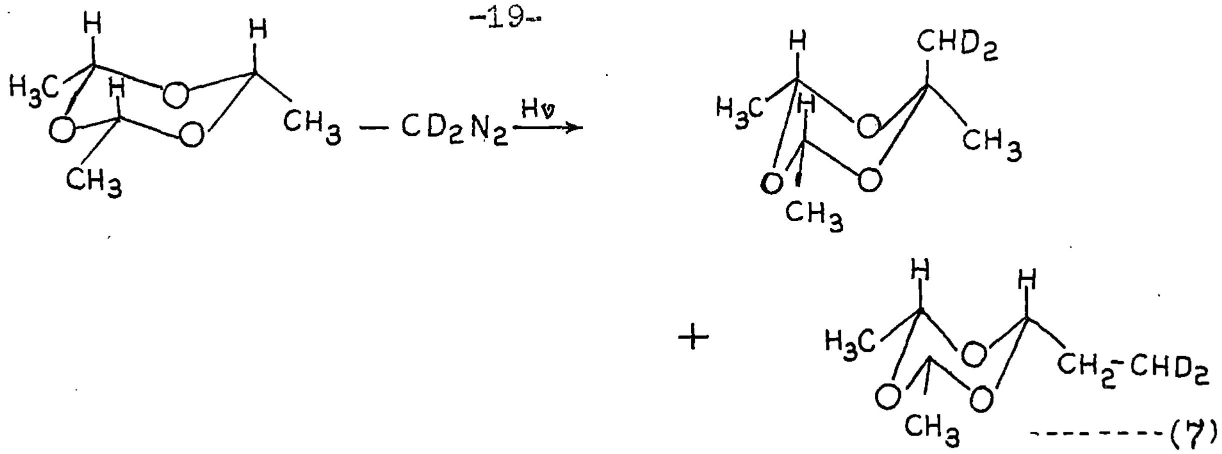


$$:CH_2 + CH_3-\overset{\overset{CH_3}{|}}{C}=\overset{*}{C}H_2 \longrightarrow CH_3 + \underline{CH_2-\overset{\overset{CH_3}{|}}{C}-\overset{*}{C}H_2}$$

$$\longrightarrow CH_3-CH_2-\underset{\underset{CH_3}{|}}{C}=\underset{*}{C}H_2 + CH_2=\underset{\underset{CH_3}{|}}{C}-CH_2-\overset{*}{C}H_3 \qquad .. (6)$$

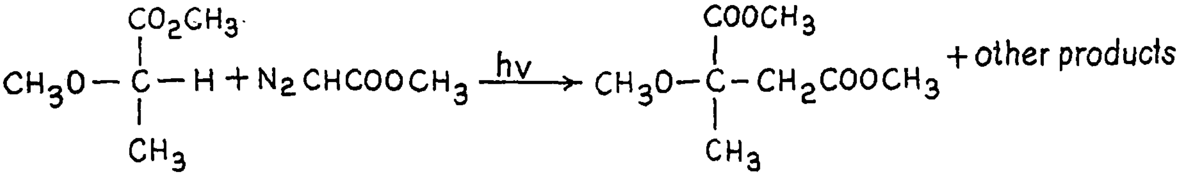
This is also supported by the work of Bell and Kistiakowsky who found $C_2H_2D_4$ to be the major product from the photolysis of diazomethane in the presence of methane - d_4 (38).

But insertion reaction mechanism is a concerted one which have shown by Kirmse and Buschoff who have demonstrated that the insertion into. C-H bonds retains steric configurations about the carbon atom (39). (Eqn. 7)



--------(7)

Another example of retention of configuration was given by Doering and Helgen (40). So retention of configuration is consistent with a one step insertion mechanism. (Eqn. 8)



$$CH_3O-\overset{\displaystyle CO_2CH_3}{\underset{\displaystyle CH_3}{C}}-H + N_2CHCOOCH_3 \xrightarrow{hv} CH_3O-\overset{\displaystyle COOCH_3}{\underset{\displaystyle CH_3}{C}}-CH_2COOCH_3 + \text{other products}$$

.. (8)

Even intramolecular 3° C-H insertion goes with retention of configuration (44). Although the evidence is strong that, at least in solution, methylene often inserts primarily in a concerted reaction, Frey showed some time ago that products derived from all possible radical coupling reaction are formed in gas phase experiments (41) [Eqn. 9]

