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METAL SALT CATALYZED CARBENOID—XIII[1]

ON THE MECHANISMS OF CYCLOPROPANATION AND ALLYLIC C-H INSERTIONS BY DIAZO ESTERS IN THE PRESENCE OF OLEFINS AND HOMOGENEOUS COPPER CATALYSTS

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Abstract—Evidence is presented demonstrating the existence of two paths to the title processes which arise from a common intermediate. A rationale involving catalyzed addition of the diazo compound to the olefin and carbenoid addition to the olefin is proposed. The penultimate intermediate has one new C–C bond formed. It is partitioned between products by forming the second C–C bond or formation of a hydrocarbenoid allyl complex which collapses to the allylic C–H insertion products. Cyclopropanation occurs stereospecifically. The proposed mechanism accounts for the stereospecificity of cyclopropanation, the variance of *syn/anti* ratios with catalyst concentration when diazoacetic ester is employed and optical inductions with chiral catalysts. The question of whether the alleged carbenoid and/or the penultimate intermediate contain N_2 is not answered although it is felt that a cupro-cyclobutane intermediate is the most probable intermediate before product partitioning.

INTRODUCTION

The use of copper and its salts for the catalytic decomposition of diazoalkanes is well known.[4-7] Surprisingly little is known about the mechanisms of the processes involved and that which is generally known is based upon interpretations which tend to be oversimplified[8-10] or which neglect reasonable alternative explanations.[9-12] Previously we have presented sufficient evidence to support this contention.[13-24] Although the present work has greatly increased our knowledge of the general mechanisms of carbene transfer for rather simple processes, there continues to be far more unknown than known. With time, work will undoubtedly yield more refined interpretations than those proposed here but at present it is possible to set forth with confidence mechanistic interpretations for copper salt catalyzed cyclopropanations with diazoacetic ester and diazomalonic esters.

We have revealed that the product distribution between cyclopropanes, allylic C–H insertions, olefin formation and ethane formation and overall yields are functions of the catalyst concentrations.[13,15,16,20,21] What is not widely recognized is the fact that the observed behavior places severe restrictions on mechanistic hypotheses to the point where one can now make some fairly definitive statements for the reactions of diazomalonic esters and diazoacetic esters with olefins in the presence of copper catalysts. Our results have been obtained by examining the relationships between catalysts concentrations and product yields. The important features of the product yield versus catalyst concentration plots (Figs. 1-3) and the reactions themselves, include the following: (a) there are two maxima for cyclopropanation and allylic C–H insertions (b) the partial rates (allylic C–H insertion ÷ cyclopropanation) at both maxima are the same or very nearly the same in all cases (see Tables 1 and 2 for

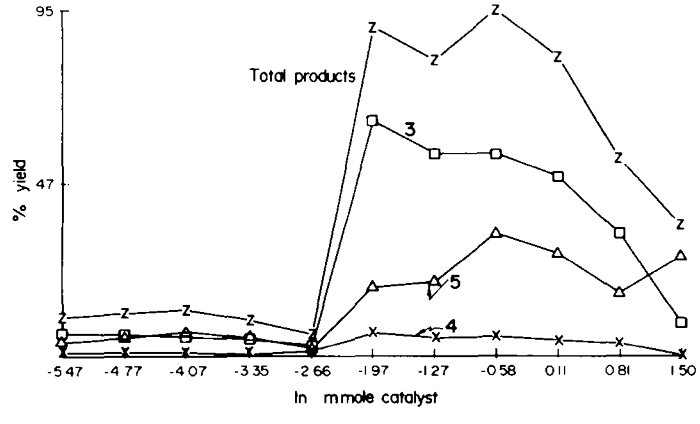


Fig. 1. Product distribution and yields as a function of $[(CH_3O)_3P]_2$-CuI concentration in the reaction of dimethyl diazomalonate with cyclohexene.

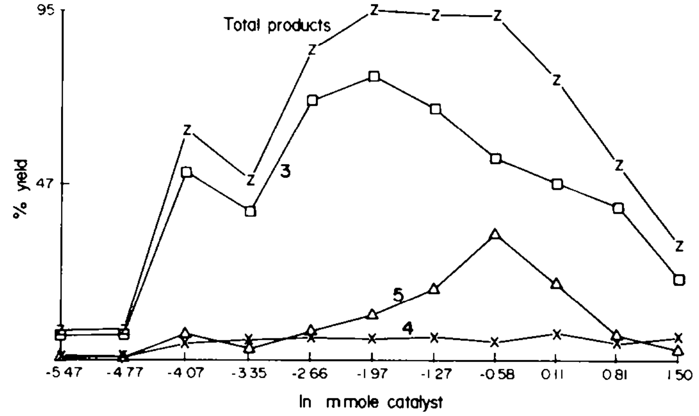


Fig. 2. Product distribution and yields as a function of Cu(AcAc)$_2$ concentration in the reaction of dimethyl diazomalonate with cyclohexene.

