

Scheme-1

When a diazoketone loses nitrogen a sextet of electrons remains on the carbon atom which was linked to the diazo group. The α -ketocarbene thus formed is capable of undergoing the most diverse reactions, depending on the conditions under which nitrogen elimination takes place (thermal, photolytic or metal catalysed) Scheme-1 summarizes the preparative possibilities employed to date.

(a) If the α -keto carbene stabilizes itself by an intramolecular rearrangement, a ketene is formed (86) (Wolff rearrangement) which can then react further, e.g. in the presence of water gives carboxylic acid.

(b) Intramolecular hydrogen displacement produces unsaturated ketones from carbenes of the form $R-CO-\overset{\ominus}{C}-CH_2-R'$ (37).

(c) Dimerisation and trimerization give 1,2,diacyl ethylenes and triacyl cyclopropane, respectively (88).

(d) At elevated temperatures, α -keto carbenes can enlarge the ring of hydri^uene (89).

(e) Substitution of certain heterocyclic and isocyclic rings (90).

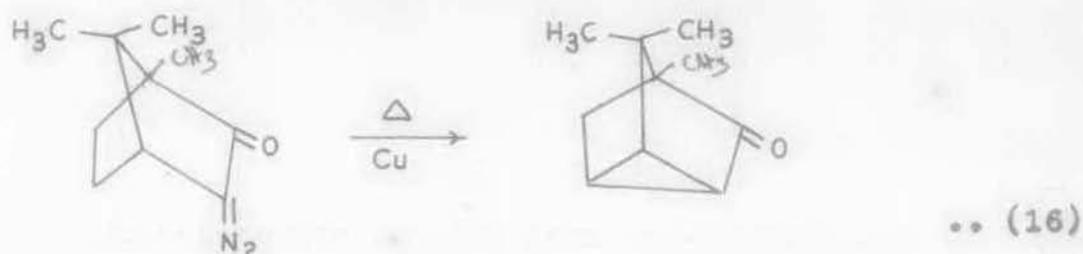
(f) α -Keto carbenes can react with compounds containing a double bond, to form derivatives of cyclopropane (91).

(g) Decomposition of diazoketones with copper powder in the presence of amines, alcohols, or mercaptans gives ~~rise~~ rise to α -amino ketones α -ketal ethers, or α -ketal thio

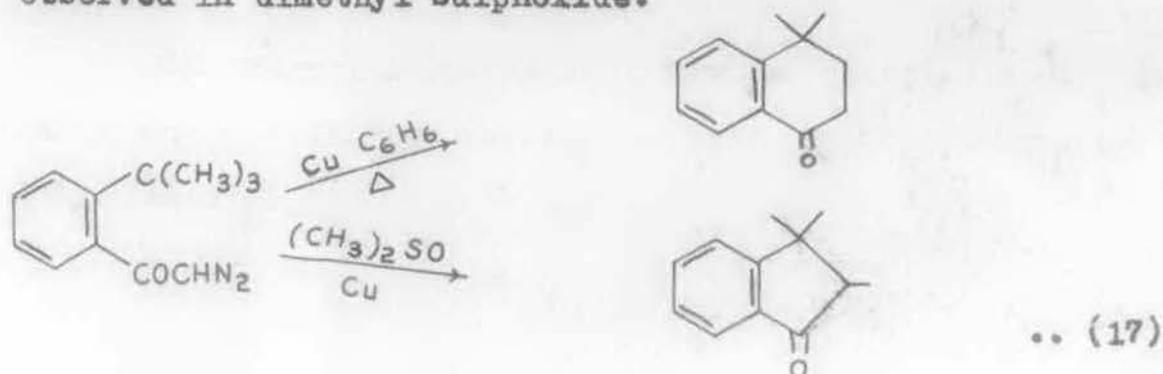
ethers respectively (92). Other reactions proceeding in similar manner are discussed subsequently.

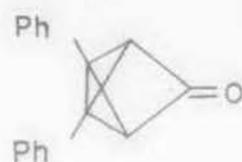
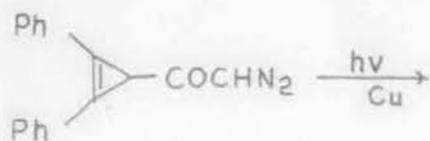
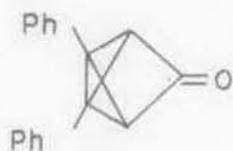
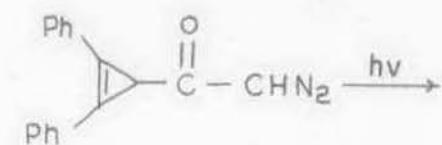
Insertion and addition reaction of carbenes
(Keto-carbenes)

Pyrolysis of diazocamphor leads to intramolecular insertion of the divalent carbon into neighbouring carbon-hydrogen bonds (Eqn. 16). The tricyclic structure of the product was established by Bredt and Holz (93).