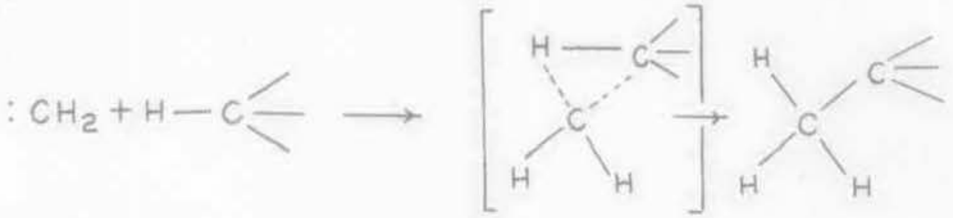
$$\begin{aligned}
&CH_2 + RH \longrightarrow \dot{C}H_3 + \dot{R} + \dot{R}' \quad \text{other radicals}\\
&\dot{C}H_3 + \dot{R} \longrightarrow CH_3R\\
&\dot{C}H_3 + \dot{R}' \longrightarrow CH_3R'\\
&2\dot{C}H_3 \longrightarrow CH_3CH_3 \qquad ..\ (\text{Eqn. 9})\\
&2\dot{R}' \longrightarrow R'R'\\
&\dot{R} + \dot{R}' \longrightarrow R-R'
\end{aligned}$$

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

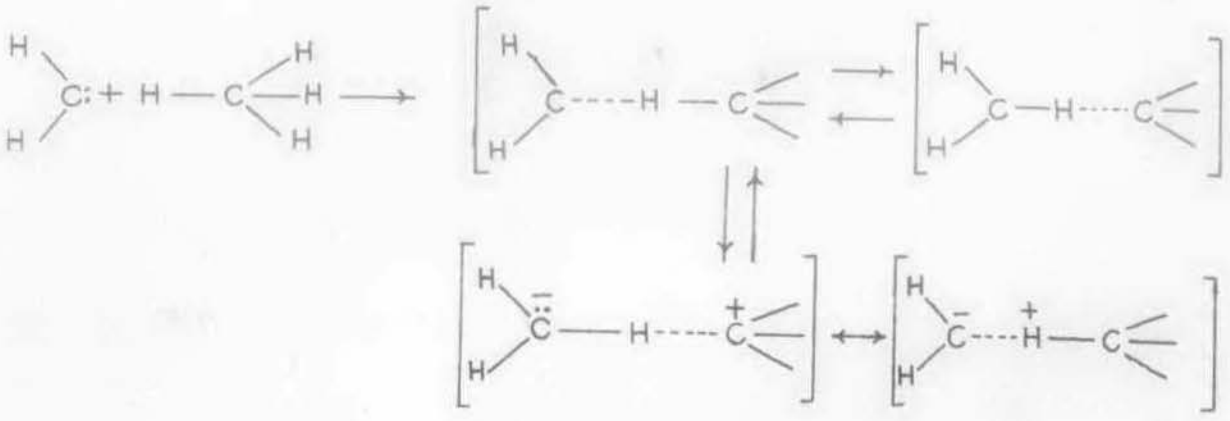
Observation in 1969 of emission and enhanced absorption in the NMR benzylic proton signal from an irradiated solution of diphenyl diazomethane in toluene was important both for the understanding of the chemically induced dyanamic nuclear polarization (CIDNP) phenomenon and for the verification of hydrogen abstraction by triplet carbenes (42).

Section-C : Nature of the transition state for C-H insertion and addition of carbene to double bonds.

Two hypothesis concerning the transition state for C-H direct insertion have been presented. Doering and Skell, having demonstrated that methylene is a vigorous electrophile, proposed a triangular transition state for direct insertion (43,44,45,37). The trianguler transition state accommodates the one step nature of singlet methylene insertion.



Demore and Benson on the other hand have proposed end on attack of the C-H bond. A transition state with diradical character is probably intended, with stabilisation due to contribution by ionic terms to the wave function (36).



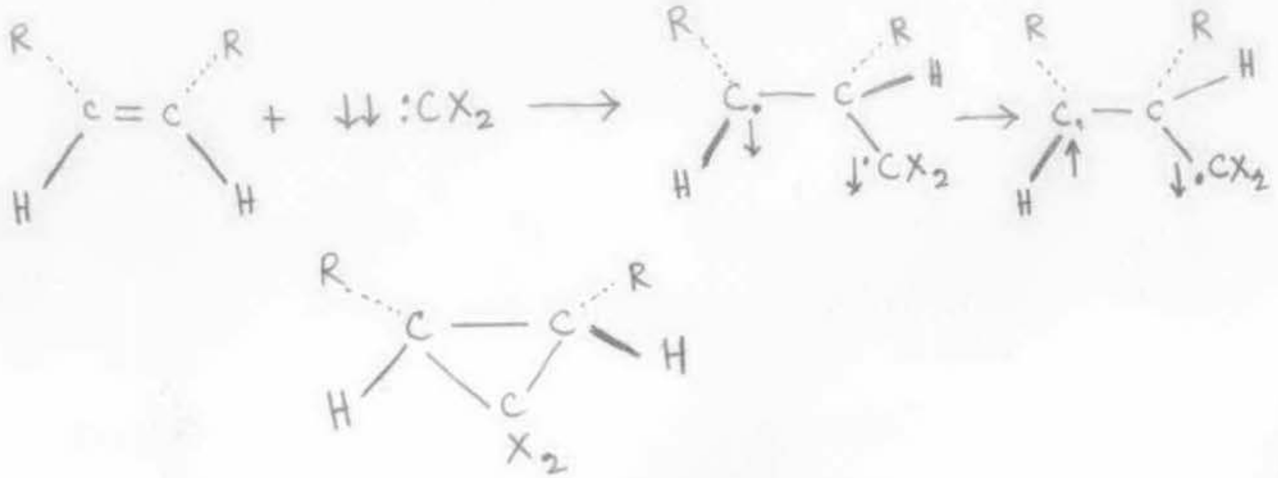
Some confusion has arisen as to whether an intermediate radical pair rather than a transition state was intended. Stereospecific insertion seems to preclude the formation of a radical pair of finite life time. The mechanism is much like that favoured by Hofmann on theoretical grounds (45). Three kinds of evidence have been brought to bear on the micro mechanism of concerted C-H insertion by singlet methylene (46,47,48). One step, three centre, direct insertion mechanism is common for singlet carbenes, ($^3CH_2$) reacts with two step abstraction recombination mechanism. Ylide mechanism is possible when atoms with one pair electrons are present at or near the substrates reactive site.

