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Metal salt catalyzed carbenoids II

Robert Stephen McDaniel Jr.

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METAL SALT CATALYZED CARBENOIDS II

by

ROBERT STEPHEN McDANIEL, JR., 1946-

A DISSERTATION

Presented to the Faculty of the Graduate School of the

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In Partial fulfillment of the Requirements for the Degree

DOCTOR OF PHILOSOPHY

in

CHEMISTRY

1974

D S Wulf
Bruce Poling
L. M. Nicholson
J O Stoffer

' "Tempus adest nunc," Rosmarus inquit, "multa loquendi
reges caules, cothurnos, classem, sigillos.
Cur mare si ferventius sestuat, sou subus alae." '

Lewis Carrol

translation by K. M. Thomas

ABSTRACT

The interaction of diazomalonic esters with olefins in the presence of homogeneous Cu(II) catalyst species has been examined relating to olefin structure effects and catalyst structure effects using partial rate data as a method of determining the mechanistic aspects of the various reactions.

It has been possible to examine the mechanistic details of cyclopropanation, C-H insertion, and both "dimer" forming reactions.

Cyclopropanation proceeds via a transition state including olefin, copper (II), ligands, and carbene C-H insertion results from hydrogen abstraction prior to collapse of the transition state. "Dimer" is formed by the attack of diazo compound on the carbenoid carbon, with subsequent *trans* elimination of nitrogen and catalyst.

The first copper catalyzed decomposition of a Δ-1 pyrazoline has been observed.

ACKNOWLEDGEMENTS

The author wishes to express his gratitude to Dr. David S. Wulfman, under whose direction this dissertation was prepared.

For providing the financial support, the author wishes to thank Dr. William H. Webb and the Department of Chemistry for teaching assistantships; the University of Missouri-Rolla and the Dean of the Graduate School, Dr. Robert F. McFarland, for summer assistantships in 1972 and 1973; Dr. Robert Carlisle and I.A.E.S.T.E., for the privilege of working at Reactor Centrum Nederland in the summer of 1971.

Special thanks are due to my wife Katherine for her encouragement, assistance in completing my literature search, and proofreading and typing this dissertation.

The author wishes to acknowledge Bro. William Chewning, S.M. for initating an interest in chemistry.

The author wishes to dedicate this work to Fatima without whom none of this would be possible.

TABLE OF CONTENTS

Table of Contents (continued) Page

Table of Contents (continued) Page

LIST OF ILLUSTRATIONS

Figures Page

LIST OF TABLES

INTRODUCTION

Diazo compounds and their reactions have been known for almost one hundred years. Since that time scores of investigators have examined various aspects of thermal, photolytic, and catalyzed diazo decompositions.

In 1952 Yates[1] first postulated the intermediacy of a copper-carbene complex. It was not until 1964 that the term "carbenoid" appeared in the literature[2]. This term has now obtained general usage to describe a metal complexed divalent carbon species, as opposed to the uncomplexed or free carbene.

During the last decade or so, much attention has turned to the reactions of carbenoid chemistry. Nevertheless, while it has been recognized that carbenoids are not simple, divalent carbon species, their exact nature has remained a mystery. In particular, the relationship between the substrate, metal ion, ligands, and the divalent carbon has not been precisely defined.

The actual valence of the catalyst metal has often been the subject of debate. This aspect is frequently complicated by the observation that different diazo compounds often require different metals and/or valence states for catalyzed decompositions. Indeed, work is often complicated by the observation that despite the original valence of the catalyst, several, or all, valence states may be observed at the completion of the reaction.

It has also been shown that extremely small differences in reaction conditions (temperature, the presence of peroxides or their formation, solubilities, ionic strength, common ions, etc.) can seriously affect the outcome of a carbenoid reaction. Thus it can be extremely difficult to make accurate extrapolation between work done on different systems at greatly different concentrations.

The overall purpose of this work was to ellucidate the mechanistic aspects of the copper catalyzed decomposition of diazo malonate. Realizing the impossibility of offering absolute proof of any given mechanism, experiments were designed to differentiate between various reaction paths and thereby narrowing the field of choice.

The specific problems involved in this research were the establishment of the correct copper state for the catalysis of the decomposition of diazo malonates, ascertaining evidences of the coordination of the transition state, differentiating between the requirements of a unimolecular carbene transfer step and a biomolecular carbene transfer step and establishing guidelines for the mechanistic aspects of "dimer" and "reduced dimer" formation.

I HISTORICAL

A. Carbene

The literature on diazo chemistry and carbenes through 1971 has been thoroughly reviewed by several authors[3,4,5,6,7,8,9] and so no rigorous attempt to present the literature will be made. Nevertheless, some of the salient historical data will be presented here.

The fundamental reactions of carbenes were discovered by Buchner in the 1880's. In 1885 Buchner and Curtius[10] pyrolyzed ethyl diazoacetate in the presence of benzene derivatives and produced the esters which were later "identified" as norcaradienes[11] (Figure 1). By 1903, Buchner had reported the formation of a cyclopropane by the reaction of diazoacetic ester and styrene[12].

Staudinger and Kupfer[13] proposed the presence of a free carbene in the thermal reaction of diazomethane and carbon monoxide which produced, explosively, a trace of ketene.

Metals and their salts were demonstrated to catalyze the decomposition of diazoacetic esters[14,15,16]. Arndt and Eistert[17] used silver, copper, or platinum as catalysts for the Wolff rearrangement of diazo ketones. Yates[1] decomposed diazoketones in the presence of alcohol yielding O-H insertion products, without rearrangement. Yates postulated the intermediacy of a carbene resulting from the interaction of the diazoketone and copper.

By the mid 50's, the so-called Buchner esters[11] had been reexamined by Doering *et al.*[18] who identified the products as substituted tropilidenes instead of norcaradienes.

Shell and Etter[19] found that carboethoxy carbene reacts stereospecifically with *cis* or *trans*-2-butene by *cis* addition, and that it reacts slightly faster with the more highly substituted olefins.

The relative reaction rates of dicarboethoxycarbene with olefins was reported by Neale[20] (Table I). Neale reported stereospecific *cis* addition to the isomeric 2-butenes without insertion products. He also claimed no isolable products from copper catalyzed decomposition of diazomalonic ester in olefins.

Solvent effects in the reaction of methylene with benzene (Figure 2) were reported by Russell and Hendry[21] (Table II). This variance was ascribed to πcloud stabilization of methylene by the aromatic solvents. This concept is supported by the observation of Schollkopf[22] that the rate of addition of halocarboethoxy carbene is a function of the ionization potential of the olefin.

B. Carbenoids

A variety of different metals and their salts have been employed as useful catalysts in diazo decompositions. Despite the broad range of metals which can be employed, their synthetic utility is often limited by their non

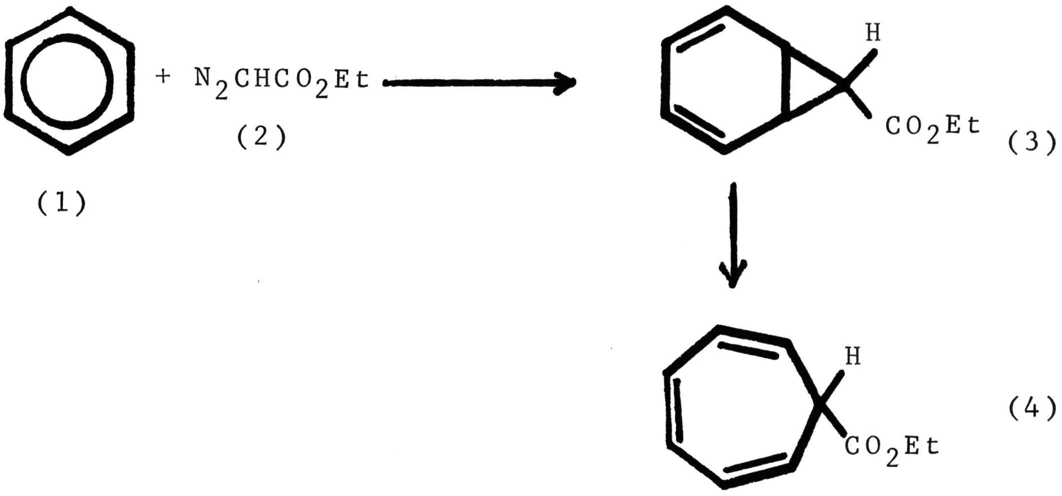


Figure 1. Buchner Ester Formation[11,18]

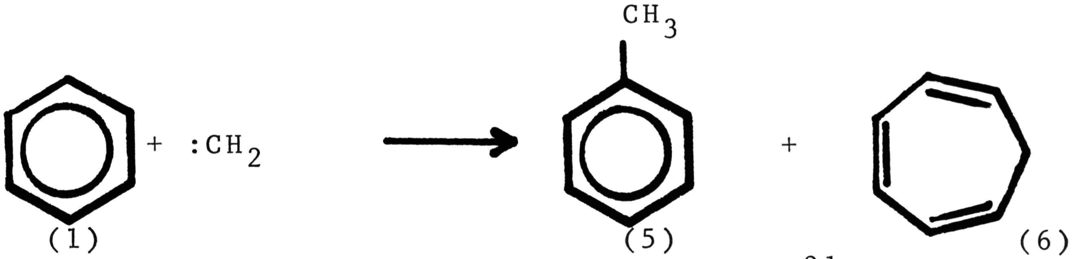


Figure 2. Tropilidene Formation[21]

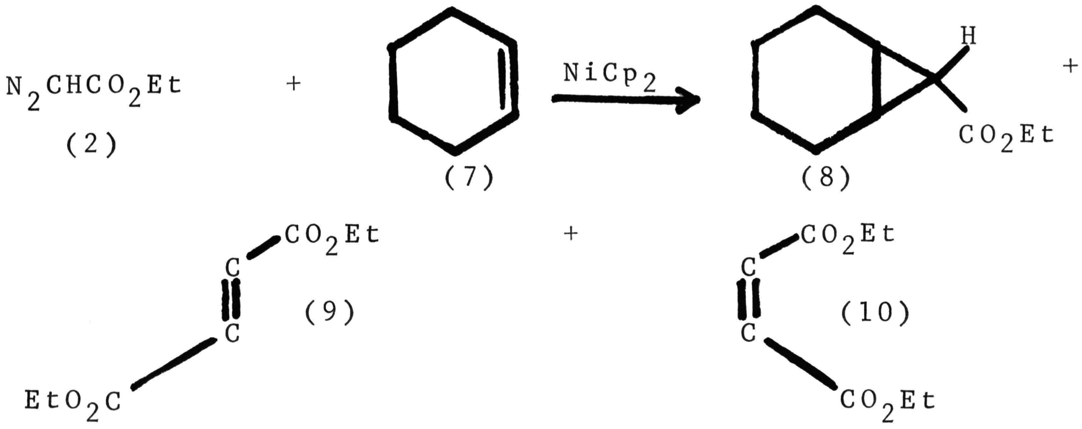


Figure 3. Nickelocene Catalysis[23]

TABLE I

REACTION RATE OF DICARBOETHOXY CARBENE WITH OLEFIN[20]

Olefin	Rate
isobutylene	13.7
Butadiene	10.6
cis-2-butene	5.13
trans-2-butene	2.93
Cyclohexene	2.44
1-butene	1.00

TABLE II

SOLVENT EFFECTS IN THE METHYLENE/BENZENE REACTION[21]

Solvent (conditions)	Tropilidene:Toluene
None (vapor phase)	3.3
Benzene (liquid phase)	4.8
t-Butylnaphthalene-Benzene	7.0

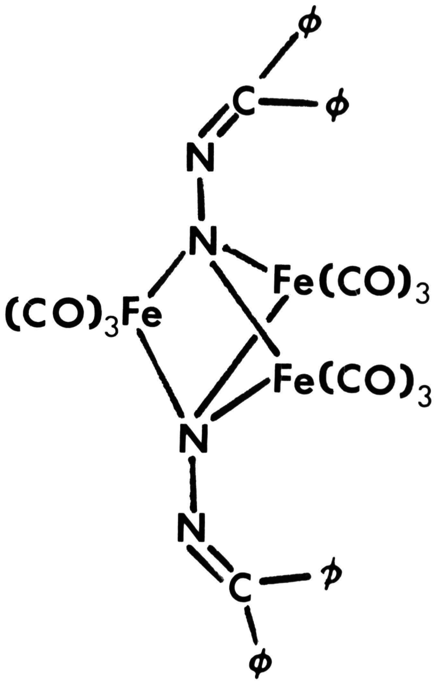
catalytic behavior with one or more classes of diazo compounds. For instance, Werner and Richards[23] found that Nickelocene ($NiCp_2$) catalyzed diazomethane decomposition to produce only polymer, even in cyclohexene solution. However, Nickelocene catalyzes cyclopropanation with diazopropene or ethyl diazoacetate and olefins. At the same time, diphenyldiazomethane and diazofluorene do not decompose catalytically with Nickelocene. Werner and Richards attributed this failure to steric factors.