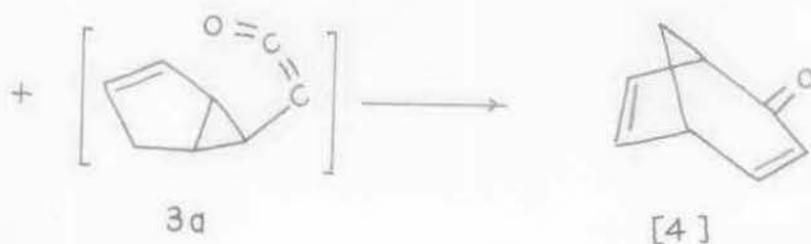
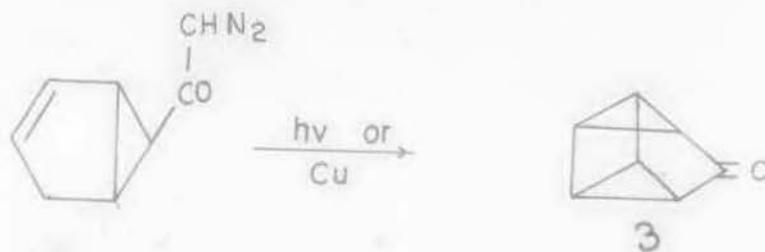
Intramolecular insertion has also been reported with tertbutyl diazo acetophenone (94) [Eqn. 17]. In a nonpolar solvent, benzene C-H insertion occurred with formation of product where as a small amount of apparent C-C insertion was observed in dimethyl sulphoxide.





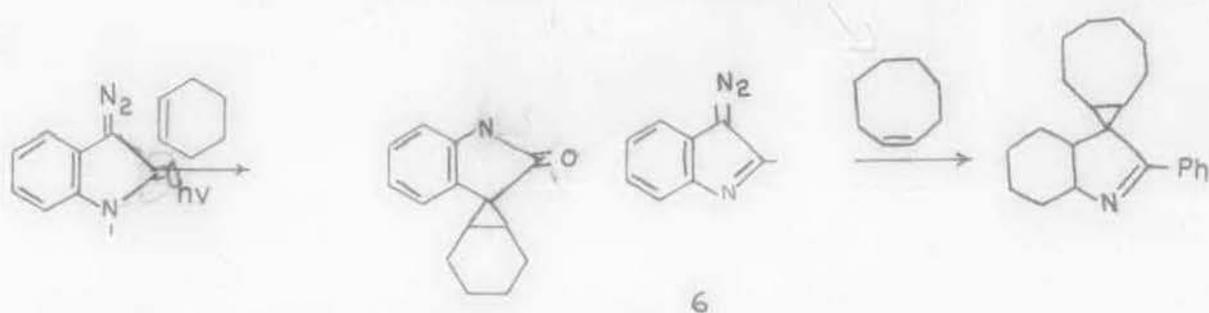
.. (20)

Freeman and Kuper observed a similar reaction 3 and also isolated 4 the product of rearrangement of 3a itself formed by Wolf rearrangement (99, 100) [Eqn. 21].

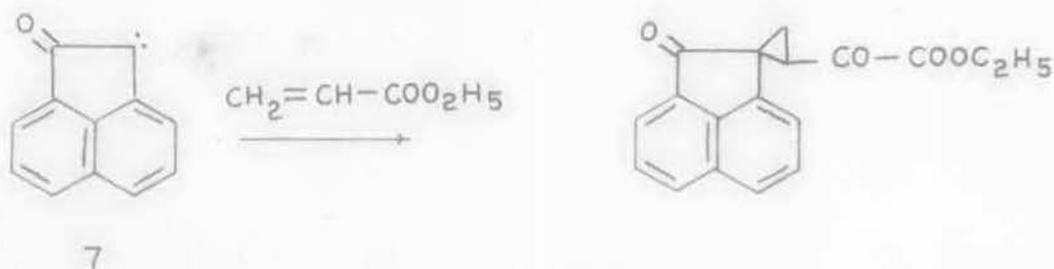


.. (21)

Photolysis of diazoketone 5 in cyclohexane or 1,1-diphenyl ethylene gives adducts presumably because the mobility of an amide in the Wolf rearrangement is low (101) and imine 6 gives a carbene which adds to ^{octene} cyclohexene (102).

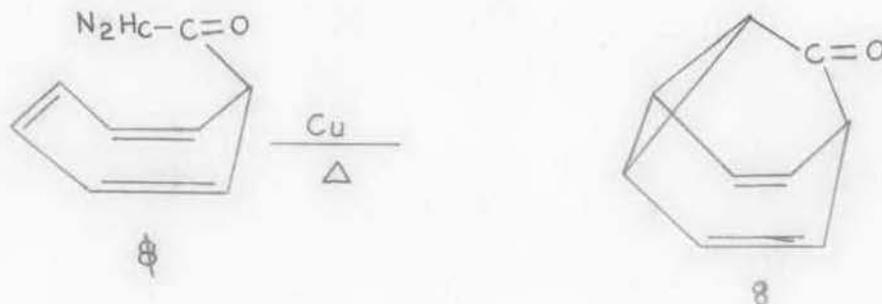


Additions are common when a copper catalyst is employed, but occasionally uncatalysed additions are successful. These are often suspect. For instance, addition of 7 to olefins was reported on thermal decomposition of diazo acenaphthalene (103).