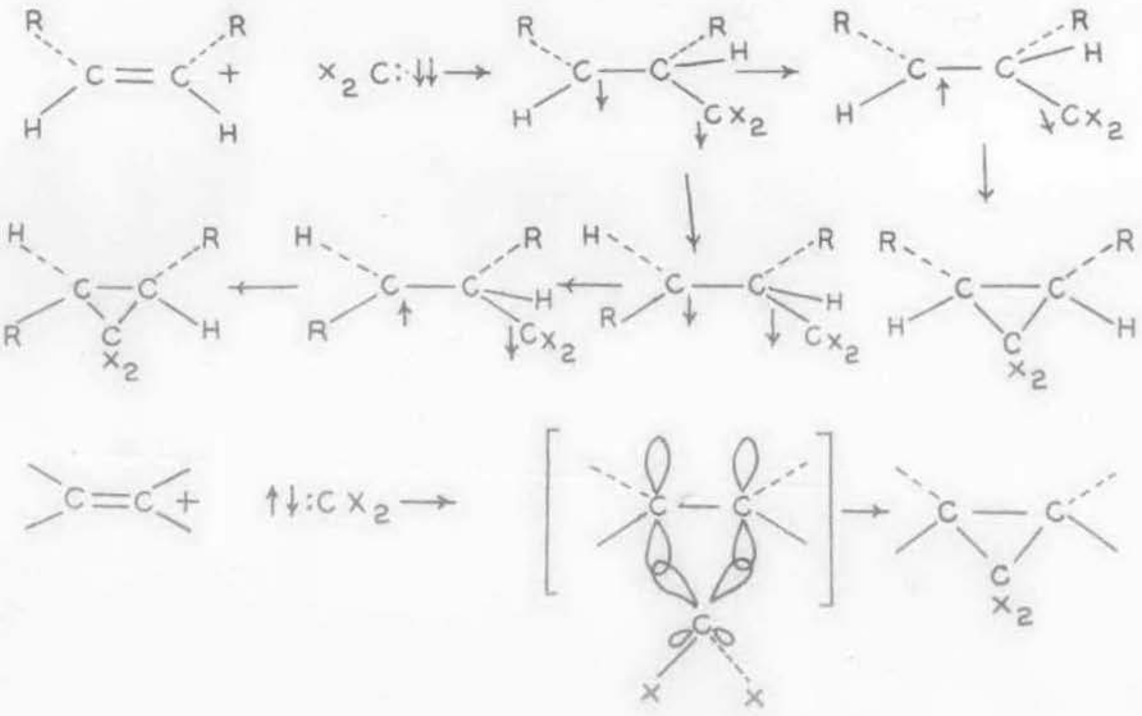
ADDITION TO DOUBLE BONDS

Soon after the discovery of the addition reaction it was proposed by Skell and co-workers that singlet and triplet carbenes could differ both in their selectivity (49) and in the stereospecificity of addition to olefins (43).

In 1956 Skell and Woodward proposed that the spin state of carbene can be deduced from the stereochemistry of cyclopropane formation (43). The generalization has come to be known as the Skell rule. The rule states that singlet carbenes are expected to add to a olefin in single step and therefore preserve the cis-trans stereochemistry of the olefin in the cyclopropane product. Conversely, it was argued that since a triplet carbene cannot give a singlet ground state cyclopropane in a single fast step, two step addition must occur. Rotation about single bonds in the diradical intermediate should be rapid compared with spin inversion followed by ring closer, and therefore non stereospecific addition by triplet carbenes was expected. Both these cases are shown in Fig. 7.

Empirically, Skell's rule has been found to be very successful. Although a singlet carbene may add to an olefin in a single step, there is no selection rule prohibiting spin conservation, step wise path. Conversely, although a triplet carbene very likely does add in two steps, the result could be stereospecific addition, if spin inversion and ring closure are sufficiently rapid. A two step reaction will indeed always give non stereospecific addition in the gas phase. Thus if stereospecific addition in the gas phase is observed, the reaction of a singlet carbene is indicated. The converse need not hold, nonstereospecific addition in the gas phase is not diagonostic of a triplet.