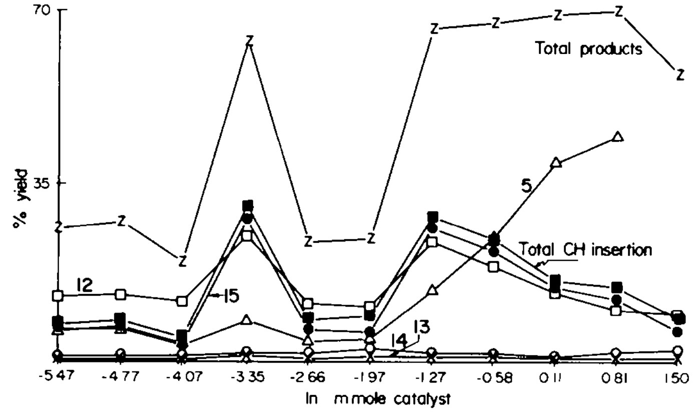


Fig. 3. Product distribution and yields in the reaction of dimethyl diazomalonate with 1-methylcyclohexene using (CH$_3$O)$_3$P–CuCl as catalyst in refluxing hexafluorobenzene at 83° (90 mole HFT).

Table 1. Product distribution and yields in the reaction of dimethyl diazomalonate with 1-methylcyclohexene using (CH$_3$O)$_3$P · CuCl as catalyst at 110°

Catalyst (mmol)	**12**	**13**	**14**	**15**	**5**
0.0042	21.53 (1.00)	1.51 (0.070)	7.78 (0.361)	19.54 (0.904)	4.03 (0.187)
0.0085	23.07 (1.00)	1.68 (0.073)	8.72 (0.378)	20.12 (0.874)	3.84 (0.166)
0.0170	22.34 (1.00)	1.63 (0.073)	8.45 (0.378)	19.59 (0.877)	2.48 (0.111)
0.0350	21.80 (1.00)	1.68 (0.077)	8.05 (0.369)	18.91 (0.868)	3.56 (0.163)
0.0700	23.21 (1.00)	1.80 (0.077)	8.38 (0.361)	20.39 (0.878)	3.69 (0.159)
0.1400	20.39 (1.00)	1.45 (0.071)	7.11 (0.349)	16.90 (0.830)	4.78 (0.234)
0.2800	20.12 (1.00)	1.54 (0.077)	7.98 (0.396)	19.45 (0.965)	3.84 (0.191)
0.5600	19.38 (1.00)	1.49 (0.077)	7.44 (0.384)	18.7[illegible] (0.966)	5.08 (0.262)
1.120	18.51 (1.00)	1.01 (0.055)	7.63 (0.358)	14.89 (0.805)	7.77 (0.420)
2.240	8.72 (1.00)	0.40 (0.046)	3.76 (0.431)	9.05 (1.04)	22.67 (2.60)
4.480	6.77 (1.00)	0.00	2.07 (0.307)	4.81 (0.715)	19.32 (2.87)

examples), (c) the dependence of dimer formation is of higher order kinetically than allylic C–H insertion and cyclopropanation relative to catalyst over a large concentration range, (d) with diazoacetic ester the *syn*/*anti* ratio for cyclopropanation is a function of catalyst concentration (Table 3), (e) the *cis*/*trans* ratio for olefin formation from diazoacetic ester is a function of catalyst concentration (Tables 3 and 4), (f) at very high catalyst concentrations the ability of dimer formation to compete with allylic C–H insertion and cyclopropanation processes decreases, (g) cyclopropanation occurs stereospecifically over a range of conditions, (h) the effect of temperature upon allylic C–H insertion and cyclopropanation processes is different (low T favors allylic C–H insertion) and therefore partitioning between products is not occurring after the rate determining step (with pyrazoline thermolyses partitioning occurs afterwards[25]).