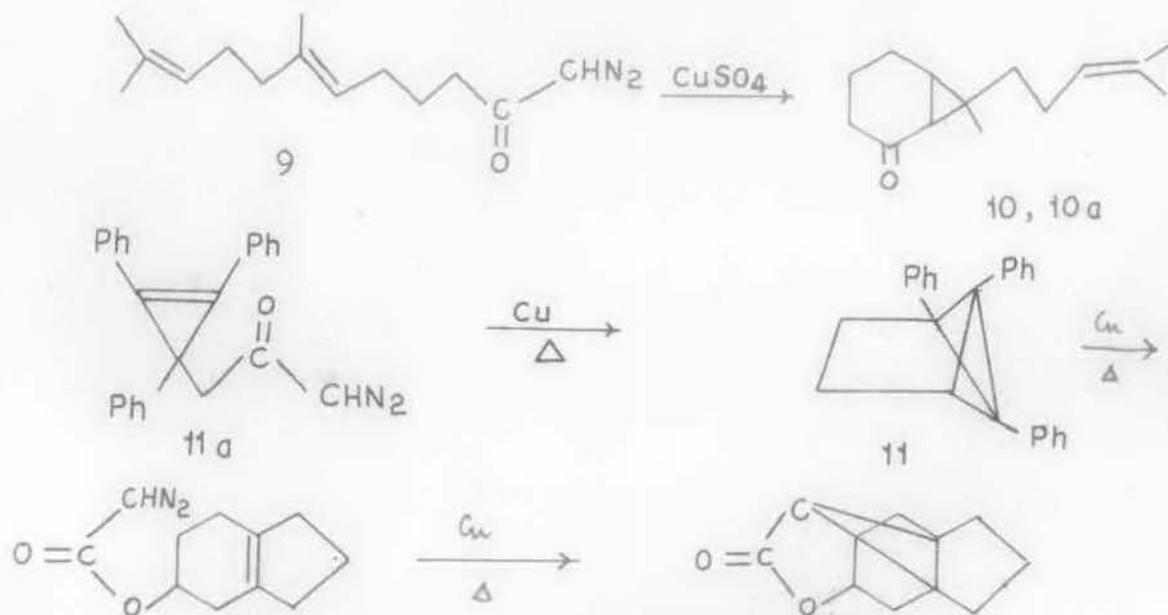


Olefins not bearing electron withdrawing groups do not form cyclopropanes. However, the intermediary of pyrazolines seems quite possible.

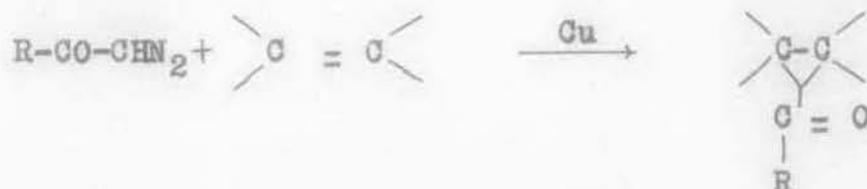
Doering et al (104) used the reaction to make barbalone 8, a precursor of bullvalene.



Mori and Matsui (105) achieved a 59% yield of epimers 10 and 10a the copper/copper sulphate - catalysed decomposition of 9 and the prebenzvalene 11 was made from the copper-catalysed decomposition of 11a by Monahan (106). Similar reactions were performed by House and Blankley (107).

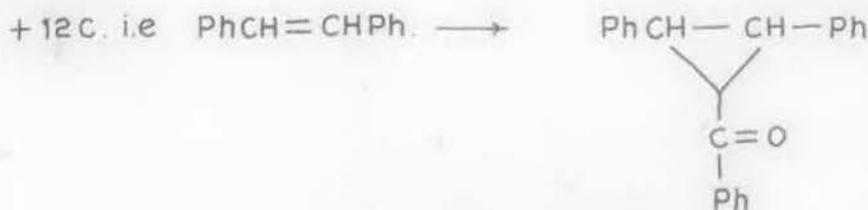
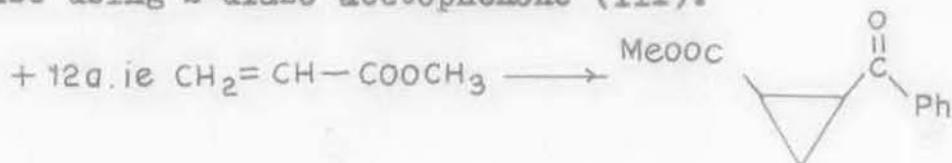


Acetyl carbene, generated by copper-catalysed decomposition of diazoacetone, added easily to olefins such as styrene, cyclohexene, cyclopentene (108). The presence of acetoxy groups did not interfere with this reaction.



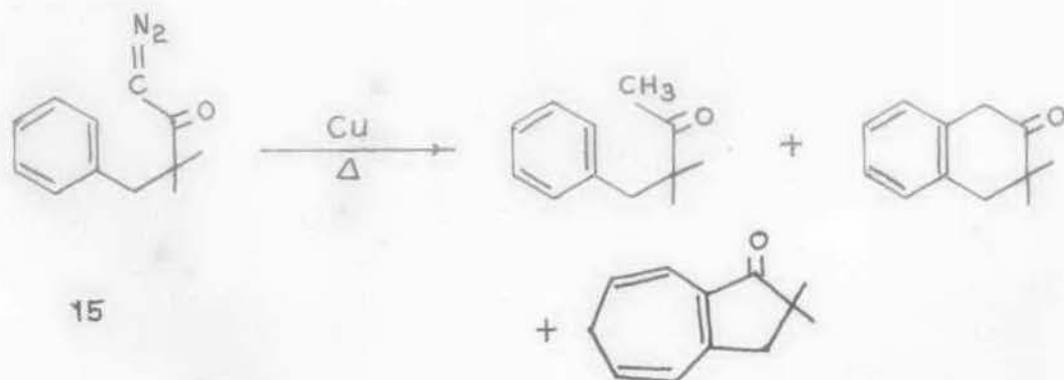
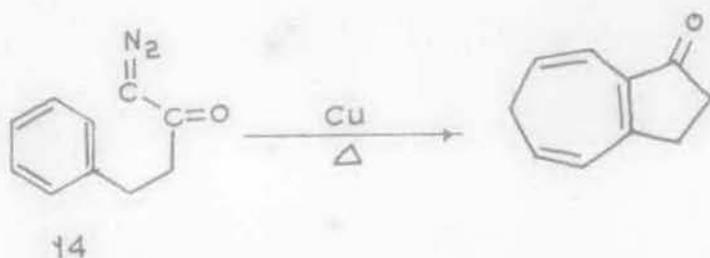
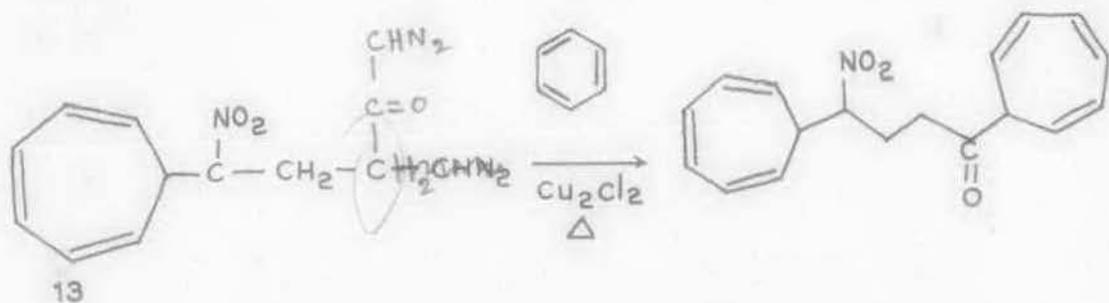
Benzoyl carbene (109) and p-phenyl benzoyl carbene (110) were found to react with olefins even in the uncatalysed pyrolysis of the related diazoketones, but the yields were considerably improved by the presence of copper powder.