Transition state

Fig. 7

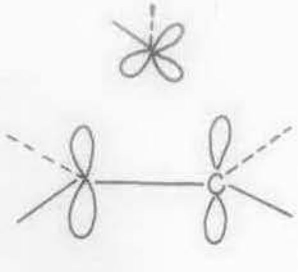
In solution predictions are more difficult because of wide variations in inter system crossing rates. To assign nonstereospecific addition to a triplet carbene, stereospecific addition by the singlet must also be demonstrated. Thus, for only in the cases of methylene itself, fluorenylidene, dicyano methylene and most recently dicarbomethoxy methylene and substituted cyclopenta dienyledenes has the stereospecificity of the addition of both singlet and triplet has been shown to conform to the Skell rule.

Stereospecific addition of methylene is obtained in the irradiation of gaseous mixtures of diazomethane and cis or trans-2-butene (50). In the liquid phase the stereospecificity is believed to be even higher, the "wrong" isomer in the gas phase coming principally from the geometrical isomerisation of the vibrationally excited primary adduct. This result was interpreted as indicating that methylene from diazomethane reacts while in its lowest singlet state, which was recognised as not necessarily being its ground state (35,51). This was the experimental basis for the Skell's rule.

Section-D : Effects of carbene reactions

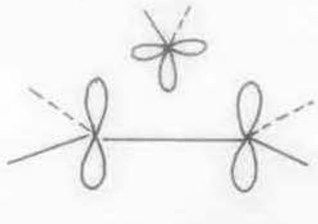
(a) Effects mainly electronic in origin:

Carbene addition to an olefin has been regarded as an electrophilic process. A theoretical analysis of the addition of $^1CH_2$ to ethylene suggests initiation of the reaction as in Fig. 8, a " approach" in which the vacant P orbital of the carbene begins to overlap with the π system. As the reactants move along the reaction coordinate toward product geometry the π approach goes over to Fig. 9, a " δ approach" (52).



π approach

Fig- 8



σ- approach

Fig- 9

The important point is the nature of the initial stage, the π approach, in which transfer of electron density from the olefin's π -system to the carbenes P orbital occurs; this is an electrophilic addition. More recent calculation suggest that π - approach Fig. 10 is energetically preferable to π -approach Fig. 11, in the addition of $^1CH_2$ to ethylene (53). Addition of CF_2 is calculated to follow a similar course, with less charge transfer from olefin to carbene at the transition state.

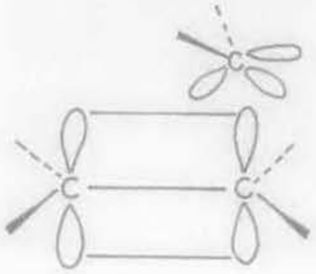


Fig. 10

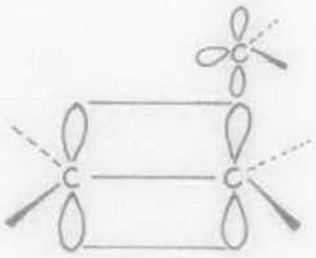


Fig. 11

Experimentally, the charge separation in generalised transition state Fig. 12 can be probed by variation of either olefinic substituents, R_1 - R_4 or carbenic substituents X and Y. This procedure, however, can alter both steric and electronic factors; the separation d changes in response to altered carbenic or olefinic reactivity.

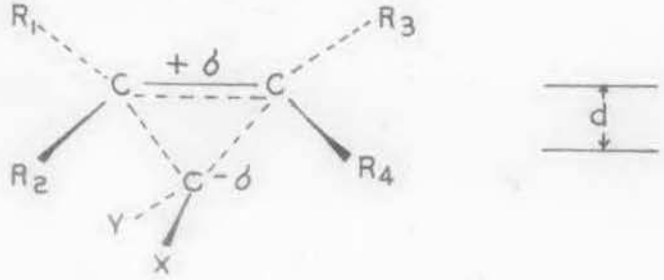
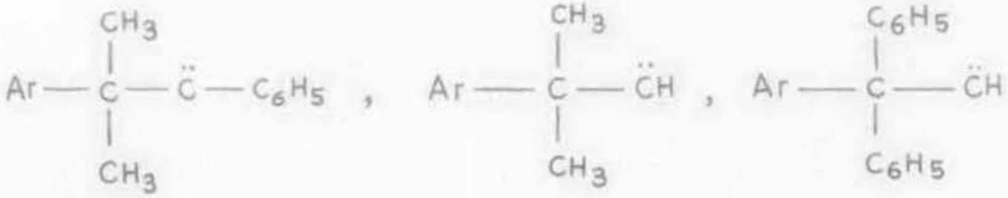


Fig. 12

It has been shown that 1,2 aryl migratory aptitude of the aryl group to an electron deficient centre, the carbenic P orbital is increased with a donating substituents on the aryl ring (54,55,56).



$$Ar-\overset{CH_3}{\underset{CH_3}{C}}-\ddot{C}-C_6H_5\ ,\quad Ar-\overset{CH_3}{\underset{CH_3}{C}}-\ddot{C}H\ ,\quad Ar-\overset{C_6H_5}{\underset{C_6H_5}{C}}-\ddot{C}H$$

This reaction may be viewed as intramolecular attack by the carbenic P-orbital on the aryl π-system at C-1.