When one examines these facts in detail one is forced to

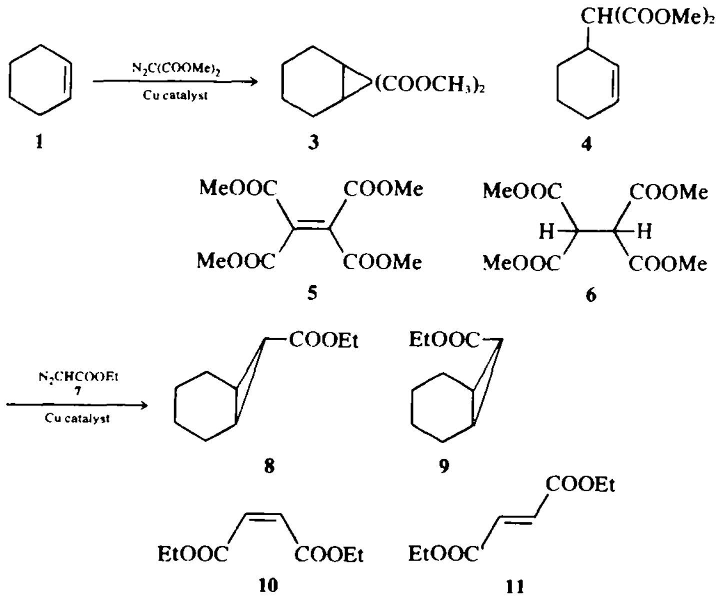
Table 2. Product distribution and yields in the reaction of dimethyl diazomalonate with 1-methylcyclohexene using $(CH_3O)_3P \cdot CuCl$ as catalyst in refluxing hexafluorobenzene

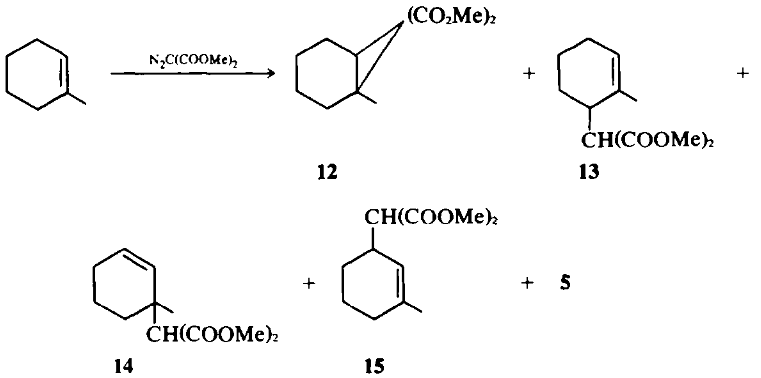
Catalyst (mmol)	12	13	14	15	5
0.0042	12.74 (1.00)	0.21 (0.017)	0.94 (0.074)	6.14 (0.480)	6.09 (0.478)
0.0085	13.08 (1.00)	0.23 (0.017)	0.98 (0.075)	6.77 (0.518)	6.40 (0.489)
0.0170	11.74 (1.00)	0.34 (0.029)	1.01 (0.086)	3.35 (0.286)	3.10 (0.264)
0.0350	24.62 (1.00)	1.08 (0.044)	1.62 (0.066)	27.84 (1.13)	7.99 (0.324)
0.0700	11.34 (1.00)	0.45 (0.039)	1.56 (0.137)	6.20 (0.546)	3.91 (0.345)
0.140	10.73 (1.00)	0.91 (0.084)	2.45 (0.228)	5.59 (0.521)	4.39 (0.409)
0.280	23.34 (1.00)	0.75 (0.032)	1.50 (0.064)	26.16 (1.12)	13.87 (0.594)
0.560	18.58 (1.00)	0.84 (0.043)	1.56 (0.084)	21.53 (1.16)	24.28 (1.31)
1.120	13.41 (1.00)	0.53 (0.039)	0.83 (0.061)	14.49 (1.08)	39.14 (2.92)
2.240	10.06 (1.00)	0.56 (0.055)	1.79 (0.178)	12.27 (1.22)	44.47 (4.42)
4.480	9.19 (1.00)	0.59 (0.064)	2.23 (0.243)	5.88 (0.640)	38.65 (4.21)

Table 3. Products and yields

mmole of cat. and N	8		9		8/9	10		11		10/11
	Absolute	Relative	Absolute	Relative	Ratio	Absolute	Relative	Absolute	Relative	Ratio
N-1										
0.14	7.80	1	0.65	0.083	12.0	0.088	0.011	0.123	0.015	0.715
5.0	2.91	1	1.16	0.390	2.51	0.218	0.075	0.710	0.244	0.307
N-2										
0.14	7.87	1	0.684	0.087	11.5	0.100	0.012	0.150	0.019	0.667
5.0	0.965	1	0.946	0.960	1.02	0.077	0.079	0.254	0.263	0.304
N-3										
0.14	6.05	1	0.533	0.066	15.1	0.067	0.008	0.111	0.013	0.608
5.0	0.333	1	0.832	2.50	0.400	none		none		

Absolute yields relative to internal standard.
Real yield is approximately 10x Absolute.