This reaction has been applied in an intermolecular sense using 2-diazo acetophenone (111).

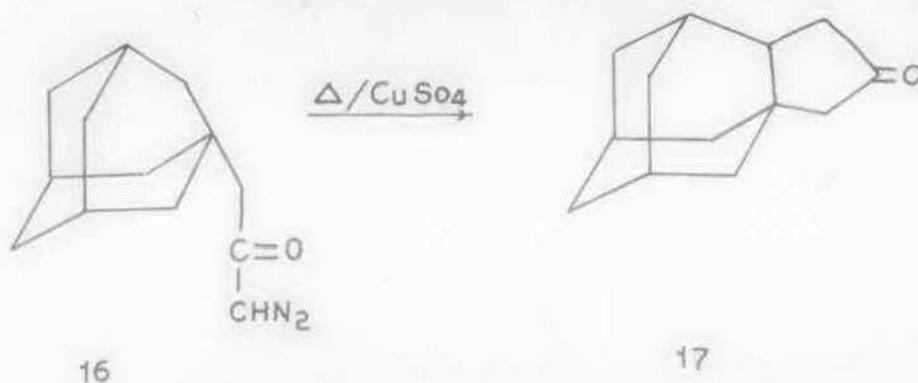


Cis and trans product

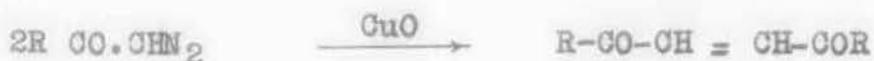
Addition of keto carbenes to aromatic systems have generally failed, even copper catalysed. But it has recently been demonstrated that both intermolecular (112) and intramolecular (113) reactions are possible.



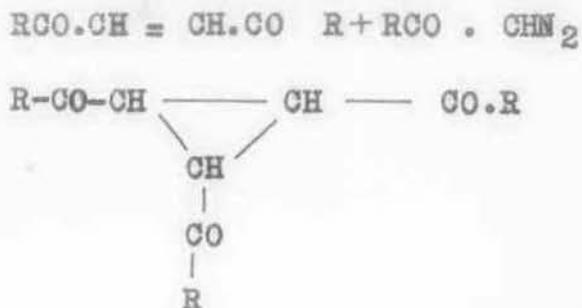
Copper sulphate-catalysed decomposition of 16 yields 17 which is the intramolecular insertion reaction.



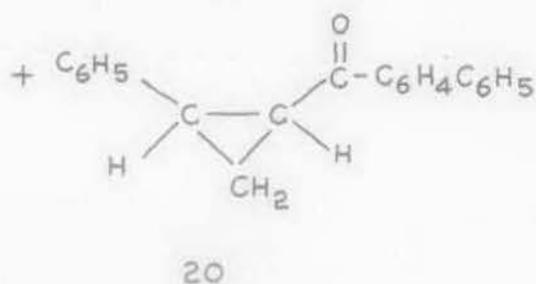
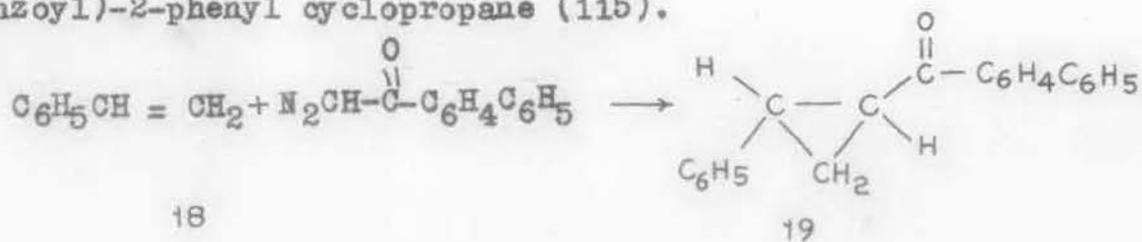
Diazoketones have been converted to diacyethylene by treatment with cupric oxide in inert solvent, such as benzene, toluene (114).