The intramolecular reactions of thermally generated carbethoxy carbene with benzene derivatives, are correlated by Hammet treatment, $P = 0.38$ (σ_p^+) (57). Here too the carbene acts as an electrophile, impinging on the aromatic π-system.

Expectations are clear for variation of olefinic substituents; olefin reactivity will parallel π-electron availability. The substrate ability to bear a positive charge in Fig. 12 will be paramount.

Additions of CCl_2 (80°C) to Fig. 13a, b and c are correlated by ρ ; values are -0.619, -0.53 and -0.378 respectively. These ρ values are much smaller than the observed in CCl_2 additions to alkenes (58). There, substituent variation is accomplished directly at the reaction centre; response is great.

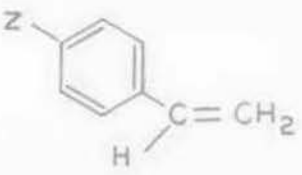


Fig- 13a

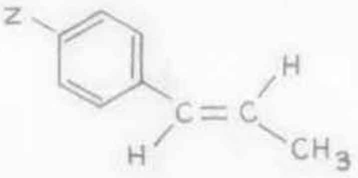


Fig- 13b

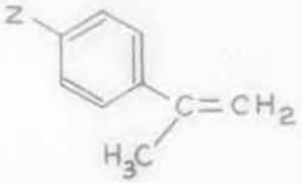


Fig- 13c

For 13a-c, the effect of substituent variation on reactivity is attenuated because it is mediated by the aromatic system. The order of increasingly negative ρ , $C < b < a$, which is the order of decreasing substrate reactivity. Substrate "a" should yield the most "advanced" transition state, with largest charge separation; the strongest response to substituent variation is expected. After incorporation the concept of Hoffmann (52,53) the transition for CCl_2 addition to 13 C is represented Fig. 14 (59).

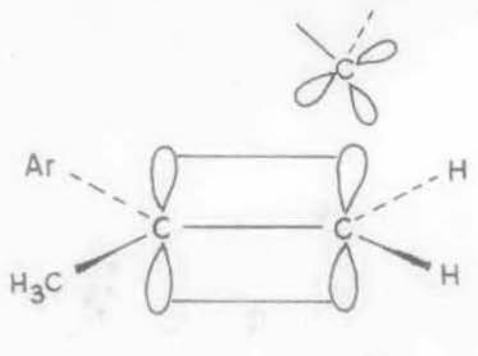


Fig- 14

Some carbenes like thioxanthenylidene (140) are nucleophilic also M.O calculations show nucleophilic character and triplet ground state for these carbenes (92).

Steric effect:

Both steric and electronic effects must be considered in order to correlate relative addition rates with substrate structure (60).

A 1-cyclohexyl substituent is 7.4 times less effective than a 1-methyl substituent at promoting the addition of CCl_2 to cyclohexene (61). Even phenyl, which should help electronically is less effective than methyl and 1- α-napthyl substitution retards the addition. These trends must be largely steric in origin. Similarly CBr_2 experience greater steric hindrance to addition than does CCl_2 (62). Relative to cyclohexene styrene, and 2,4,6-trimethyl styrene are equally reactive toward CCl_2. Toward CBr_2, styrene is more than three times as reactive. The hindrance arises at the ortho substituents.

Sadler cites a related effect of ortho substituents (63). The reactivity sequence for additions of $:CCl_2$ to α-methyl styrene derivatives is unsubstituted $>$ 2-methoxy $>$ 2-methyl $\approx$ 2,2-dimethoxy (68). A progressive twisting of the isopropenyl group from the plane of the aromatic ring is suggested. This steric inhibition of resonance decreases possible stabilisation of the transition state. Direct hindrance to $:CCl_2$ approach is also possible. The coplanarity of aryl and olefinic groups enforced on 1-methylenetetralin and 1-methylene indene by their fused ring structures maximises favourable resonance interaction. These olefins are more reactive than 1-methyl styrene toward $:CCl_2$.

Steric hindrance is responsible for the decreasing rates of addition of CCl_2 to various alkenes at the same substitution level as the chain of single substituent is lengthened (64). For example, replacement of methyl by ethyl halves the reactivity.

The low rate of addition of 2,2-diphenyl cyclopropylidene to tetramethyl ethylene (65) is attributed to steric hindrance caused by opposition of carbenes phenyl substituents and the olefinic alkyl groups. Cis-Butene and cyclohexene, which permit the phenyls to pair off with olefinic protons, react more rapidly than tetra methyl ethylene.