conclude that there must be at least three paths to cyclopropane formation. Two of these involve a single common intermediate which is formed before product partitioning between allylic C–H insertion and cyclopropanation and involves a single molecule of catalyst. A third process involving two molecules of catalyst must be occurring at high catalyst concentrations. There exists only a very small probability that some processes are occurring by dissociation of an intermediate to a free carbene. Thus we argue that the data for allylic C–H insertion and cyclopropanation processes can best be resolved by employing two formal bimolecular carbene transfer processes (**MT-2**), a formal termolecular process (**MTE-2**) and possibly a unimolecular process (**MT-1**).[26]

The question of the valence state of the copper is of little import for the present study. However it is clear from related studies that the problem must be treated thoroughly before the full mechanistic details of the reactions can be elucidated. At present we believe the valence state is dependent upon the ligands attached to copper and the substituents on the carbene. In cases where delocalization by the carbene substituents is favorable, copper (II) may be the major catalytic species but when this is not possible, copper(I) may be the catalyst.

RESULTS AND DISCUSSION

Early in our studies it became obvious that unlike many catalyzed processes, the yields of the various products from copper catalyzed reactions of diazomalonic esters had a strong dependence upon catalyst structure and concentration. This somewhat justified the *a priori* assumption that a carbenoid rather than a free carbene process was involved. However, subsequent studies revealed that unsensitized photolyses of diazomalonic esters do not furnish solely the free carbene[21] and this weakened all arguments that differences between photolyses, thermolyses and catalyzed processes were evidence of a carbenoid. Kirmse[4] has cautioned chemists about assuming the nitrogen has departed in alleged carbene reactions. In the present case it is not possible to establish whether a copper-carbene complex or a copper-diazo compound complex is one of the key active reactants. We shall assume a carbenoid intermediate for convenience but it is not *conditio sine qua non.* Alternative pathways are given in Schemes 3–5.

The initial observation that there are two maxima in yield versus catalyst concentration plots for both ACHI[†] and CYP[‡] processes was surprising and lead to our examining other catalyst systems for the same phenomenon. It appears to be general with dimethyl diazomalonate. It was observed with trialkylphosphite copper(I) complexes, triarylphosphite copper(I) complexes and with copper(II) acetylacetonato complexes. Thus formal catalyst valence state is not a determining factor.

The dependence of dimer formations upon catalysts concentrations was surprising. Addition of diazo compound was carried out dropwise at very nearly the same rate at which nitrogen evolution was occurring when low catalyst concentrations were employed. Thus an increase in catalyst concentration with constant drop rate should cause a decrease in concentration of free diazo ester with an associated increase in carbenoid concentration.

Since dimer formation competed favorably with cyclopropanation and allylic C–H insertion processes one might assume a simple second order dependence upon carbenoid for this process. However, results with ethyl diazoacetate revealed the presence of two paths to dimer formation (the *cis/trans* ratio is a function of catalyst concentration). Thus it would appear highly unlikely that the process leading to dimer at low catalyst concentrations involves two molecules of carbenoid. (If the process for dimer formation involved only one molecule of carbenoid, the competition with allylic C–H insertion and cyclopropanation would have remained relatively constant and might actually decrease as the diazo compound would be consumed more rapidly to form carbenoid at high catalyst concentrations). The failure to observe a relatively constant partitioning of a common intermediate was taken as clear evidence that the overall rate expression for dimer formation was one of the general forms given in Scheme 1. This would lead to two different transition states which undoubtedly would exhibit differing preferences for the *cis* and *trans* dimers when unsymmetrical diazo compounds were employed. (This point is treated in detail in a following paper[27]).

It is impossible to obtain a double maxima plot from a single process but it is reasonable to have separate processes which maximize.[28] The single process interpretation would require the observation of a double maximization of the activity of the key intermediate

$$\text{Rate df} \propto [\text{Catalyst}][\text{Diazo}]^2 + [\text{Catalyst}]^2[\text{Diazo}]^2 \tag{1}$$

or

$$[\text{Carbenoid}][\text{Diazo}] + [\text{Carbenoid}][\text{Diazo}][\text{Catalyst}] \tag{2}$$

or

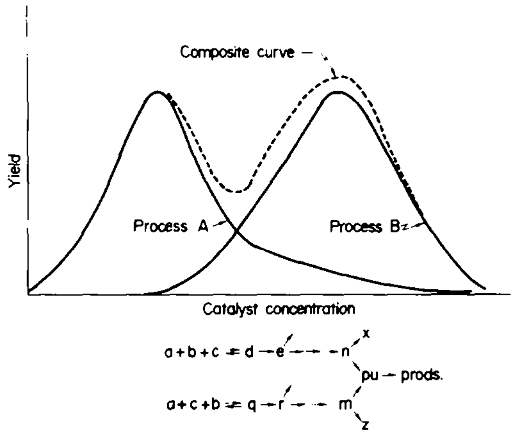
$$[\text{Carbenoid}][\text{Diazo}] + [\text{Carbenoid}]^2 \tag{3}$$

Scheme 1. Possible rate expressions.