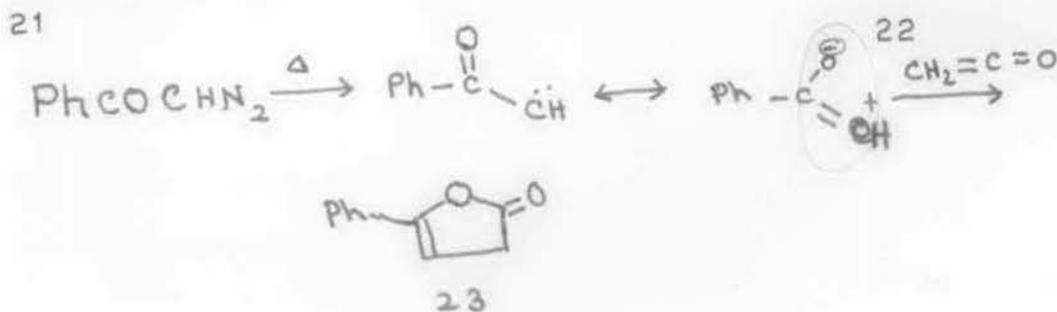
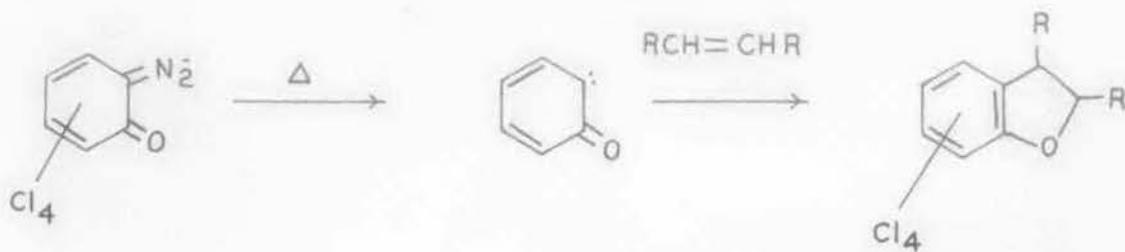
Trimer is also formed with excess diazoketones.



α -dialzo-4-phenyl acetophenone reacted with a large excess of styrene at 140° to yield cis and trans-1-(4'-phenyl benzoyl)-2-phenyl cyclopropane (115).



Cyclic diazo keto carbene of the following type has been found to be trapped by the olefins in the following fashion and addition to stilbenes is nearly stereospecific (116).



1,3 dipolar additions are common and are often catalysed by copper (117). 1,3 dipolar addition is probably responsible for the formation of 23 (118).

Section-B : Mechanistic pattern of Keto carbene addition to double bonds.

External reactions are facilitated by copper catalyst (Probably by the formation of an olefin-carbene-copper complex).

Mat Suje Takebayashi et al (111) found that when α -dialdo acetophenone reacts with olefin such as vinyl acetate, cyclo hexene and cis and trans stilbenes, several products were being formed in presence of bis (acetyl acetonates) copper. 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 seems to be not so large.

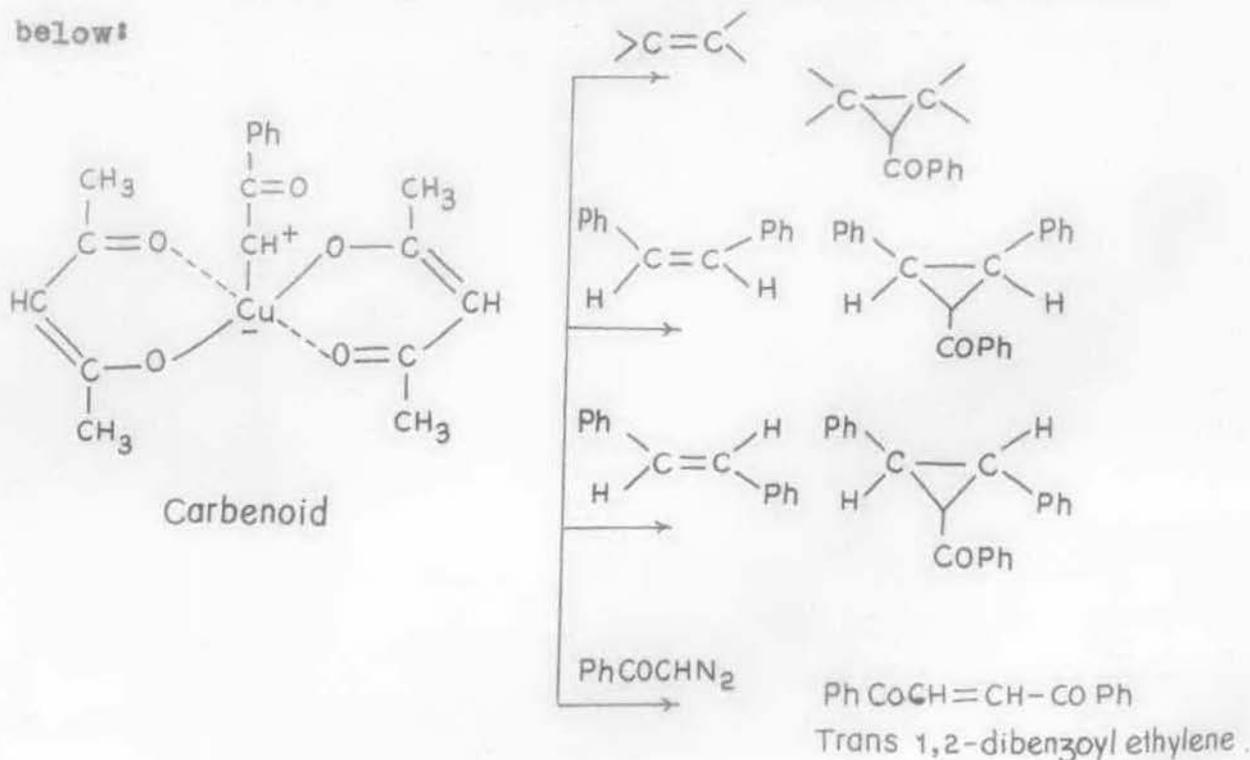
The cis and trans 1,2 dibenzoyl ethylenes may be formed by the reaction of α -dialdo ketone with carbenoid species. In the case of "mixed method" when no substrate having enough reactivity to the carbenoid is present except α -dialdo acetophenone in the reaction system. Groundmann, and Trischmann (126) have reported that the copper powder catalysed decomposition of