Dimethyl ethylidene carbene is most interesting. If the carbenic centre is Sp hybridized, then the vacant p-orbital is in the plane of the methyl carbons. In a transition state, Fig.16, these methyl groups impinge on the olefinic substituents. This picture rationalizes the very slow rate of addition of Fig. 15 to tetra methyl ethylene.

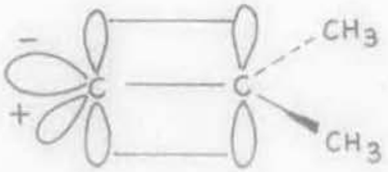


Fig. 15

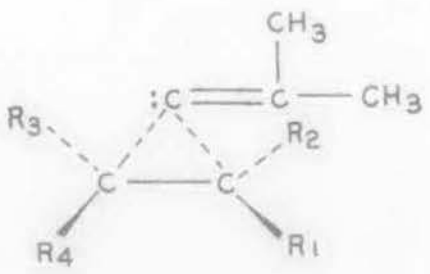


Fig. 16

Here no arrangement approximating to Fig. 16 avoids costly steric interactions. The more facile addition of15 to cyclopentene, compared with 1-methyl cyclopentene can be similarly explained (66). However, it is not clear why addition of 15 to tetra methyl allene is 45 times more rapid than addition of 15 with tetra methyl ethylene.

Photolytically generated aryl carbenes (67) do not exibit characteristic steric effects with simple alkenes.

There appears to be a substantial over all selectivity difference between photolytically (68) and thermally (69) generated carbethoxy carbene. The former does not discriminate between cis and trans butene; the latter prefers cis-butene by a factor of 2.3. The role of steric effects here is not yet defined.

Effect of Carbenic Substituents

The second "handle" for probing Fig. 12 is variation of carbenic substituents properly. Substituted carbenes develop the olefins irrespective of their potential reactivity difference.

2,2 diphenyl cyclo propylidene (65) and dimethylethylidene carbene show far more selectivity of dimethyl vinylidene carbene (70) appears to lie between that at CCl_2 and CBr_2. Resonance stabilization of the carbene Fig. 17 is suggested to account for its selectivity; the vacant carbenic P orbital is part of an allylic cation system.

Fig. 17

Singlet carbonyl carbene (71) is perhaps more selective than ${}^1CH_2$, for it reacts, 2.17 times faster with tetra methyl ethylene than with ethylene (71).

The substituted Phenyl carbenes also show only modest ability to distinguish between simple alkenes (72). The isobutene trans-butene reactivity ratio varies with carbenic aryl substituent in the order, m-Cl $\rangle$ p-Cl $\rangle$ H $\rangle$ p-CH_3 $\rangle$ O-CH_3, which parallels the expected order of increasing carbene stability. Representing these carbenes as in Fig. 18, the system is seen to be isoelectronic with a benzylic cation. It follows that Fig. 18, Z = OCH_3, should be the most stabilised and selective species.

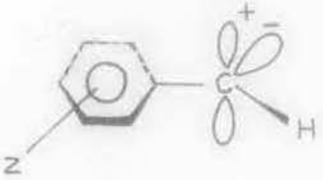


Fig. 18

The greater selectivity of bromo carboethoxy carbene compound with carboethoxy carbene, suggests stabilization as in Fig. 19 in addition to stabilization due to the carboethoxy substituent.

The latter factor Fig. 20 is presumably responsible for stabilising carbethoxy carbene relative to CH_2; that is it has somewhat greater selectivity in the C-H insertion reaction (73).

Fig. 19

Fig. 20

Little of this slectivity difference appears in the addition reactions, however, dicarbomethoxy carbene is more selective than either CH_2 or carboethoxy carbene toward the C-H bond (73). It is also more selective in addition reaction. The added selectivity presumably corresponds to extension of the stabilization depicted in Fig. 20 by the second carboalkoxy group.

In a sense, then, there is a "competition" between the substituents X and Y and the olefinic π bond over donation of electrons to the carbenic P-orbital; the balance of this competition changes during the course of addition of Fig. 21 to an olefin.

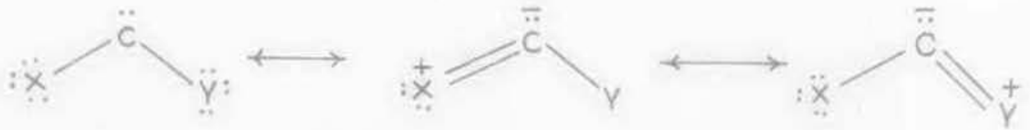


Fig. 21

The more strongly X and Y interact with the carbenic centre, the higher will be the activation energy for addition to a π bond. The transition state will be further advanced along the reaction coordinate, and more important will be the ability of the olefinic carbon atoms to support a positive charge. Thus strong resonance interaction in Fig. 21 will "develop" olefin structure reactivity sequence. Doering recognised this long ago when he spoke of relative relative carbene selectivity as reflecting the "internal stabilisation" of the carbene.