[†] ACHI ≡ Allylic C–H Insertion.

[‡] CYP ≡ CYcloPropanation.

which is clearly a violation of the Second Law. A very simple rationalization involves the superposition of two processes which involve several steps and which ultimately furnish the same products (Scheme 2). If one

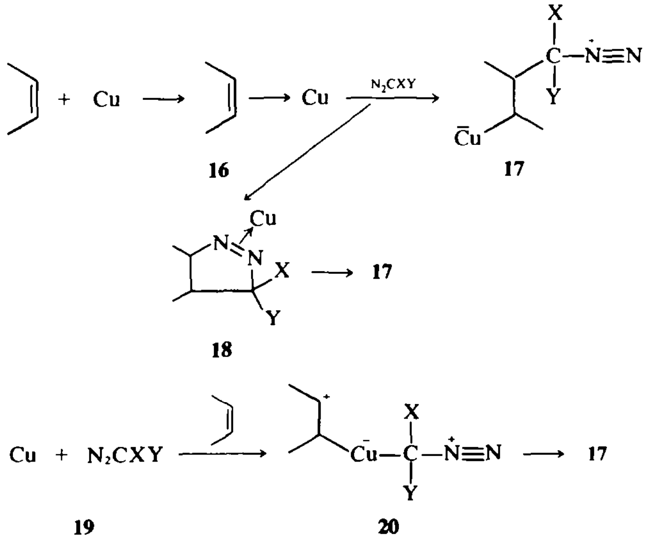


Scheme 2.

envisages the reactants A, B and C coming together in two different two-step processes (A + (B + C) and (A + C) + B) to ultimately furnish ABC, which then goes to products, one obtains such a situation. With multistep consecutive and multistep branched consecutive reactions it is possible to optimize the steady state concentrations of the various intermediates.[28] One would expect that the maximization of the concentration of an intermediate leading to a desired product would lead to the optimization of the yield of that product. If two such processes exist in parallel, the superposition of the individual yield versus variable plots can give rise to the type of plot obtained. If in addition, each path leads to a single common intermediate, the same or very nearly the same partitionings between products will be observed if there exist only minor conformational differences between the intermediates leading to the penultimate intermediate. Thus the two intermediates might well furnish different amounts of *syn* and *anti* isomers as a secondary consequence of conformational memory from earlier steps, but, unless the substrate is particularly sensitive to a longer ranging steric effect, the distribution between cyclopropanation and allylic C–H insertions will remain nearly the same. Similarly, the levels of optical induction would be the same if the induction occurs as a consequence of the asymmetry of the product forming step and not the intermediate forming step. The situation with diazomalonate is somewhat simplified because of the geminal substitution pattern. The data in Tables 1 and 2 clearly demonstrates that the same partitioning is occurring at the time of both maximizations. The data is well within ± 5% and this probably represents the limit of accuracy for the experiments as performed.

At low catalyst concentrations the catalyst is completely (or nearly completely) tied to olefin and the diazo compound reacts with complexed olefin.† At higher concentrations the olefin does not remove the catalyst so successfully and the diazo compound can react at an appreciable rate with catalyst. A very simple explanation involves catalyzed pyrazoline formation at low concentrations of catalyst with little contribution from carbenoid processes and predominantly carbenoid processes at higher catalyst concentrations. Both could lead to a common intermediate (Schemes 3–6) in which a single C–C bond has been formed and partitioning then can occur to furnish the allylic C–H insertion and cyclopropanation products. The objection that pyrazolines do not decompose catalytically with copper salts is not valid[23,24] (Scheme 7). The argument that optical inductions were not substrate concentration dependent in the work of Nozaki[10] is consistent with this argument for no evidence is available to indicate that all experiments were not performed at high catalyst concentrating. With both paths the optical inductions would be similar if not identical.

The proposal of two paths accounts for the variation in *syn*/*anti* ratios as a function of catalyst concentration



Scheme 3.