The Nickelocene catalyzed decomposition of ethyl diazoacetate in cyclohexene gives maleate, fumarate, and norcarane in the ratio 2.6:1.4:1.0 (Figure 3). Copper catalysis normally gives higher yields of the more stable fumarate.

Nickel carbonyl decomposes most diazo compounds. Reaction with ethyl diazoacetate and cyclohexene gives only fumarate and norcarane in a ratio of 6.1:1.0[23].

Iron dipivaloylmethide decomposes diazomethane in cyclohexene to produce low yields of norcarane[24,25] free from C-H insertion products. Ferrocene, however, does not catalyze the reactions[26]. Iron carbonyls fail to decompose phenyldiazomethane; however diphenyldiazomethane forms a stable complex (Figure 4).

Dicyclopentadienyl chromium reacts rapidly with one equivalent of ethyl diazoacetate, and slowly with excess diazoacetate, to form fumarate, maleate, and norcarane in



(11)

Figure 4. Phenyldiazomethane-Iron Carbonyl Complex[26]

the ratio 1.5:0.6:1.0. It does not rapidly decompose diazomethane, and no polymethylene, ethylene, or volatile hydrocarbons are produced.

Copper (0), Copper (I), and Copper (II) have been studied extensively as catalysts for a variety of diazo decompositions. It has recently been shown[6] that homogeneous catalyst systems are superior in so far as the isolation of identifyable products is concerned when diazomalonic ester is employed.

Takebayashi et al.[27,28] used $Cu(AcAc)_2$ to decompose α-diazoacetophenone in various substrates. The carbene chelate[12] was postulated as the intermediate. The carbenoid did not add to benzene or diphenylacetylene. The usual dimeric products[13,14,15] along with the dimer of diphenylketene were also found (Figure 5).

Peace[6] showed $Cu(AcAc)_2$ to be a superior catalyst for the decomposition of dimethyl diazomalonate in cyclohexene. However, Nozaki et al.[29] found that the $Cu(AcAc)_2$ failed to catalyze the reaction of diphenyl diazomethane with either cyclohexene or ethylvinyl ether. Cyclohexanone enamine did add the carbenoid to give 62% cyclopropane derivative.

Peace[6] found that at optimum concentrations, this catalyst doubled the yield obtained with heterogeneous catalysts. He also noted the formation of a small amount of metallic copper during the reaction, which implies the presence of all three valence states of copper.

Nozaki[30,31] also used a chiral copper (II) complex, bis-N-(R)-α-phenethy(salicylaldiminato) copper (II) for the decomposition of diazo compounds. This chiral complex catalyzed the decomposition of ethyl diazoacetate in the presence of styrene or 2-phenyloxetane to give asymmetric products (Figure 6), with optical yields of 6-8%. Similar optical yields resulted when the catalyst was used with diazomethane and either cis, trans, trans-1,5,9-cyclododecatriene or trans-propenylbenzene. The author discounted the presence of free carbene on the basis of dilution data.

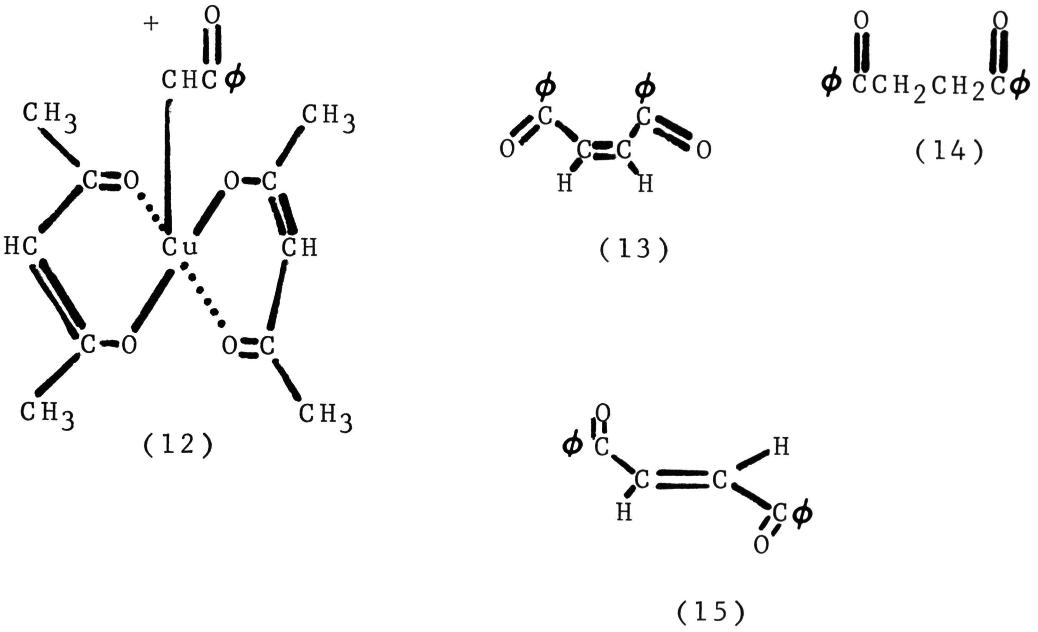


Figure 5. Takebayashi's Products[13,14,15]

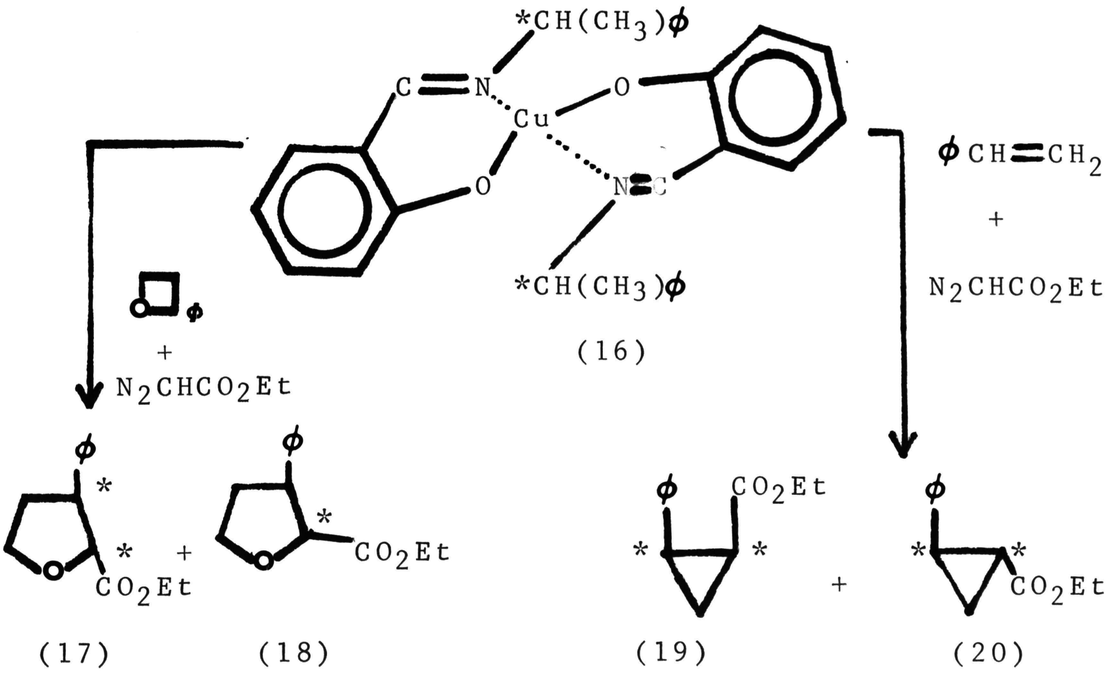


Figure 6. Nozaki's Reactions[30,31]

Cooke and Fisher[32] used a stable transition metal-carbene complex as a starting material to synthesize the chiral phosphine-metal-carbene complex: (-)(R)-methylphenylpropylphosphine (phenylmethoxy-carbene) tetracarbonyl chromium (Figure 7). This complex reacted with diethyl fumarate to yield the optically active cyclopropane[22].

Moser[33,34] used optically active tribornylphosphite copper (I) chloride (Figure 8) to catalyze the decomposition of ethyl diazoacetate in styrene. The resulting cyclopropane was produced in low (3%) optical yield. Moser claimed his results require a transition state in which catalyst, carbene, and olefin are all present.

Hammond[35] found the copper (II) dipivaloylmethide complex (Figure 9) inferior to copper salts for the reaction of α-diazoacetophenone with cyclohexene.

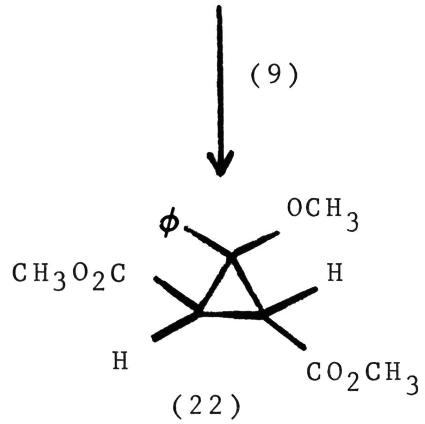
A betaine intermediate has been postulated for the $Cu(AcAc)_2$ catalyzed decomposition of various α-diazoacetophenones [36,37]. In one case[37] the betaine intermediate was trapped with a conjugated diene.

Ethyl diazoacetate can react with $Cu(AcAc)_2$[38]. The main product (Figure 10) results from the reaction of one carbenoid with two acetylacetone molecules. Diethyl maleate, but no fumarate was isolated in 45% yield.