Section-E : General procedure for carbene generation

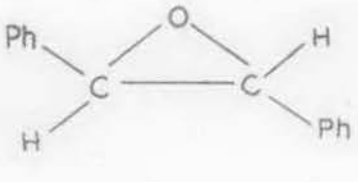
A variety of methods is available for the generation of carbenes, but for synthetic purposes they are usually obtained by thermal or photolytic decomposition of diazoalkanes, or by α-elimination of hydrogen halide from a haloform or of halogen from a gem-dihalide by action of base or a metal. In many of these latter reactions it is doubtful whether a "free" carbene is actually formed. 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 of carbenes are usually called Simmons-Smith reactant. Dichloro carbene addition- Svia -Makosza reaction (129a, be, c, d) are also interesting. Thermal decomposition of diazoalkanes ([illegible]) 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. Another convenient and widely used route to alkyl carbenes is by thermal or photolytic. Decomposition of the lithium or sodium salts of toluene p-sulphonyl hydrazones (76). The diazo alkane is first formed and decomposes under the reaction conditions. Keto carbenes and alkoxy carbenes are usually produced by heating or photolysing diazoketones and diazoesters. Generally, the reactions for generation may be classed as : Decomposition reactions (thermal or radiative activation) and elimination reactions (Participation of a reactant such as base). Sources are diazoalkanes, Diazirnes, alkylhalides, ylides, olefins, tosyl hydrazones, organometallics and the like.

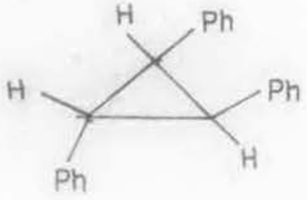
A common precursor is the diazo compounds $RR'CN_2$. These are obtained either from amines, by way of nitroso urethans nitroso amides or nitroso ureas or from carbonyl, via the oxidation of their hydrazones. Photolysis of these derivatives affords singlet carbenes. Except for diaryl species, they react in this state. Carbenes may also be generated by Bamford-Stevens reaction (130).

The decomposition of diazo compounds with copper or copper salts leads to carbene -copper complexes. These derivatives often add to olefins stereospecifically and are less energetic than the free carbenes.

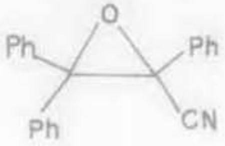
Diazirines, isomeric forms of diazo~~ethanes~~alkanes, afford carbenes less conveniently than the corresponding diazoalkanes (131a,b,c).

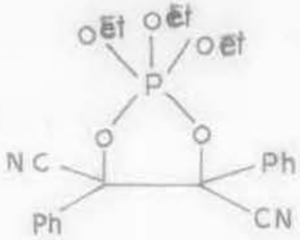
Photolysis of phenylbromodiazirine is a convenient source of phenylbromocarbene (Ph - C - Br) (132). Phenyl carbene may be generated by photolytic decomposition of following (133).





Cyanocarbene (Ph-C-CN) is produced by the photolysis of suitable oxirane(131 c) or from 1,3,2-dioxaphosph (v) alane (134).





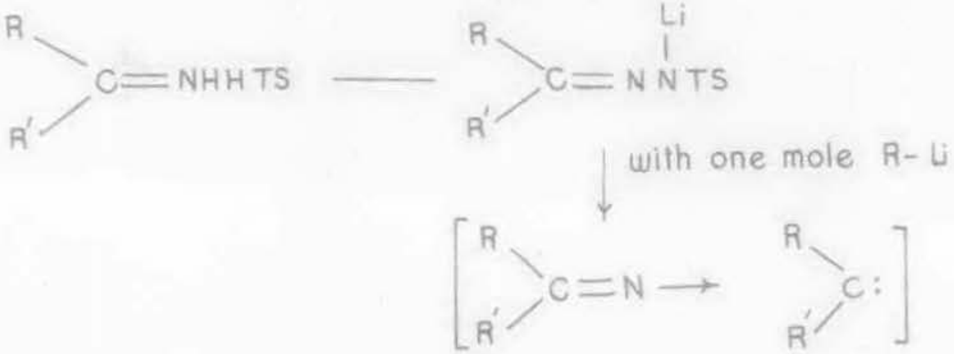
Singlet carbene is generated by the photolysis of arylcyclopropane. The reaction of esters of trichloro acetic acid with alkoxide produces dichloro carbene (78).