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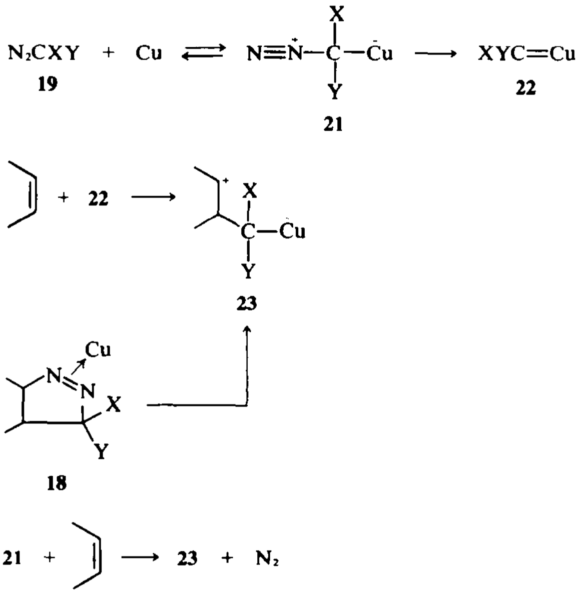
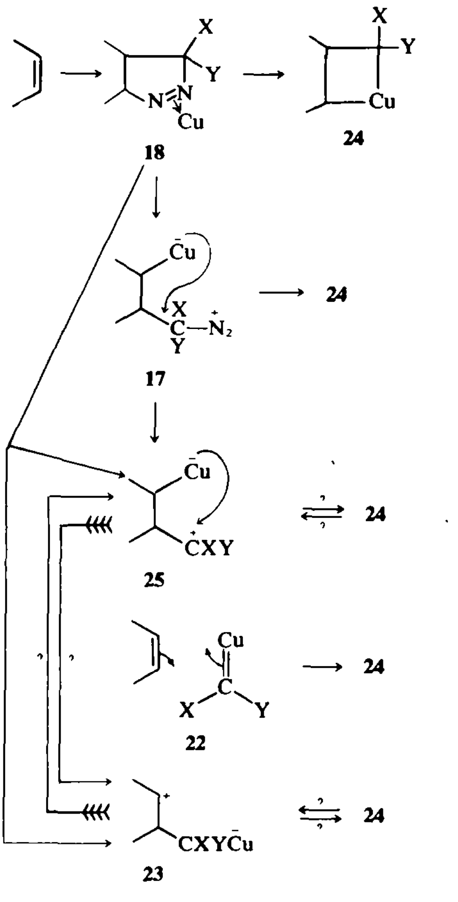
† This is consistent with the observation of D'yakonov[29] and by Kochi[9] that olefins retards the rate of reaction. The retardation of nitrogen evolution when a 1,3 dipolarophile is employed as the olefin, (such as diethylfumarate or diethyl maleate[24]) is most probably a consequence of the formation of Δ^2 pyrazolines. Since such olefins are invariably formed from diazocarbonyl compounds, it is not surprising to find a diminuation in rate of nitrogen evolution as the reaction approaches completion.



Scheme 4.



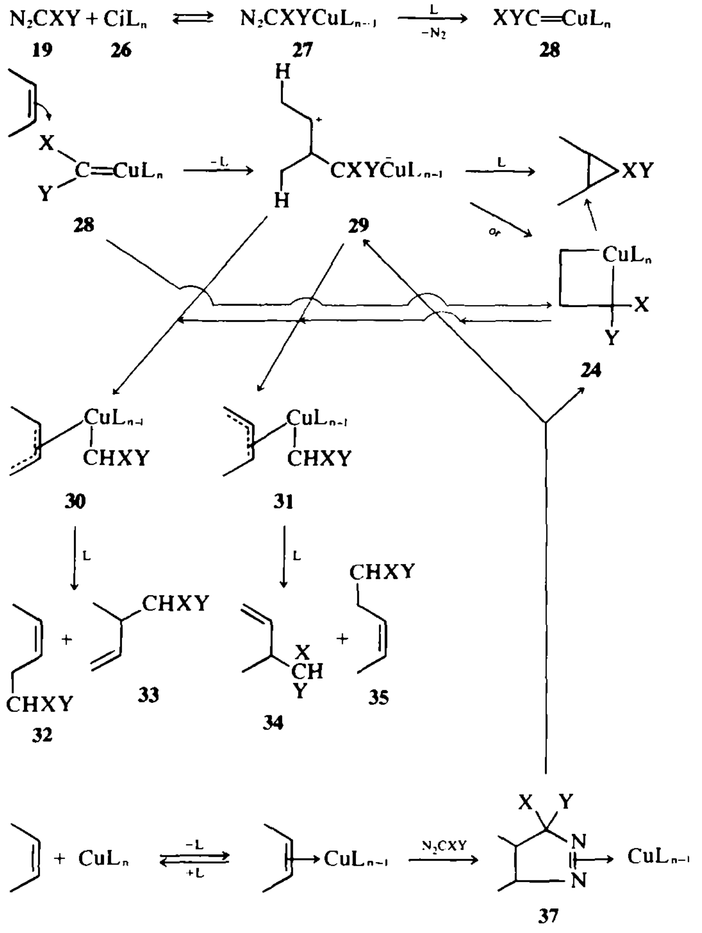
Scheme 5.