Simple arylcopper reactions of ethyl diazoacetate also produced 40% maleate. Fluorinated arylcopper

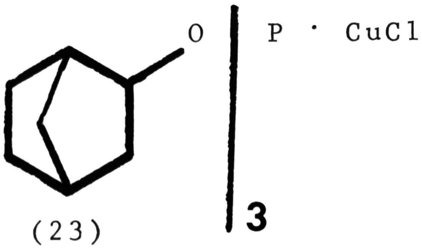
$Cr(CO)_4(P(CH_3)(\phi)(Pr))\text{-}C(OCH_3)\phi$

(21)



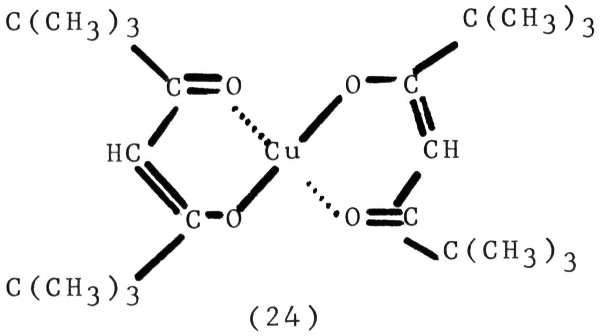
(22)

Figure 7. Cooke and Fisher's Reaction[32]



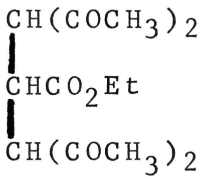
(23)

Figure 8. Tribornylphosphite Copper (I) Chloride[33,34]



(24)

Figure 9. Copper (II) Dipivaloylmethide[35]



$$\begin{array}{l} CH(COCH_3)_2 \\ | \\ CHCO_2Et \\ | \\ CH(COCH_3)_2 \end{array}$$

(25)

Figure 10. Ethyl Diazoacetate and $Cu(AcAc)_2$ [38]

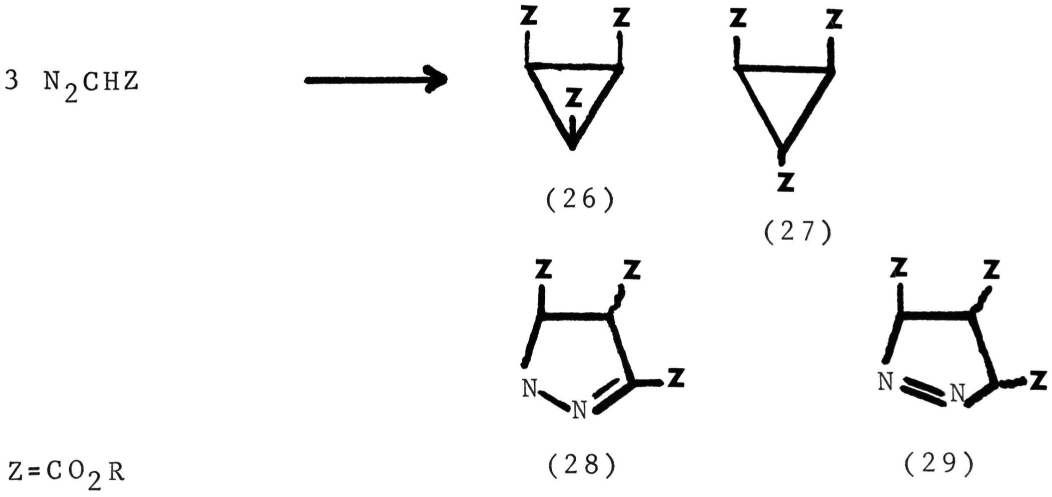


Figure 11. Dimeric Products

compounds, however, gave a 1:1 ratio of maleate to fumarate[39,40].

C. Dimeric Processes

Some of the most common by products of carbene and carbenoid reactions are formally derived from carbene dimerization. Under certain circumstances these olefins and/or their saturated analogs can be obtained as the major reaction products. Unfortunately, since these products are rarely desired, attention is seldom paid to them, no matter from what intermediate they may be derived. In many cases trimeric or even higher order condensation products have resulted.

Peace[6] has shown that at certain high catalyst concentrations, dimethyl diazomalonate gives the dimer tetracarbomethoxy ethylene as the major product. In this case neither the cyclopropane nor the pyrazoline trimer have been found. Attempts to prepare either analog resulted only in further dimer formation. No literature reference has been found to hexacarbomethoxycyclopropane.

Diazoacetates frequently give large amounts of maleates and/or fumarates. Here catalyst selection will largely dictate the relative amounts of dimeric products [23,26,41,42,43] (Table III). In some cases, the thermodynamically more stable fumarate isomer does not appear[38].

In the case of diazoacetates, three types of compounds formally derived from three molecules of diazo

TABLE III

RATIO OF PRODUCTS FROM CATALYZED DECOMPOSITION OF ETHYL DIAZOACETATE

CATALYST	DIETHYL FUMARATE	DIETHYL MALEATE	ETHYL NORCARANE-CARBOXYLATE
$NiCp_2$	1.4	2.6	1.0
$Ni(CO)_4$	6.0	---	1.0
Cu	0.57	0.67	1.0
CuBr	0.5	0.5	1.0
$CuSO_4$	0.7	0.5	1.0
ZnI_2	1.4	0.6	1.0
$CrCp_2$	1.5	0.6	1.0

Cp=Cyclopentadiene

compound can arise: two isomeric cyclopropane derivatives and Δ-1 or Δ-2 pyrazolines resulting from 1,3 additions across the double bond of the dimer (Figure 11).

Only in recent times has confusion resulted from the isolation of the pyrazoline trimer. Buchner[44,45,46,47] and co-workers first identified the trimeric pyrazoline as the rearranged ester of Δ-2-pyrazoline-3,4,5-tricarboxylic acid. Reaction of diazoacetate with either maleate or fumarate yielded the same stable material. Heating this pyrazoline well above its melting point furnished the trans-cyclopropanetricarboxylic ester[48,49,50]. In the past few years the chemical literature has been misquoted[5,26] and the Δ-1-pyrazoline been cited.

As a result of this work and work in our own laboratory, Kochi's[51] claim to have isolated 2-3% cis-triethyl cyclopropane-1,2,3-tricarboxylate free from the trans isomer must be viewed with some doubt.

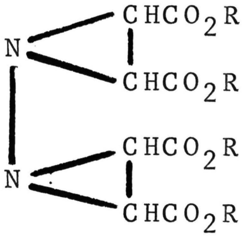
Curtius[52] reported a tetrameric compound from the thermal decomposition of diazoacetate of the formula $C_{12}H_{16}N_2O_8$. The tetrameric structure (Figure 12) was postulated.

Schenck and Ritter[53] investigated the photolysis of carbomethoxycarbene and identified a tetrameric product as either compound 31 or 32 (Figure 13).

A decomposition of ethyl diazoacetate by copper-bronze produced, among other products, a material which was hydrolized and converted to the methyl ester and identified as methyl cyclobutane-1,2,3,4-tetracarboxylate[54,55].

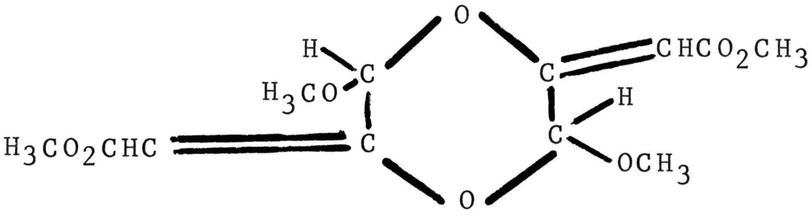
Forbes and Wood[49] examined by products from the thermal decomposition of ethyl diazoacetate in N-alkane. Polymeric material of the formula $N_2(CHCO_2Et)_{12}$ was found, but not identified. The presence of the nitrogen in a pyrazoline ring was discounted since prolonged heating at 240° C did not reduce the nitrogen content. The <u>trans</u>-pyrazoline and/or it's decomposition product, the <u>trans</u>-cyclopropane was also identified as is usual in thermal decompositions, especially in the presence of copper catalysts[42,45,47,49,50,52].

Structures of the type of 33 (Figure 14) have also been found in copper catalyzed reactions of ethyl diazoacetate.

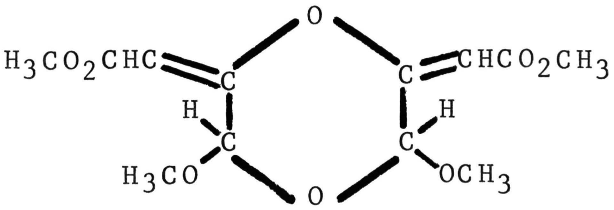


(30)

Figure 12. Diazoacetate Tetramer[52]

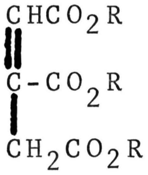


(31)



(32)

Figure 13. Carbomethoxy Carbene Tetramer[53]



(33)

Figure 14. Diazoacetate Trimer[49]

II RESULTS AND DISCUSSION

A. Cyclopropanation

The copper catalyzed decomposition of diazo compounds in the presence of olefins normally proceeds via one of three pathways: cyclopropanation, dimerization yielding olefinic products, or C-H insertion reactions with olefin substrates, catalyst, or additional diazo compound (Figure 15).

Most of the work in the field has been concerned with the mechanistic aspects of the cyclopropanation reaction since this obviously has the greatest synthetic utility.

Dimerization processes, on the other hand, are rarely used synthetically[57] and quite often cited in the literature principally to account for low cyclopropane yields. It is also necessary to account for the fate of the initial diazo compound when evaluating mechanisms. For this reason carbenoid reactions in this laboratory are routinely run at 0.14 millimole of catalyst for fifty milliliters of olefin, a concentration which has been shown to give routinely the highest yield of all identifiable products[6].

Difficulties in the field of catalyzed diazo decomposition arise from the inability of researchers to draw parallels from similar work with other systems. That is, a given transition metal or valence state may decompose

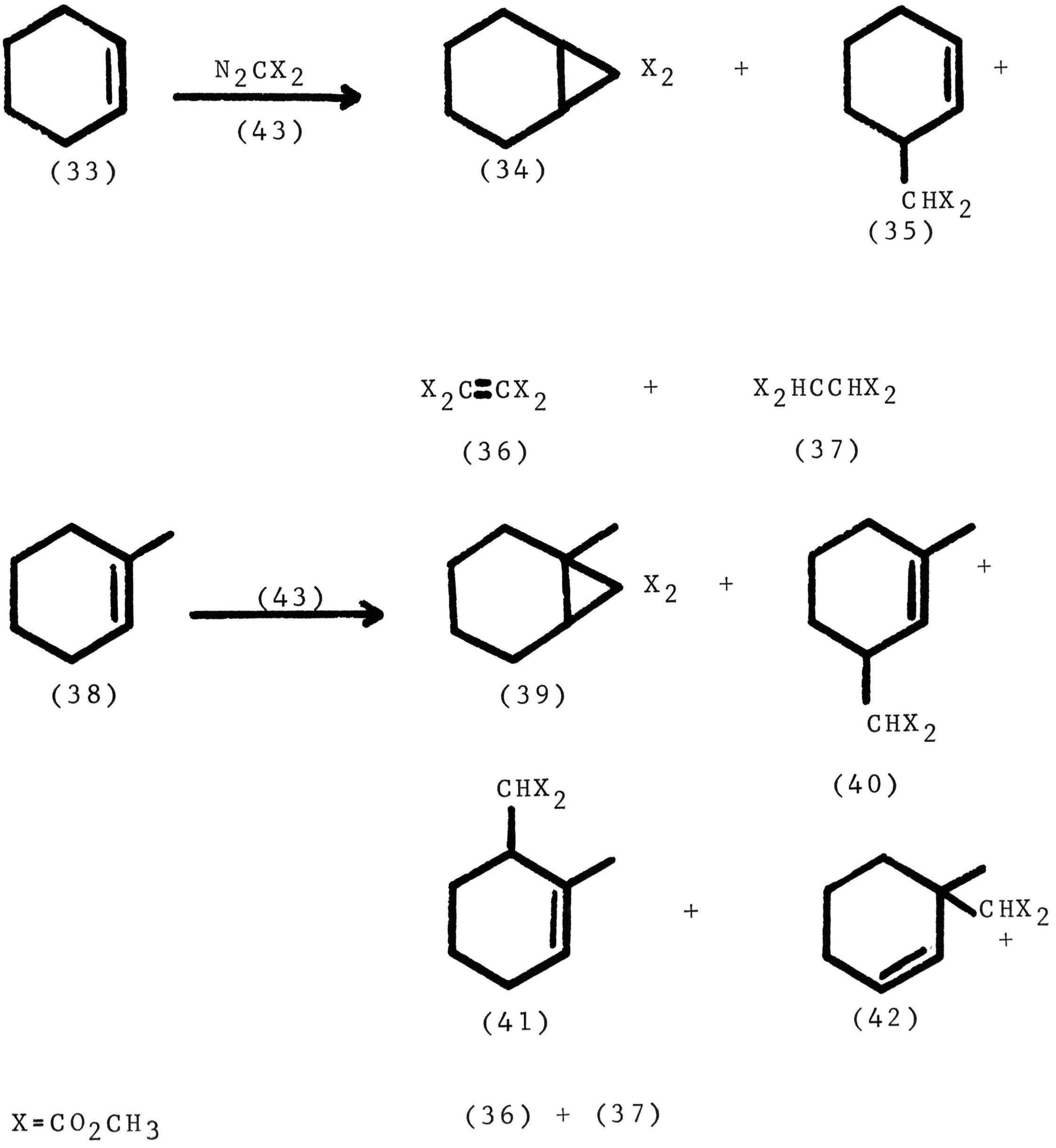


Figure 15. Products From Cyclohexene and 1-Methylcyclohexene

some diazo compounds, but not others, regardless of their stabilities. Copper catalyzed decompositions are complicated by the fact that all valence states of copper are normally found after a reaction. Additionally, Peace[6] has demonstrated the dependence of product distribution on catalyst concentration, using both copper (I) and copper (II) catalysts.