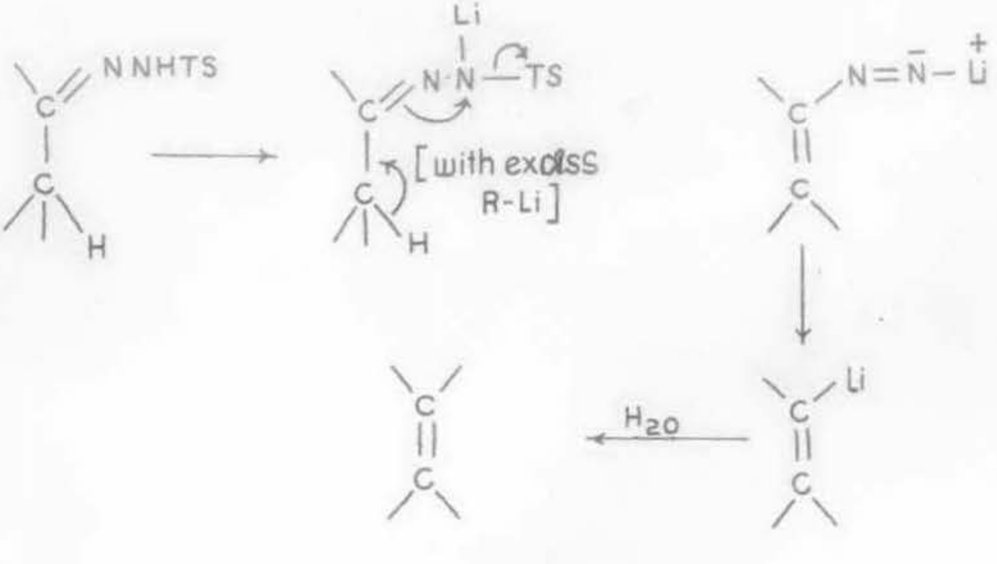
One of the most convenient method for generating halogenocarbenes is the thermal decomposition of organometallic precursors (135 a, b).

$$\phi H-Hg-CCl_2-Br \longrightarrow \phi H-Hg-Br + :CCl_2$$

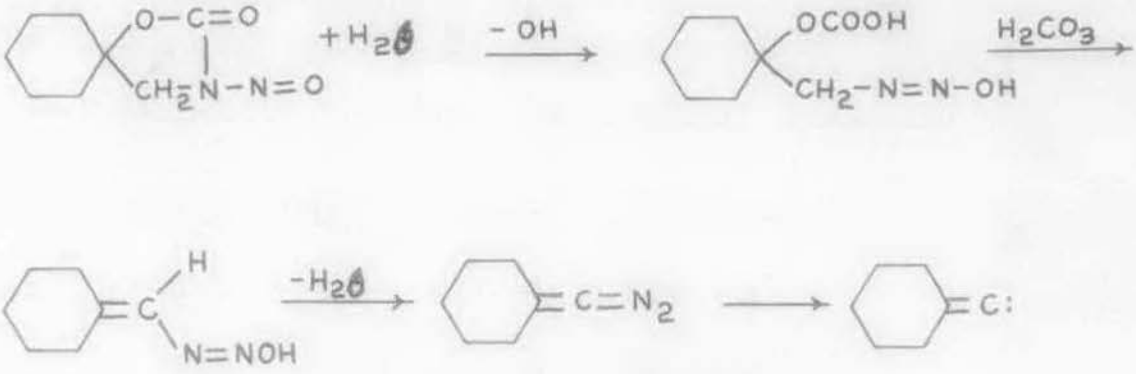
$$\phi H-Hg-CBr_3 \longrightarrow \phi H-Hg-Br + :CBr_2$$

Organolithium reagent gives ϕH-C-H carbene with ϕHCH I_2, whereas pH-C-Cl is obtained from pHCH Cl_2, in the latter reaction organolithium works as a base, removing a proton. Whereas with tosylhydrazone, organolithium compound react in two ways depending on whether it reacts with only one mole or with an excess of organolithium:





Vinyl carbenes can be generated in various ways the initial work by Newman which involves the reaction of bases with nitro oxazolidinones (136 a,b).



Basic hydrolysis of haloforms results in the generation of dialkylcarbenes <u>via</u> the intermediate carbanion (137).

$$\mathrm{CHCl_3} + :\mathrm{B} \longrightarrow :{}^{-}\mathrm{CCl_3} + \mathrm{BH}$$

$$:\mathrm{CCl_3} \longrightarrow :\mathrm{CCl_2} + \mathrm{Cl^-}$$

Olofson *et al* have reported interesting synthesis of carbene by treatment of stable cations, viz. $(\mathrm{Mes})_2\ \overset{+}{\mathrm{CH}}\ \overset{-}{\mathrm{BF_4}}$) with base (138).

$$(\mathrm{MeS})^{+}_{2}\ \mathrm{CH}\ {}^{-}\mathrm{BF_4} \xrightarrow{\text{Base}} (\mathrm{MeS})_2\ \mathrm{C}:$$

$$(\mathrm{MeO})^{+}_{2}\ \mathrm{CH}\ \mathrm{BF_4^-} \xrightarrow{\text{Base}} (\mathrm{MeO})_2\ \mathrm{C}:$$

d. Thermal and photo chemical reactions are also the generating source of dihalo carbene which are shown by the following reactions (79,80). [Eqn. 15]

$$Cl_3C-SiCl_3 \xrightarrow{250^\circ} SiCl_4 + {:}CCl_2 \qquad \ldots (15)$$

$$Ph-Hg-CX_3 \xrightarrow{80^\circ} Ph-Hg-X + {:}CX_2 \quad (X = Cl,\ Br)$$