[*syn*/*anti* partitioning and optical inductions are not the same things].

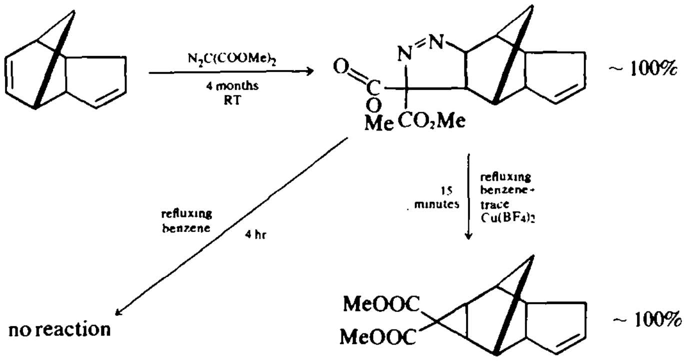
The fact that the dimer forming reaction does not overwhelm the allylic C–H insertion and cyclopropanation processes at very high catalyst concentrations is consistent with the presence of a third process having the same dependence upon catalyst as dimer formation. The possible rationalization that the initial situations do not involve catalyst in the product determining stages of the process is clearly not tenable. A direct consequence of such an hypothesis is the requirement that the two processes leading to the penultimate intermediate are of a **MT-1** type while the carbenoid is only capable of interacting upon diazo compound to form dimer. The dimer formation processes do not occur in the absence of catalyst for sensitized and unsensitized photolyses or for thermolyses. In addition, the catalyzed processes occur approximately 10^3 times faster than the uncatalyzed thermolyses at 90°. Thus, the observed behavior is totally consistent with the presence of a formal **MTE-2** process.

The situation at low catalyst concentrations is more confused because there clearly is an opportunity for thermal processes to compete with catalyzed processes. Consequently, it is not surprising to observe an appreciable change in the partial rate data at the very lowest catalyst concentrations. We feel it is extremely unlikely that that data represents the presence of a **MT-1** process. Under these conditions the mole fraction of substrate to diazo compound and catalyst is at a maximum. For a **MT-1** process to be of importance relative to a **MT-2** process, one must decrease the possibility of collision between substrate and the active species, not increase it. For the overall process, the weight assigned to a **MT-1** process must clearly be small. At high catalyst concentrations, the probability of recombination becomes higher at the same time that **MTE-2** processes become of increasing importance. Because the partial rate data is constant for allylic C–H insertion and cyclopropanation over the major range of catalyst concentration, it is clear that a **MT-1** process is making little if any contribution under those conditions as well.

Any mechanistic scheme which is proposed for the reactions of diazomalonic esters and ethyl diazoacetate must account for the above observations and lead to stereospecific cyclopropanation and stereospecific non-allylic C–H insertions.[31] In the case of diazoacetic ester, it is not possible to examine the processes with the same



Scheme 6.



Scheme 7.

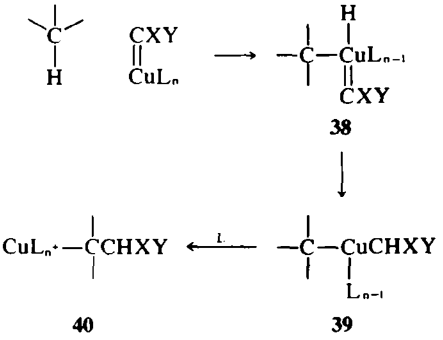
thoroughness as employed with dimethyl diazomalonate because allylic C–H insertion is not an important process and the resulting partial rate data is not obtainable with sufficient accuracy. However, the variation of the *syn/anti* ratio with catalyst concentration clearly establishes the presence of a dual path to products. With a single process there is no way to account for variations in product distribution. The failure of others to observe or account for this phenomenon is undoubtedly a consequence of employing heterogenous conditions, a single catalyst concentration or insensitivity with the substrate employed. (For example, we found the *cis/trans* ratio for cyclopropanation of styrene with diazoacetic ester relatively insensitive over a wide range of catalyst concentrations although a very real trend was observed[22]).

The observations of optical inductions with chiral ligand being employed to form the catalyst used to decompose ethyl diazoacetate and diazomethane in the presence of styrene has been widely accepted as evidence for the intermediacy of a copper carbenoid.[4,5,7,8,10,30] In one case dilution experiments were performed to demonstrate that the carbene was not free.[10] However, that approach does not distinguish between complexation of a diazo compound or substrate or complexation of a carbene or other intermediate. It simply establishes the presence of the copper complex in the vicinity of the portion of the substrate undergoing cyclopropanation.