There is no a priori reason to assume that a single catalyst will decompose different diazo compounds, e.g. diazoacetate and diazomalonate, via the same pathway. Indeed, different researchers might alter the reaction path simply by inadvertant presence or absence of small amounts of impurity, e.g. peroxide in the case of copper (I) catalysis.

It has been previously shown in these laboratories that in reactions with diazo malonate, the presence of peroxides is highly beneficial when utilizing copper (I) complexes, while the effectiveness of copper (II) compounds is unaffected[6]. This is a definite indication that soluble copper (II) species are more active catalysts, if not the actual catalysts in these reactions.

The implications of much of the previous work on diazoacetate decompositions are uncertain. Moser[33,34] used a catalyst concentration far above that established in our laboratory as optimum, and the chemical purity of his catalysts has not been established in the literature.

Kochi's[51] work with ethyl diazoacetate is similarly confusing. While claiming in situ reduction of copper (II) compounds, he intentionally used olefin neither freed from peroxide nor degassed; nor was any distinction made as to the optimum catalyst concentrations in his studies. His rather unusual claim to have detected traces (2-3%) of triethyl cis-1,2,3-cyclopropanetricarboxylate as a reaction by-product would be unique in the face of the work of other researchers. Additions of diazoacetate to maleate or fumarate leads to the same Δ-2-pyrazoline which thermally decomposes to the trans-cyclopropane. Previous reports of this trimeric by-product in copper catalysis reactions indicated the pyrazoline and/or the trans-cyclopropane[42,44,45,47,49]. For these reasons, the real importance of Kochi's work is yet to be determined.

The specific problems involving cyclopropanation were to add evidence to the nature of the catalytic species, to formulate possible and plausible mechanisms for the process, and to obtain data contradictory to most of the possibilities. To be more specific, the copper cation and whatever ligands may be associated with it, the carbenoid carbon, and the olefinic substrate must all be accounted for as contributing or not contributing in the transition state of the cyclopropanation reaction.

Basic to the study of carbenoid or carbene transfer reactions, is the understanding of the two basic pathways open for the reaction. The first possibility involves the formation of the carbenoid species with subsequent autodissociation to free carbene. This can be called a unimolecular carbene transfer (CT-1). This process would involve the diazo-copper complexation, loss of nitrogen to form the carbenoid, and finally the autodissociation to free carbene. The rate determining step could be any of these processes, for there is no a priori reason to specify a particular step. The second possible transfer reaction type is a bimolecular carbene transfer (CT-2) involving one molecule of olefin substrate and one molecule of carbenoid. Again, the rate determining step is uncertain. There is the diazo-copper complexation, loss of nitrogen to carbenoid, and the inter- or intramolecular attack of olefin on carbenoid. This attack could occur in either a concerted or nonconcerted manner.

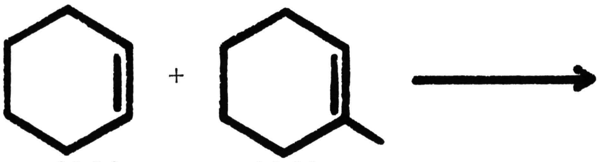
There also exists the very real possibility that more than one such mechanism does occur in the same reaction vessel. In this case steric and/or electronic differences in the catalyst or substrate may alter the partitioning. Thus, the dependence of product distribution on catalyst structure is not, in itself, proof of a pure CT-2 reaction. A mixed path, however, means that products not common to both paths may disappear in a given reaction when one path predominates. In a CT-1 reaction, of course, the relative amounts of any product type must be independent of the catalyst.

The first major evidence that the transition state of the cyclopropanation reactions involved both the carbene and the metal ion resulted from optical induction experiments. When optically active soluble copper (I)[1] or copper (II)[31] catalysts were employed in the diazoacetate-styrene reaction, the products included low yields of potically active cyclopropanes. The lower optical yield involving the copper (I) phosphite catalyst was attributed to the greater distance from the asymmetric center to the reaction center. In the light of our work, an alternate explanation would involve the necessary catalyst modification from copper (I) to copper (II) which could result in the partial destruction of the asymmetric ligancy of the copper. A second ramification of these results would be the necessity of retaining these chiral ligands attached to copper throughout the course of the reaction. In the asymmetric synthesis of 1-methyl-2-phenyl cyclopropane[31], the optical yield of the product remained constant using (N-(R)-α-Phenethylsalicylaldiminato) copper (II) catalysis of diazomethane in <u>trans</u>-propenylbenzene. This indicates primarily that the chiral ligands are fully retained throughout the course of the reaction. The alternative would be an initial high optical yield followed by alteration of the catalyst's chiral coordination with a subsequent steadily decreasing level of optical induction. Nozaki[31] also reported that the optical yields remained constant on dilution with n-hexane. This is interpreted to rule out the possibility of a free carbene with the optical induction resulting from asymmetric solvation by the soluble, optically active catalyst.

When a 1:1 mole ratio of cyclohexene and a 1-methylcyclohexene was reacted with dimethyl diazomalonate photochemically and in the presence of a series of soluble copper (II) catalysts, the norcarane product distribution was found to vary greatly with the type of catalysts (Table IV).

The disparity between the catalyzed and photochemical results indicate that different intermediates are involved (i.e. carbenoid vs carbene). The immediate supposition of a metal complexed divalent carbon species is strengthened by the variation of the product ratio depending on the substituents on copper. This also tends to indicate that the ligands remain closely associated with copper during the reaction course. Additionally, the catalysts exhibit a marked selectivity in a mixed substrate. The transition state must therefore reflect this selectivity and can be rationalized merely by requiring the presence of all three reacting species. Thus, the metal ion, divalent carbon or diazo compound, as well as the olefin must participate in the transition state. This does not

TABLE IV
COMPETITION VERSUS CONDITIONS



(33) (38)

(34) + (39)

CATALYST	SOLVENT	TEMP. °C	PRODUCT DISTRIBUTION 39:34
$CuCl \cdot P(OCH_3)_3$	NEAT	REFLUX	1:4.90
$Cu(BF_4)_2$	NEAT	REFLUX	1:13.82
$Cu(BF_4)_2$	C_6F_6	REFLUX	1:2.29
$Cu(AcAc)_2$	NEAT	REFLUX	1:2.73
$Cu(AcAc\text{-}F_3)_2$	NEAT	REFLUX	1:2.96
$Cu(AcAc\text{-}F_6)_2$	NEAT	REFLUX	1:2.58
Photolysis	NEAT	REFLUX	1.1:1
Photolysis (ϕ_2CO)	NEAT	35°	2:1
Photolysis	NEAT	35°	3:1

necessarily propose the presence of the reacting olefin prior to bond formation. The reaction could be initiated by attack of olefin from the solvent sphere upon the carbenoid.

Hexafluorobenzene is well known for forming charge transfer complexes by acting as an electron acceptor[57]; an increase in the stability of the complex with increasing donor capacity has been noted[58]. Hexafluorobenzene stabilization of the transition state involving the more electron rich 1-methylcyclohexene would account for the leveling effect this solvent has on selectivity.

This enhanced stability is also substantiated by the observation of Peace[6] that with high catalyst concentration in hexafluorobenzene dimer formation (normally the major product at high catalyst concentration) is suppressed.

Marchand[59] points out that a mechanism which has not been rigorously excluded involves a metal complexed olefin which suffers rate determining attack by uncomplexed diazo compound, and the resulting complexed pyrazoline could then undergo a facile collapse to product (Figure 16).

Although no reference to copper catalyzed pyrazoline decomposition was found in the literature, it was decided to test the hypothesis. The Δ-1-pyrazoline (44) resulting from the 1,3-dipolar addition of dimethyl diazomalonate.

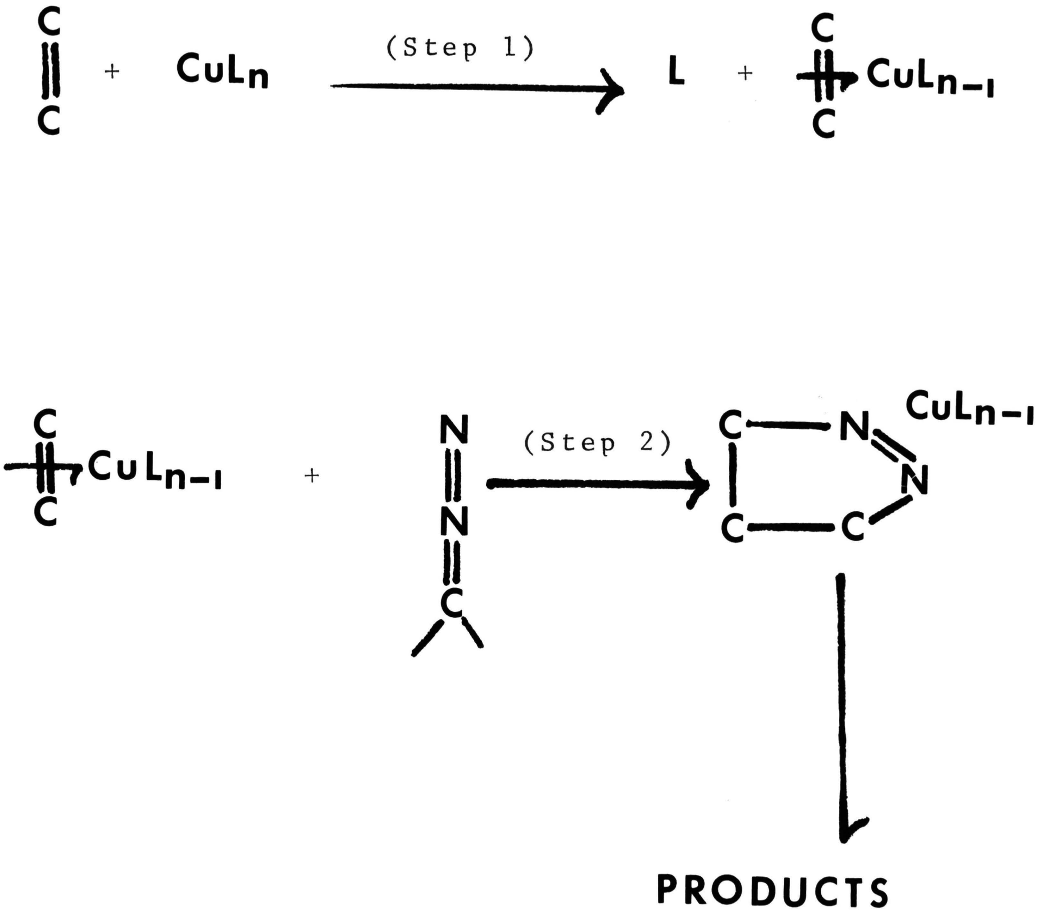


Figure 16. Pyrazoline Mechanism

to 3a,4,7,7a-tetrahydro-4,7-methanoindene (dicyclopentadiene, (43)) was stable in refluxing benzene in the absence of $Cu(BF_4)_2$ catalysis. These conditions closely approximated normal reaction conditions. Addition of $Cu(BF_4)_2$ was followed almost at once by gas evolution. NMR and mass spectral studies of the product indicate the expected cyclopropane derivative (45) (Figure 17). Thus there is no a priori reason to discount this mechanistic possibility. The formation of insertion products via this route will be discussed later. Under the same conditions, triethyl-Δ-2-pyrazoline-3,4,5-tricarboxylate was recovered unchanged.