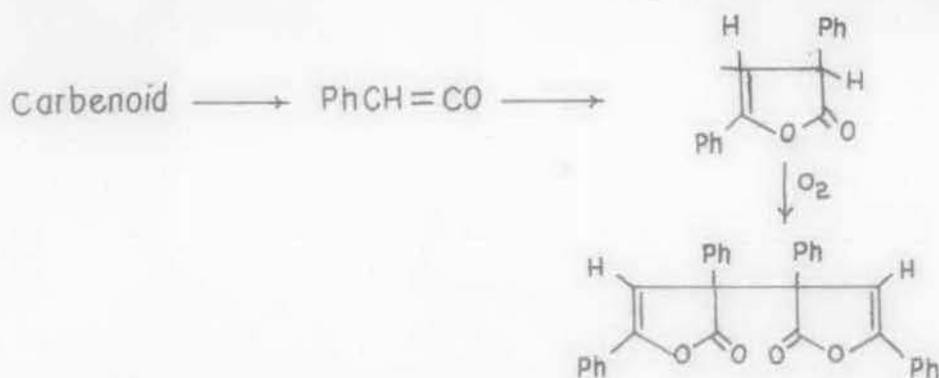
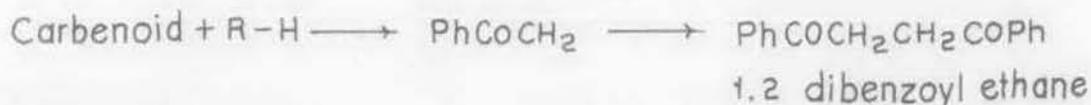
α -dialzo acetophenone in various solvents gives trans-1,2 dibenzoyl ethylene.

On the other hand, dilactone was observed in the reaction of α -dialzo acetophenone 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 lead to phenyl ketene by concerted phenyl migration. Phenyl ketene reacts with dialzo acetophenone and finally affords dilactone.

The formation of 1,2 dibenzoyl ethane is explained by the dimerization of relatively stable phenacyl radical, which is formed by the hydrogen abstraction of the carbenoid from the solvents or substrates.

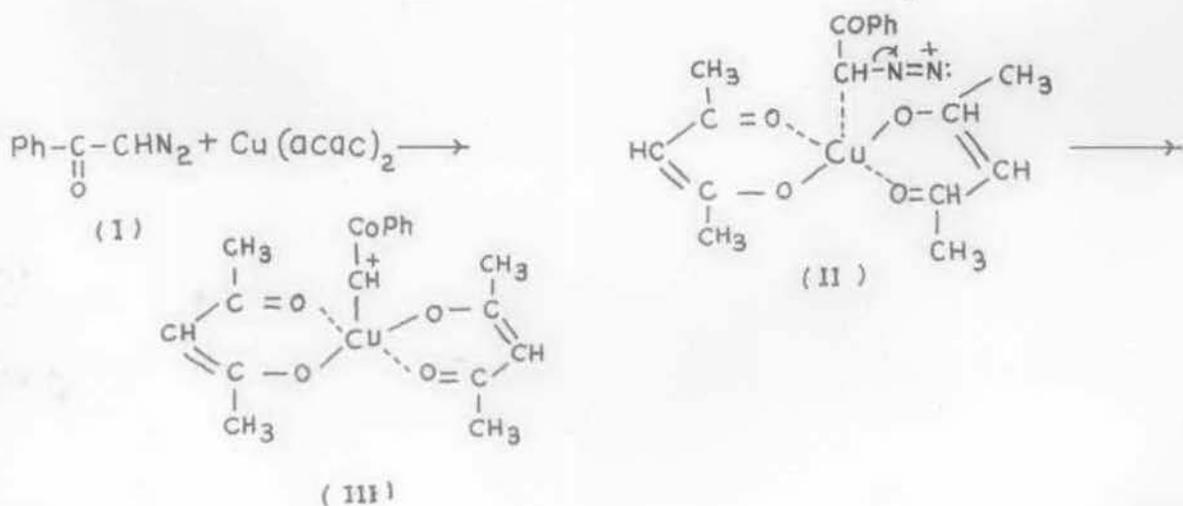
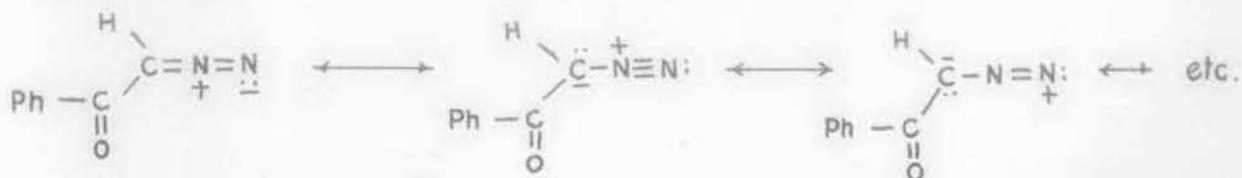
The formation of the products obtained is summarised below:





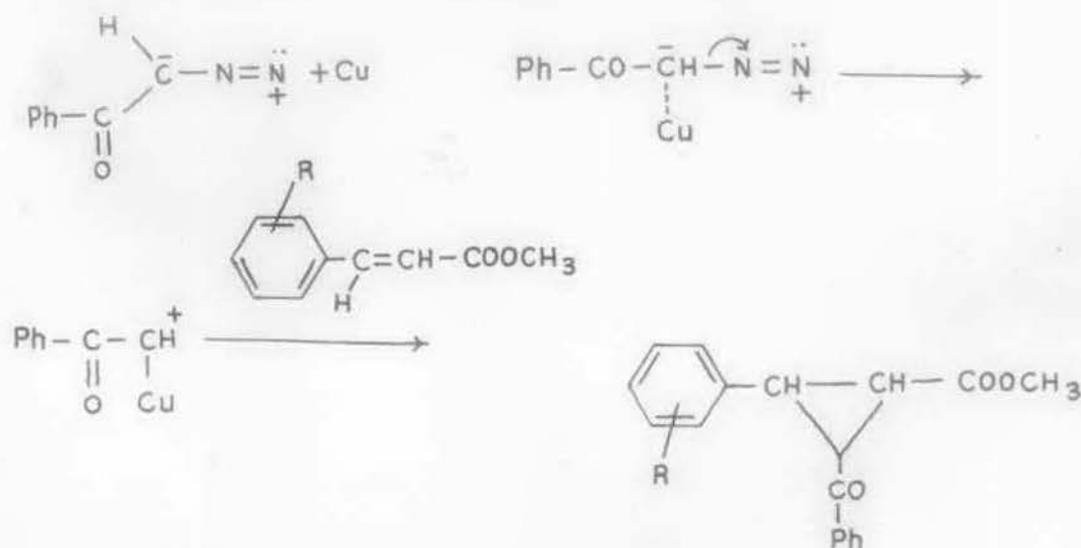
The following mechanism has been proposed for the formation of carbenoid intermediate. Copper chelates such as $\text{Cu}(\text{acac})_2$ and $\text{Cu}(\text{DMG})_2$ have been recognised to have a plane structure of 4 co-ordination.

α -dialzo acetophenone has the following resonance structure:



The diazo ketone coordinates with its α -carbon atom to the metal atom of copper chelates, thus giving an intermediate complex (II); the complex loses its nitrogen immediately to afford a keto carbene complex (III). The bond between the keto carbene and the copper atom of the complex is not so strong that the complex may react with olefins to give cyclopropyl ketones.

We have prepared cyclopropyl ketones with olefins of the following type and α -diazo acetophenone in presence of active copper powder, anhydrous copper sulphate and cuprous chloride. In all cases we observed cyclopropyl ketones together with trans-1,2 dibenzoyl ethylene, so it may be concluded that a parallel mechanism hold in these cases. Here the α -carbon atom of the 2-diazo acetophenone coordinates with the copper atom giving rise to keto carbene Cu-complex. This then reacts with olefinic double bond to give cyclopropyl ketones. The reaction mechanism can be depicted as follows:

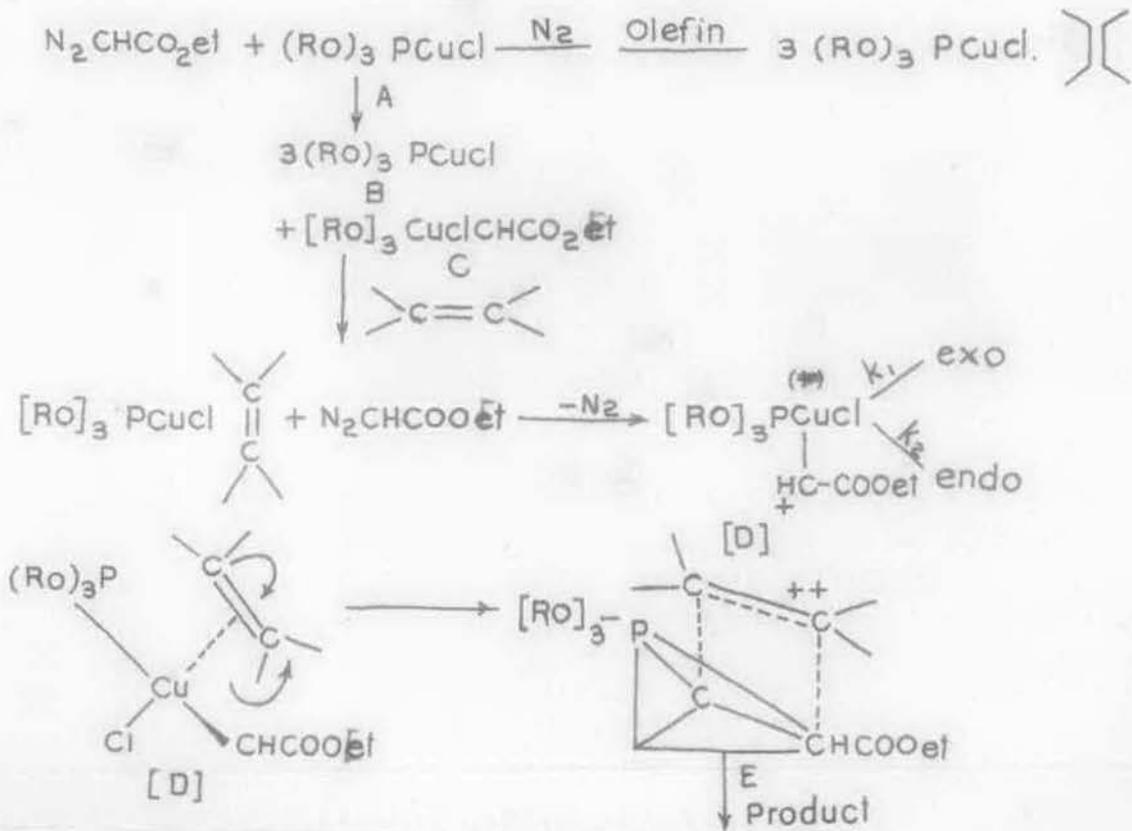


Dyakonov and co-workers (139) have shown Kinetically that the catalytic species in the type of reaction of cyclohexene and ethyl diazo acetate is not the starting copper complex, but an intermediate derived there. Of all the several mechanisms for the formation of cyclopropane product from the decomposition of ethyl diazo acetate in cyclohexene the overall path depicted in scheme 2(140) below best explains the experimental data.

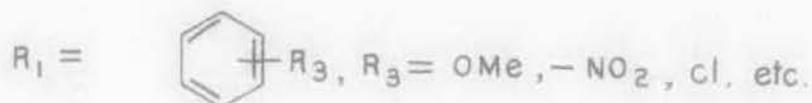
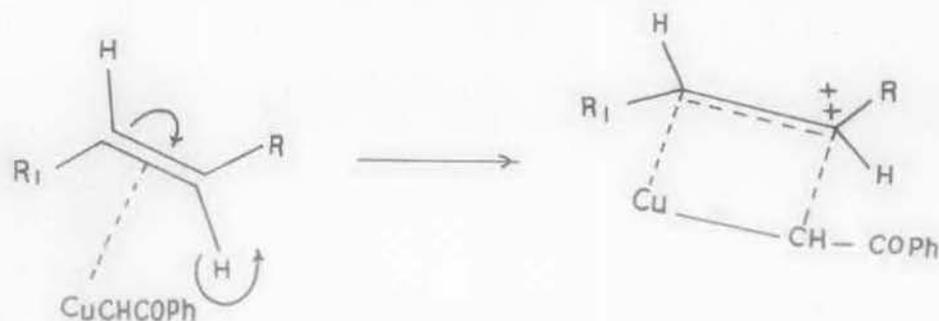
Concerning the 1st step in the scheme it is quite reasonable that the coordinately satisfied tetrameric (141, 142) copper complex A is cleaved by diazo alkane to form 3 mole of coordinately unsaturated monomer, and 1 mole of mono saturated carbene-metal complex. Since the reactive monomer B is formed in a huge excess of cyclohexene and Cu(1) forms strong olefin complexes, the most reasonable step is to coordinate with either 1 or 2 mole of cyclohexene to form intermediate complex-C. This complex cannot form the product directly, therefore it is reasonable that it reacts further with ethyl diazo acetate to form the final intermediate D, before product formation. This intermediate D depicted in scheme 2 is tetrahedral and co-ordinately satisfied. Since the central metal atom is Cu(1) complexes is 4 and tetrahedral (143). In this complex D, the olefin as well as the carbene could be coordinated via a donation back donation type of bonding. This requires donation of 2-electrons in SP^2 orbital from a singlet carbene

and a back donation of electrons from a dxz orbital of the metal into vacant Pz orbital of the carbene carbon. Stable carbene complex of this type with various ^{metals} of the central metal atom have been reported (144) and the X-ray study indicates Sp^2 hybridisation of the carbene carbon and $d\pi - p\pi$ bonding (145).

Scheme 2



Hence in our study, exact transition state would be



Mechanism of catalytic decomposition of diazo acetophenone in the presence of copper salts must be different from the photolytic processes. Cowan et al (124) showed that catalytic decomposition of α -diazo acetophenone in presence of cyclohexene leads to formation of norcaryl phenyl ketone, usually in much larger yield than was obtained by either direct or sensitized photolysis. Products expected from hydrogen abstraction from the alkene was not found. Catalytic decomposition in the presence of the butenes also led to higher yields of cyclopropyl

ketones than were obtained in the photochemical experiments. They also observed that catalytic decomposition in presence of trans butene yields a trans product i.e. addition of keto carbene to the trans butene has taken place stereospecifically. But in the case cis-butene, no stereospecific addition was found. Phenacylchloride is also produced when cuprous chloride was used as the catalyst.

The relatively high stereospecificity of a keto carbene addition to 2-butenes might be indicative of the singlet keto carbene intermediary. The reagent involved seems to be more selective than triplet carbene believed to be the active intermediate photolysis. It is most probable that the active reagent is an organometallic compound such as PhCOCHCu or $\text{C}_5\text{H}_5\text{COCHCuCl}_2$. The latter reagent would be a logical precursor of phenacyl chloride which would be structurally analogous to the CH_2I_2 formed by the diazomethane and zinc iodide. The fact that the catalytic addition with cis-2-butene are not entirely stereospecific indicates that the catalysed reaction proceed with a mixture of mechanisms i.e. singlet keto carbene and triplet keto-carbene both being involved in the catalytic decomposition of diazo acetophenone.

Now as addition of keto carbene to trans olefins (E) is entirely stereospecific, we have taken trans (E) olefins in our studies as to avoid a greater number of products with cis olefin (Z type).