A series of copper (II) complexes of 1,3 diones and copper (II) salts of organic acids was examined for catalyst efficiency in the decomposition of dimethyl diazomalonate in cyclohexene. The results are summarized in Table V. The copper salts showed very similar catalytic activity as would be predicted from the lower (two) number of coordination sites demanded by the ligands. The 1,3 diones, however, require four coordination sites. The fact that the relative yield of norcarane falls drastically in the case of copper (II) dipivaloylmethane is indicative of severe steric interaction. Based on available x-ray crystallographic data and molecular models, intramolecular distances can be estimated. In the case of acetylacetone, the distance between terminal protons

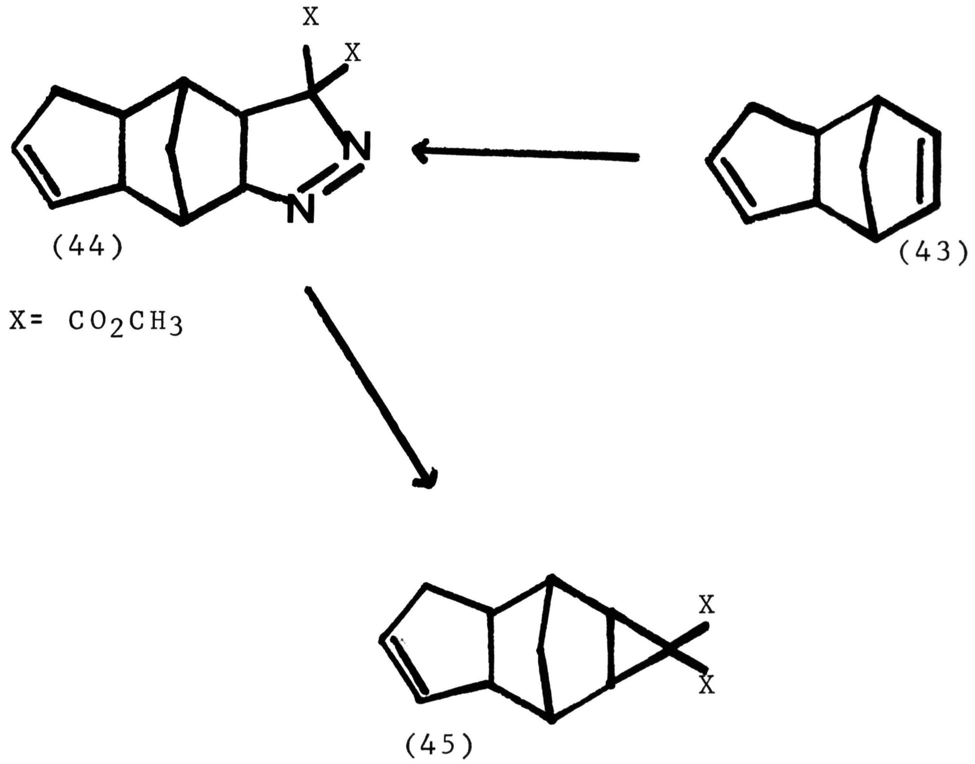


Figure 17. Copper Catalyzed Pyrazoline Decomposition

is estimated at 5.1Å. For dipivaloylmethane, the distance falls to 3.2Å.

The data in Table V is also indicative of the fate of the ligands associated with the copper catalyst. The high steric dependence of the reaction products requires that the 1,3-dione-copper (II) complex remain associated during the course of the reaction. Attack of olefin would require displacement of the ligand at only one point of attachment, with recoordination after the reaction had gone to product.

This data is in agreement with the optical induction studies.

B. Dimerization

Tetracarbomethoxyethylene, the carbene dimer from dimethyl diazomalonate, can arise via several general paths (Figure 18): the action of free carbene on carbenoid, the action of diazo-compound on carbenoid, or the action of carbenoid on carbenoid.

The results of a series of photochemical reactions of dimethyl diazomalonate in cyclohexene are given in Table VI. The data clearly indicates that only negligable quantities of dimer arise in the absence of copper salts.

Photolysis in the presence of copper (II) affords the opportunity to observe a carbene reacting with carbenoid. The relatively small amount of dimer formed in

TABLE V

COPPER (II) CATALYST VERSUS PRODUCTS IN THE REACTION OF DIAZOMALONATE IN CYCLOHEXENE

CATALYST LIGAND	Product relative to standard (and to norcarane) (3)	(4)	(5)	(6)
Dipivaloylmethane	0.051 (1.00)	0.004 (0.09)	0.386 (7.52)	0.228 (4.43)
Acetylacetone	4.54 (1.00)	0.145 (0.03)	0.461 (0.10)	0.053 (0.01)
Acetylacetone-f_3	0.484 (1.00)	0.039 (0.08)	0.016 (0.03)	0.023 (0.05)
Acetylacetone-f_6	1.054 (1.00)	0.054 (0.05)	0.986 (0.94)	0.041 (0.04)
Thenoyltrifluoroacetylmethane	1.224 (1.00)	0.078 (0.05)	0.115 (0.09)	0.034 (0.03)
Benzoylacetylmethane	0.562 (1.00)	0.015 (0.03)	0.421 (0.75)	0.141 (0.25)
Acetate (H_2O)	1.291 (1.00)	0.112 (0.09)	0.408 (0.32)	0.105 (0.08)
Octoate	1.97 (1.00)	0.090 (0.05)	0.240 (0.12)	0.200 (0.10)
Stearate	1.859 (1.00)	0.122 (0.07)	0.231 (0.12)	0.214 (0.11)
Ethyl acetoacetate	1.581 (1.00)	0.097 (0.06)	0.500 (0.32)	0.128 (0.08)

$$R_2C\colon + \colon CR_2 \longrightarrow R_2C{=}CR_2$$

$$R_2C\colon + N_2CR_2 \longrightarrow R_2C{=}CR_2 + N_2$$

$$L_nCu{=}CR_2 + \colon CR_2 \longrightarrow R_2C{=}CR_2 + L_nCu$$

$$L_nCu{=}CR_2 + N_2CR_2 \longrightarrow R_2C{=}CR_2 + L_nCu + N_2$$

$$L_nCu{=}CR_2 + L_nCu{=}CR_2 \longrightarrow R_2C{=}CR_2 + 2L_nCu$$

Figure 18. Dimerization Paths

TABLE VI

DIMETHYL DIAZOMALONATE IN CYCLOHEXENE VERSUS CONDITIONS--PHOTOCHEMICAL

			RELATIVE YIELDS				
SENSITIZER	ENERGY	TEMP. C	(35)	(34)	(R)	(36)	(37)
NONE	--	0	0.47	1.00	0.05	T	0
		54	0.46	1.00	0.11	0	0
ACETONE	78	0	0.42	1.00	0.05	0	0
		54	0.50	1.00	0.05	0	0
BENZOPHENONE	69.3	0	0.13	1.00	0.11	0	X
		54	0.19	1.00	0.10	0	X
HFB	--	0	0.46	1.00	0.23	0	T
		54	0.47	1.00	0.39	0	T
COPPER(II)OCTOATE	--	0	0.43	1.00	0.045	0.02	T
		54	0.44	1.00	0.03	0.02	T

R=random insertion

this reaction indicates the importance of this route. The process clearly involves a thermal, copper catalyzed reaction (Figures 19,20,21).

Furthermore, the fact (Table V) that dimer is not suppressed by the steric factors which depress norcarane formation rules out its formation by only interaction of two carbenoids (Figure 21). Hammond's[35] work with diazoacetophenone and copper (II) dipivaloylmethane exhibits the same effects. With this bulky catalyst, cyclopropanation accounts for only 19% of the reaction products as opposed to 55% using cupric sulfate.

When using copper (II) catalysts with low steric requirements, dimer formation at high catalyst concentration predominates. These facts are indicative of a mixed path, with the steric requirements of the catalyst determining the partitioning.

The remaining pathways consist of an attack by diazo carbon upon either carbenoid copper or carbenoid carbon with subsequent loss of nitrogen and collapse by either a *cis* or *trans* elimination. In the case of diazomalonate these paths are indistinguishable. However, when the decomposition of ethyl diazoacetate is examined, the path can be elucidated. In this case, the ratio of *cis* (maleate) to *trans* (fumarate) has been found to vary with catalyst and with catalyst concentration. In at least one case[38], $Cu(AcAc)_2$ catalysis resulted in formation of 45%

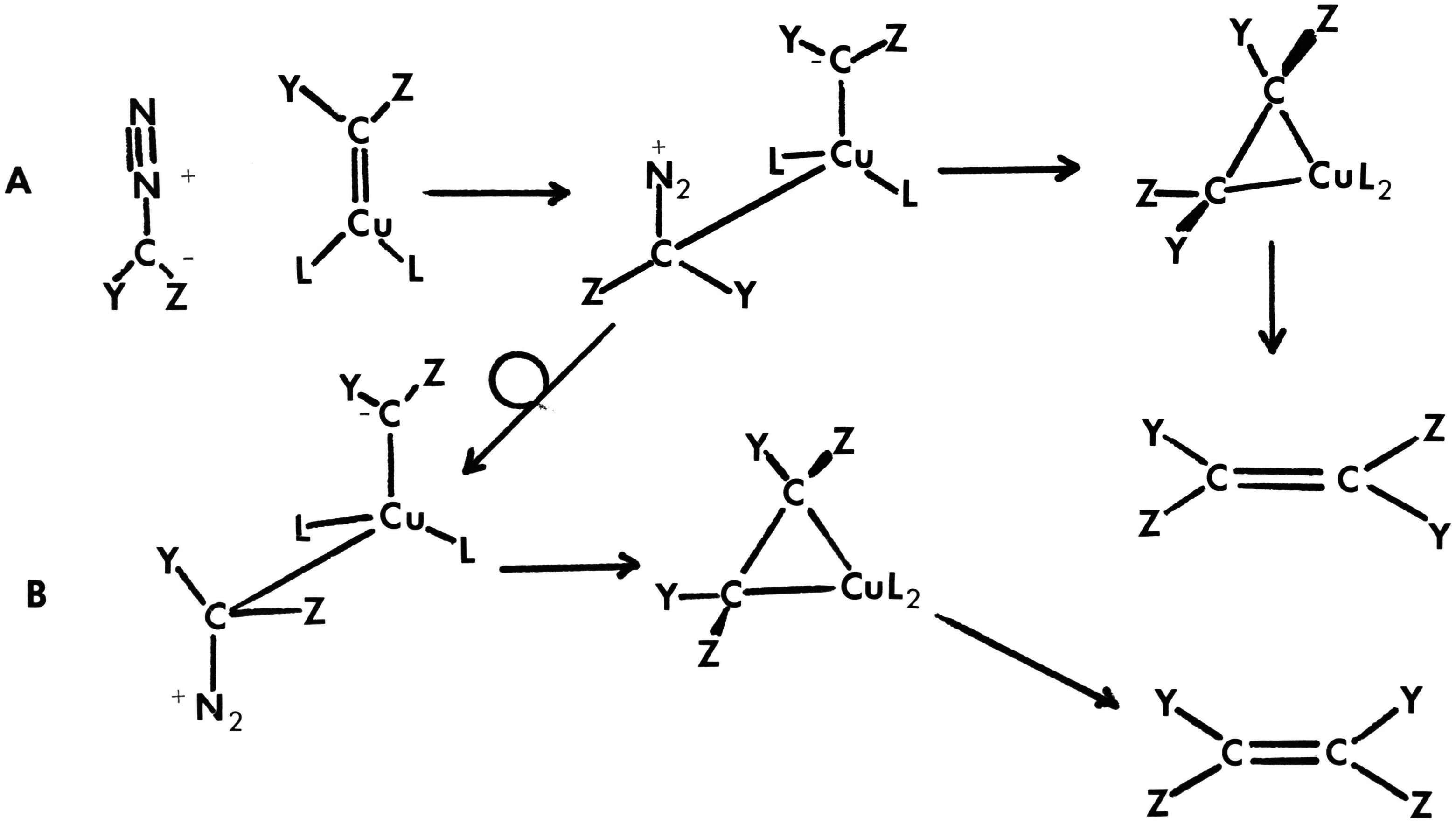


Figure 19. Dimerization Paths A and B

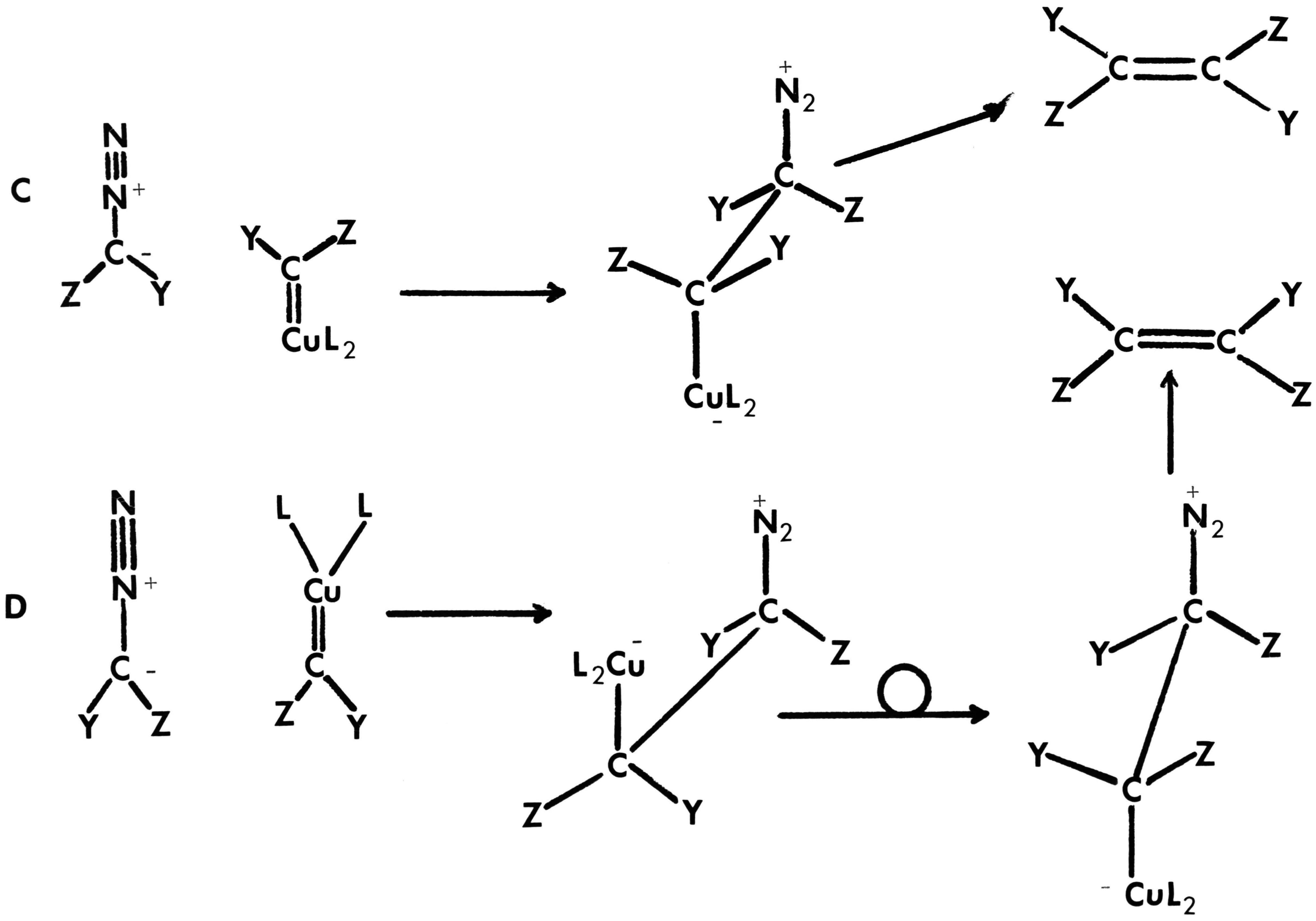


Figure 20. Dimerization Paths C and D

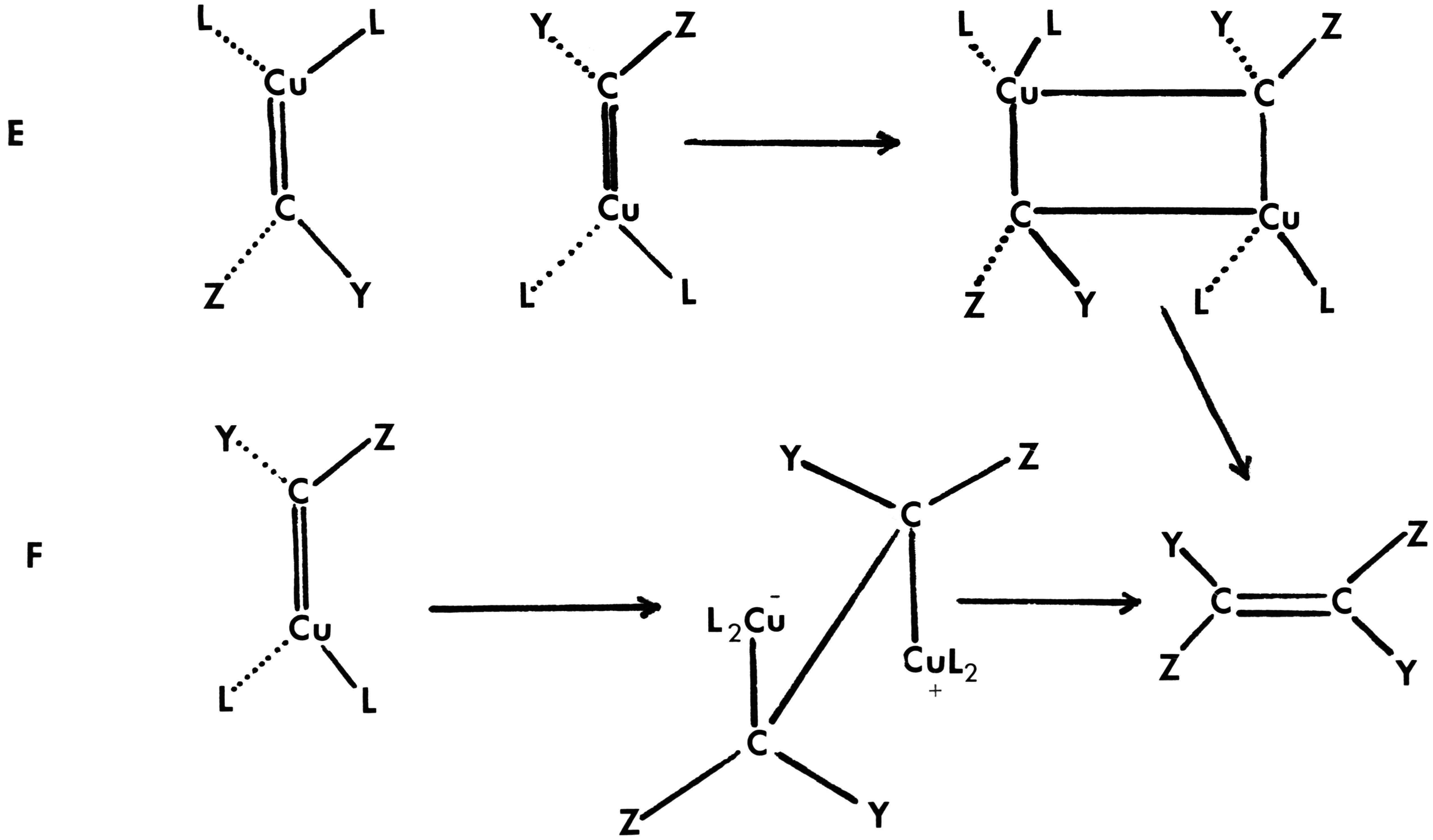


Figure 21. Dimerization Paths E and F

diethyl maleate, while the thermodynamically more stable trans isomer (fumarate) was not detected. We have seen (Table VII) that the trans/cis product ratio can vary with catalyst concentrations.

Since the product distribution implies steric control, the transition state must reflect this. Because of steric and electrostatic interactions, the approach of diazoacetate to a carbenoid will occur in the configuration which minimizes repulsion. Moreover, the greater the differences between substituents Y and Z, the greater will be the preference for a particular approach configuration.

The ligands substituted on copper will likewise effect the reaction, balancing steric factors with electrostatic effects. Both steric and electrostatic repulsion will tend to force the diazo compound to approach in an anti fashion where like groups are opposed. Paths A and B (Figure 19) suffer from the defect of necessitating attack on copper which is effectively blocked by ligands of high steric requirement. Additionally, Path A would require a cis elimination which would be an unusual requirement. Excluding Path A would then mean that the cis isomer would always be predominating, which we have shown not to be the case.

Paths C and D (Figure 20) which differ in the orientation of the nitrogen atoms in relation to carbenoid

TABLE VII

STEREOCHEMISTRY OF CARBENE DIMERS AS A FUNCTION OF CATALYST CONCENTRATION IN CYCLOHEXENE WITH $Cu(AcAc)_2$-$N_2CHCOOC_2H_5$

CATALYST CONCENTRATION Mg/50ml	$\frac{TRANS}{CIS}$
0	0.53
1	0.69
4	0.69
16	0.89
32	1.03
64	1.39
256	2.18

account via *trans* elimination for *cis* and *trans* products. The ratio of *cis* to *trans* isomers would depend upon the magnitude of the repulsion terms involved in the attack as well as the ability of the intermediate to rotate (Path D) to the *trans* configuration. Path C is, of course, the more straight forward mechanism; but either or both could be expected in the case of a given catalyst system. The presence of the *trans* catalyst species can facilitate loss of nitrogen and collapse to dimer.

C. Insertion Reactions

In dicarbomethoxy carbenoid reactions, the products which can be attributed to C-H insertion reactions are the allylic insertion products and tetracarbomethoxyethane. The latter product can arise via insertion into the C-H bond of malonic ester which is present either as an impurity in the starting diazo compound or produced in the reaction.

The insertion products (Table VIII) derived (detected) from the reaction of dimethyldiazomalonate with 1-methylcyclohexene are illustrated in Figure 15. Two different mechanisms for C-H insertion are outlined in Figure 22. No single mechanism accounts for all the observed insertion products. A hydrogen abstraction, recombination pathway calling for radical-like behavior of the carbenoid can account for compounds 40 and 41. The observation that no methyl C-H insertion occurs is explained partially

TABLE VIII

COMPETITION VERSUS CONDITIONS (50/50 MOLE PERCENT CYCLOHEXENE/1-METHYLCYCLOHEXENE)

CATALYST	CONDITIONS SOLVENT	TEMP. C	RELATIVE YIELDS (34)	(35)	(39)	(40)	(41)	(42)
$Cu(BF_4)_2$	NEAT	REFLUX	13.82	0	1	T	T	0.21
$Cu(BF_4)_2$	90% HFB	REFLUX	2.29	0	1	0.302	T	T
$Cu(AcAc)_2$	NEAT	REFLUX	2.73	0	1	0.268	T	T
$Cu(AcAc\text{-}f_3)_2$	NEAT	REFLUX	2.96	0	1	0.319	0.019	T
$Cu(AcAc\text{-}f_6)_2$	NEAT	REFLUX	2.58	0	1	0.229	0.053	T
$CuI \cdot P(OCH_3)_3$	NEAT	REFLUX	4.90	0	1	0.088	0.580	0.354
photolysis	Φ_2CO sensitized	35°C	0.500	0	1	1.284	T	1.190
photolysis	NEAT	35°C	0.333	0	1	1.410	0.938	0

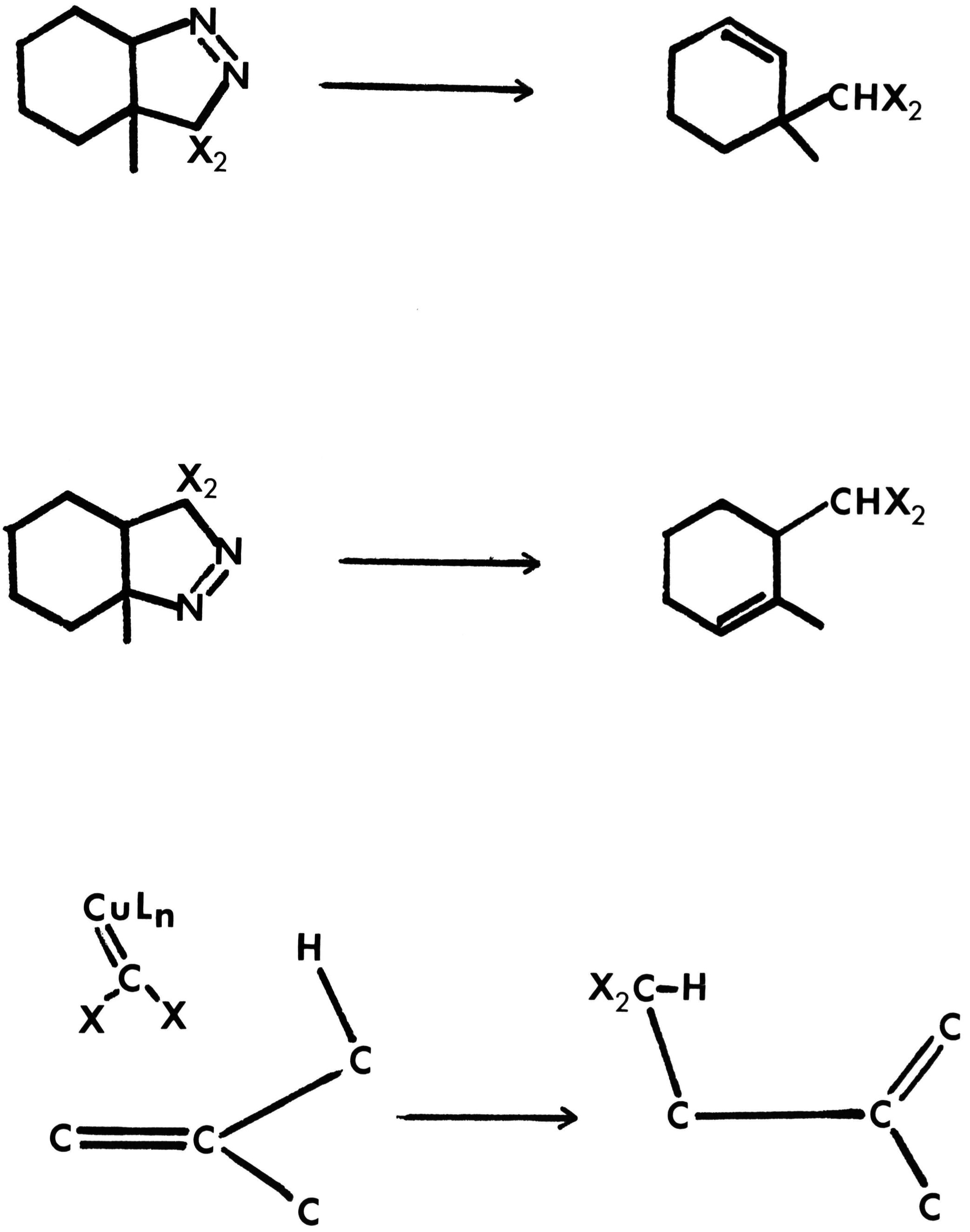


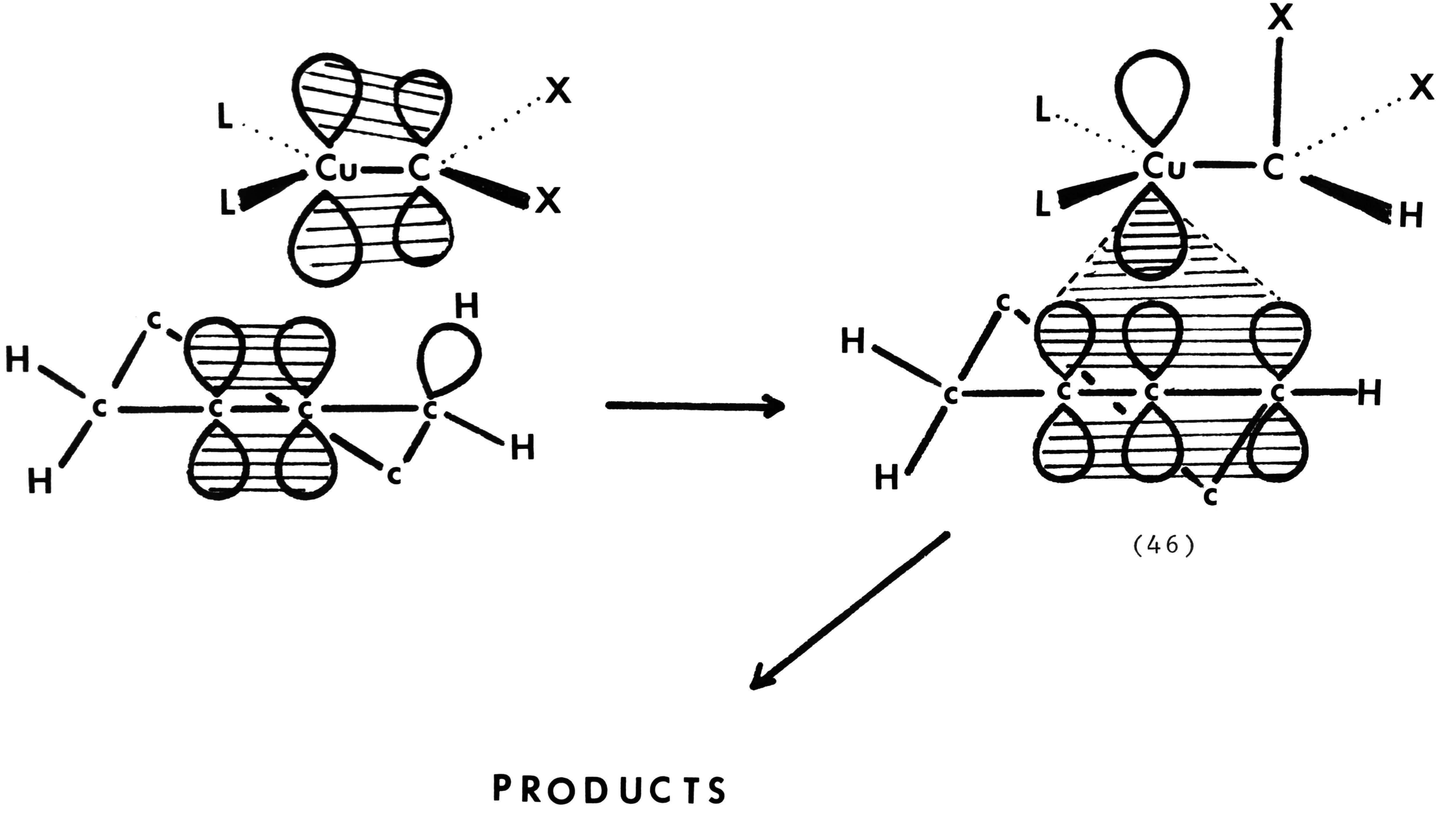
Figure 22. C-H Insertion Mechanisms

by the greater stability of the secondary, allylic radical and also by the stereochemistry of the intermediate.

The pyrazoline pathway accounts for compounds 41 and 42, depending on the relative positions of the methyl group of the olefin and the two carbomethoxy groups of the diazo compound. This would also agree with the postulate that the cyclopropanation process involves a metal complexed olefin which undergoes rates determining attack by an uncomplexed molecule of diazo compound, and the resulting complexed pyrazoline then collapses to products.

Since both mechanisms are required to account for all of the insertion products, pyrazoline and carbenoid reactions can be assumed to compete in cyclopropanation as well. The extent of this competition has not been shown.

Figure 23 will also account to a large extent for the presence of tetracarbomethoxyethane. The intermediate 46 can abstract a second proton releasing malonate which readily reacts with carbenoid to produce 37. The presence of bicyclohexenyl as detected by GC/MS in some reaction mixtures tends to support this species. Free carbene cannot contribute to the product since photolysis experiments, using the same diazomalonate source, resulted in no appreciable amounts of either dimeric species, whereas allylic and random insertion products were found. In addition, our steric effect studies showed that the nature of the ligand substitution on copper can depress



(46)

Figure 23. Hydrogen Extraction Process

either or both dimeric species, giving further evidence toward the involvement of the carbenoid in both cases.

III EXPERIMENTAL

A. Starting Materials

1. *p*-toluenesulfonyl Azide

p-toluenesulfonyl azide was prepared by the method of Doering and DePuy[61]. *p*-toluenesulfonyl chloride (1.02 kg, 5.35 moles) was dissolved in 6 l of ethanol to which a solution of sodium azide (420 g, 14 moles) in 1.8 l of water was added. The mixture was stirred together overnight, poured into a 6½ gallon carboy, and diluted with water. The oily azide separated out. The crude azide was separated, washed with three 500 ml portions of water, and washed once with 500 ml of saturated sodium chloride solution. The azide was dried over sodium sulfate and again over calcium chloride. The yield was 875 g (83%) of pale yellow azide, which was used without further purification.

2. Dimethyl Diazomalonate

A solution of 197 g (1.0 mole) of *p*-toluenesulfonyl azide, 101 g (1.0 mole) of triethylamine, and 133 g (1.0 mole) of dimethyl malonate was allowed to stand for 12 hours with occassional swirling. The resulting precipitate of *p*-toluenesulfonamide was filtered and washed with cold benzene. The benzene was then removed *in vacuo*. Hexane, 250 ml was added to precipitate remaining *p*-toluenesulfonamide. After filtration and further concentration *in vacuo*, the residue was distilled to give 131 g (90%) of yellow oil, b.p. 42-44°C/0.01 mm. The material was then redistilled slowly to remove traces of unreacted dimethyl malonate as verified by NMR.

3. Ethyl Diazoacetate

a. Ethyl diazoacetate was prepared by the method of Womack and Nelson[62]. A solution of 140 g (1.0 mole) of glycine ethyl ester hydrochloride and 3 g of sodium acetate in 150 ml of water was made. The solution was cooled to 0°C by an ice-salt bath. A cold solution of 83 g (1.2 moles) of sodium nitrite in 125 ml of water was added and the mixture stirred. Cold diethyl ether, 80 ml, was added along with 3 ml of cold 10% sulfuric acid. The ether layer was separated and washed with 50 ml of cold 10% sodium bicarbonate. The ether-acid process was repeated six times. The combined neutralized ether extracts were concentrated _in vacuo_ to remove all of the ether. The residual oil, 98 g, 85% was not used in competitions due to possible contamination by ethyl diazochloroacetate.

b. Ethyl diazoacetate was prepared by a procedure patterned after that of Searle[63]. A solution of 140 g (1.0 mole) of glycine ethyl ester hydrochloride in 250 ml of water was mixed with 600 ml of methylene chloride and cooled to 95°C in an ice-salt bath. While vibrating the solution with a Vibramixer, an ice cold solution of 83 g (1.2 moles) of sodium nitrite in 250 ml of water was added slowly. Five per cent sulfuric acid, 95 g, was then added dropwise over 5 minutes. After an additional 5 minutes the solution was transferred to an ice-cold 2 l separatory funnel and the separated organic layer was neutralized to litmus paper with saturated sodium bicarbonate solution. The aqueous layer was extracted once with 75 ml of methylene chloride. The combined organic layers were dried over anhydrous sodium sulfate and concentrated *in vacuo*. Vacuum distillation of the residual oil yielded 95 g, 84%, of ethyl diazoacetate, b.p. 30-32°C/5mm. (lit. 29-31°C/5mm) Purity was confirmed by NMR and mass spectral data.

4. Triethyl-**Δ**-2-pyrazoline-3,4,5-tricarboxylate

a. Diethyl maleate, 18 g (0.25 moles), and 1 l of diethyl ether were mixed with magnetic stirring in a 2 l round bottomed flask. A crystal of $Cu(BF_4)_2$ was added, and 29 g (0.25 moles) ethyl diazoacetate was added gradually. The reaction mixture was stirred overnight. The ether was removed *in vacuo*, leaving a yellow solid. Recrystallization from ethanol gave 42 g (90%) colorless plates, m.p. 94.5-96.5°C (lit. 93°C).[46]

b. Diethyl fumarate, 18 g (0.25 moles), and 1 l of diethyl ether were mixed with magnetic stirring in a 2 l round bottom flask. A crystal of $Cu(BF_4)_2$ was added, and 29 g (0.25 moles) ethyl diazoacetate was added gradually; the reaction mixture was stirred overnight. The ether was removed *in vacuo* leaving a yellow solid. Recrystallization from ethanol gave, in two crops, 42 g (90%)

colorless plates, m.p. 95-96.5°C. Mixed m.p. proved the two materials identical. IR and NMR were consistant with the structure.

B. Catalysts

1. Copper (II) Bis Acetylacetonate

Cupric chloride dihydrate (85 g, 0.5 moles) was disolved in 750 ml of water. 2,4-pentanedione, 100 ml, was added with vigorous stirring. The solution turned deep blue and the blue Copper (II) Bis Acetylacetonate began to rise to the surface. The mixture was stirred overnight. The dark blue crystals were filtered and air dried. Recrystallization from chloroform gave mats of blue crystals, m.p. 238-9°C (lit. 236°C decomposition)[64, 65]. The yield was 20.7 g, 24.4%.

2. Copper (II) Bis (1-phenyl-1,3-butanedioate)

1-phenyl-1,3-butanedione (12.0 g, 0.06 moles) was dissolved in 50 ml of methanol. Cupric acetate monohydrate (11.2 g, 0.06 moles) was dissolved in 100 ml of boiling water and filtered directly into the methanolic solution of the dione. A bluish-green precipitate appeared at once, was filtered onto a Buchner funnel and air dried. Recrystallization from absolute ethanol gave blue-green needles, m.p. 191.5-192.5°C decomposition. (lit. 194.5-5.5)[66] The yield of recrystallized material was 10.42 g, 80.5%.

3. Copper (II) <u>Bis</u> (1,3-diphenyl-1,3-propanedioate)

1,3-diphenyl-1,3-propanedione (11.2 g, 0.05 moles) was dissolved in 50 ml of methanol. Cupric acetate monohydrate (12 g, 0.06 moles) was dissolved in 100 ml of boiling water and filtered directly into the methanolic solution of the dione. A yellow-green precipitate appeared at once and was filtered onto a Buchner funnal and air dried. The yield of unrecrystalized material was 12.5 g, 98%, m.p. 315-317.5°C decomposition (lit. 319-27°C)[67].

4. Copper (II) <u>Bis</u> (1-thenoyl-3,3,3-trifluoroacetonate)

1,1,1, trifluoro-3-thenoyl acetone (11.1 g, 0.05 moles) was dissolved in 50 ml of methanol. Cupric acetate monohydrate (12 g, 0.06 moles) was dissolved in 100 ml of boiling water and filtered directly into the methanolic solution of the dione. A forest green precipitate formed at once. The mixture was filtered onto a Buchner funnel and air dried. Recrystallization from chloroform gave dark green fine crystals, m.p. 239-40°C, (lit. 242-3°C)[68]. The yield of recrystallized material was 8.43 g, 67%.

5. Copper (II) <u>Bis</u> (2,2,6,6-tetramethylheptane-3,5-dionate)

2,2,6,6-tetramethylheptane-3,5-dione (9.2 g, 0.05 moles) was dissolved in 50 ml of methanol. Cupric acetate monohydrate (12 g, 0.06 moles) was dissolved in 100 ml of boiling water and filtered onto a Buchner funnel and air dried. Recrystallization from absolute ethanol yielded purple crystals, m.p. 191.5-193.5°C (lit. 192-3°C) 69. The yield of recrystallized material was 7.71 g, 72%.

6. Copper (II) Bis (methyl acetoacetate)

Methyl acetoacetate (5.8 g, 0.05 moles) was dissolved in 50 ml of methanol. Cupric acetate monohydrate (12 g, 0.06 moles) was dissolved in 100 ml of boiling water and filtered directly into the methanolic solution of the dione. No product was isolated.

7. Copper (II) Bis (tert-butyl acetoacetonate)

t-Butyl acetoacetate (7.9 g, 0.05 moles) was dissolved in 50 ml of methanol. Cupric acetate monohydrate (12 g, 0.06 moles) was dissolved in 100 ml of boiling water and filtered directly into the methanolic solution of the dione. A very small amount of solid material resulted, consisting mainly of cupric acetate crystals. The mixture was not characterized.

C. Catalyst Studies

1. Catalyzed Competition Reactions of Dimethyl Diazomalonate and 1-methylcyclohexene

Clean 100 ml 3 necked round bottom flasks were prepared by washing with concentrated nitric acid, concentrated ammonium hydroxide, distilled water, and acetone. The flasks were baked out overnight in a 200°C oven to insure dryness and assembled while hot. A 1:1 molar mixture of 0.125 moles cyclohexene and 0.125 moles 1-methylcyclohexene was placed in the flask, together with 0.14

mmoles of the selected catalyst, and brought to reflux. 0.02 moles of the dimethyl diazomalonate was dissolved in an equal quantity of the olefins and added at the rate of 1 drop per 10 seconds. After addition was completed, the solution was refluxed an additional twelve hours. The reaction mixture was then concentrated in vacuo and analyzed by gas chromotography. Analysis was accomplished by comparison to known solutions. The reaction was also carried out using 0.021 moles of the 1:1 olefin mixture in 45 ml of hexafluorobenzene with 0.14 mmoles of $Cu(BF_4)_2$.

2. Catalyzed Decomposition of Ethyl Diazoacetate in Cyclohexene

Clean 100 ml round bottom flasks were prepared and assembled in the usual manner. The flask was charged with 25 ml of cyclohexene, a variable amount of $Cu(AcAc)_2$ catalyst, and brought to reflux.

A solution of 2.28 g (0.02 moles) of ethyl diazoacetate in an additional 25 ml of cyclohexene was added dropwise at the rate of 1 drop per 10 seconds. After addition was completed, reflux was continued overnight. The reaction mixture was then concentrated in vacuo and analyzed by gas chromotography. Components were identified by retention times.

3. Photolytic Decomposition of Dimethyl Diazomalonate in Cyclohexene

Clean 6 in Pyrex test tubes were prepared by washing followed by treatment with concentrated nitric acid, concentrated ammonium hydroxide and distilled water to assure the absence of copper derivatives. A solution of 6.32 g (0.04 moles) dimethyl diazomalonate and 100 ml of cyclohexene was prepared. The solution was prepared as needed. Twenty-five ml portions of stock solution were introduced into the test tubes, along with any additives. The tubes were then stoppered with rubber septa, vented, and placed in a constant temperature bath around the photolysis source (Hanovia). The reaction was followed by following the disappearance of the diazo frequency in the IR (PE-137). Usual reaction time was about ten hours. No appreciable evaporation was observed. Excess cyclohexene was then removed *in vacuo* and the product distribution determined by gas chromotography, comparing retention time to known samples. Sample runs were made at 0°C and 54°C using stock solution and samples sensitized with 0.01 moles aliquots of acetone and benzophenone and 0.07 mmoles of Copper (II) Octoate. Runs at both temperatures were also made using 90 mole per cent hexafluorobenzene as solvent.

4. Photochemical Competition Reactions of Dimethyl Diazomalonate

Clean 100 ml round bottom flasks were prepared and assembled in the usual manner. A 1:1 molar mixture of 0.25 moles cyclohexene and 0.25 moles 1-methylcyclohexene were introduced into the flask along with 0.02 moles of dimethyl diazomalonate. Irradiation was provided by a portable Hanovia ultra violet lamp. When the reaction was complete, as monitored by the disappearance of the azide band in the IR, the solution was concentrated *in vacuo* and analyzed by gas chromotography, comparing retention times to known solutions.

5. $Cu(BF_4)_2$ Catalyzed Decomposition of a Δ-1-pyrazoline

The Δ-1-pyrazoline (10 g) resulting from 1,3 dipolar addition of dicyctopentadiene and dimethyl diazomalonate (furnished by Dr. D. Wulfman, identified by NMR and MS, m.p. 125-8°C decomposition) was dissolved in 50 ml of benzene and brought to reflux. A few crystals of $Cu(BF_4)_2$ were added at which time gas evolution became noticeable. After refluxing one hour, the solvent was removed *in vacuo* yielding a dark, viscous oil which solidfied on standing for a few days. Recrystallization from methanol gave tan crystals, m.p. 87.5-89.5°C. Mass spectral data confirmed the molecular weight and identified retrograde Diels-Alder fractions. NMR (in CCl_4) showed the cyclopropyl protons at 0.9 ppm singlet area=2 and vinyl protons at 4.7 ppm, multiplet area=2. The methoxy protons appeared at 3.65 ppm, singlet area=6. The remaining signal matched well the analogous signals of dicyclopentadiene.

6. Attempted Decomposition of triethyl -Δ-2-pyrazoline-3, 4,5-tricarboxylate

30 g of triethyl-Δ-2-pyrazoline-3,4,5-tricarboxylate was dissolved in 200 ml of benzene to which a few crystals of $Cu(BF_4)_2$ had been added. The solution was refluxed overnight and the solvent removed *in vacuo*. The yellow residue was shown to be identical to the starting material by mixed melting points.

Consistant mass spectral evidence was obtained on all the pyrazolines and the catalysts prepared in this study.

IV CONCLUSIONS

The copper catalyzed decomposition of dimethyl diazomalonate in an olefin substrate has been shown to involve a variety of mechanisms. Evidence indicates that copper in the plus two valence state is a superior catalyst in these reactions.

The transition state of the cyclopropanation process contains olefin, copper (II), ligands, and carbene. The participation of free carbene by a CT-1 process was not observed. Catalysts with a high steric requirement lead to enhanced production of dimeric species at the expense of norcarane.

Cyclopropanation can result from a bimolecular carbene transfer (CT-2) reaction involving one molecule of olefin substrate and one molecule of carbenoid. Another mechanism consistant with the data requires attack of diazo compound on a copper complexed olefin molecule. The resulting pyrazoline intermediate would then collapse to cyclopropane. Observation of $Cu(BF_4)_2$ catalyzed decomposition of a Δ-1-pyrazoline lends support to this mechanism.

C-H insertion products can arise either from a radical type pyrazoline decomposition or from the carbenoid-olefin complex transition state. Both mechanisms are required to account for all of the observed insertion products. The partitioning between these two processes depends upon the nature of the ligand substitution on the catalyst.

Dimer formation can occur either by the reaction of two carbenoids or by the attack of diazo compound on the carbenoid carbon, with subsequent trans elimination of nitrogen and catalyst most likely. This mechanism accounts for the formation of up to 100% of the thermodynamically less stable cis dimer in the decomposition of ethyl diazoacetate by certain catalysts. This cis:trans ratio depends on both steric and electrostatic effects in a given system.

The carbenoid-carbenoid dimerization mechanisms can predominate in reactions employing catalysts with low steric requirements. Hindered catalysts depress cyclopropanation as well as dimerization by this mechanism.

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VITA

Robert Stephen McDaniel, Jr. was born on September 26, 1946 in Nashville, Tennessee. He moved to St. Louis, Missouri, at the age of four. There he received his primary education at St. Roch's parochial school and his secondary education at Chaminade College Preparatory School. He received his Bachelor of Science degree with a major in chemistry from the University of Notre Dame du Lac, Notre Dame, Indiana, in June, 1968.

He has been enrolled at the University of Missouri-Rolla since September of 1968. He has held a teaching assistantship in the Chemistry Department during this time. He was a working exchange student in Holland during the summer of 1971. He also received summer research assistantships from the Dean of the Graduate School in 1972 and 1973.

He married the former Katherine Wood Johnson of Colorado Springs, Colorado, in 1972.

He received his Doctor of Philosophy in organic chemistry in 1974.