Incorporation of all of the above factors permits one to arrive at the basic mechanistic hypotheses outlined in Schemes 3–6. Each of these schemes would furnish a common intermediate by two possible paths which might lead to allylic C–H insertion and cyclopropanation processes. Several possibilities exist which do not involve a carbenoid intermediate for either branch. Thus, the choice of a carbenoid for one of these paths is more a reflection of an emotional bias than empiricism.[12] All but Scheme 6 fail to account for the generation of three allylic CH insertion products when 1-methylcyclohexene is the substrate. One can not invoke a separate process to account for compound **15** because the partial rate data clearly reveals that it arises by the same path as the other two insertion products. Similarly one probably can not reasonably assign the insertion products to a reversable formation of a free carbene or carbenoid followed by "ene reactions" because such a reversal would most probably lead to non-stereospecific cyclopropanations. An economical explanation lies in the reversal only occurring simultaneous with the abstraction of the allylic hydrogen to furnish the hydrocarbenoid species **38** or the copper hydride **39** paired to an allylic ion. This then collapses with alkylation of the allylic ion by the hydrocarbenoid **38**. It seems clear that the extent of allylic C–H insertion will indeed be influenced by the anion associated with the copper for the extent to which the Cu–X bond is broken will obviously alter the affinity of both Cu and the carbene carbon for H. Although it is not possible to distinguish at this time between species **38** and **39** we favor **39** because Cu can serve in hydrogenation reactions and therefore clearly does have an affinity for hydrogen.[33] In any event **39** must be converted to **38** prior to the alkylation step. The overall reaction sequence meets all of our stated boundary conditions and is, we believe, consistent with the earlier work of others. It does not answer a number of fundamental questions regarding the fine points of carbene transfer and the fate of the nitrogen as the *proto*carbene passes along the reaction chains. It seems highly likely that a cuprocyclobutane such as **24** is formed for the process is stereospecific however the open chain system **29** might not exhibit free rotation on the time scale of cyclopropanation because the cyclopropanation step is extremely fast or because the bulk of the catalyst system makes rotation unlikely when considered in conjunction with the fact that rotation would involve increased charge separation.

Summary. In terms of the formalisms previously proposed,[27] there are two processes occurring, one of which involves an actual carbenoid (**MT-2**$_c$) and the other involves a non-carbenoid intermediate (**MT-2**$_{nc}$). These processes account for all of the allylic CH insertion products and the cyclopropane over a large range in catalyst concentrations. At very high catalyst concentrations there appears to be a **MTE-2**$_c$ process involving complexed substrate. The proposed mechanism does not distinguish between processes in which the carbenoid initially interacts with substrate through the metal (**MμS**) or the carbenoid carbon (**SMμ**) or occurs non-synchronously (**MT-2**$_{c,nsync}$) or synchronously (**MT-2**$_{c,sync}$). Similarly, no distinction is currently possible between a number of available intermediates which could be formed in the **MT-2**$_{nc}$ process.

The mechanism is not dependent upon the valence state of copper. In an earlier communication we had indicated the existence of charge separation during one of the processes and the operation of a common ion effect.[18] Such an effect can be associated with interference with any of the multi-reaction steps leading to the penultimate intermediate which will lead to a favoring of alternate reactions, or it may be associated with the rate determining step. As previously stated,[18] charge separation does play a role in partitioning between allylic CH insertion and cyclopropanation. It currently seems most probable that the *rds* for cyclopropanation involves the formation of the second C–C bond and that for allylic CH insertion involves formation of the final product by alkylation. The mechanism can be extended to account for the results of Linstrumelle, Ledon and Julia obtained where non-allylic CH insertions are involved[31] (Scheme 8). We believe a mechanism such as that shown in Scheme 8 is consistent with the earlier results of D'yakonov[29] who appears to have performed the first kinetic studies in this area. Clearly many questions remain to be answered. To obtain these, a considerable amount of ingenuity will be required.



Scheme 8.

EXPERIMENTAL

Detailed experimental conditions are presented in Paper XVI[32] of this series. Unlike the work of Moser,[8] no effort was made to free the systems from air. Such precautions were found to be deleterious[16,17,20,21] and a full treatment of this phenomenon has been presented.[21] In all experiments special precaution was taken to ensure the same operating temperature was employed (same flask, heating mantle, voltage setting, stirring bar, dropping funnel, etc.) to limit extraneous variables. All dropping rates were controlled and periodically checked to ensure the same rates were employed.

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[1a] For the preceding paper in this series, see D. S. Wulfman, *Tetrahedron* **32**, 1231 (1976). [b] Portions of this work were presented at the *First Chemical Congress of the North American Continent*. Mexico City, December (1975).

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[3a] Taken in part from the Ph.D. Dissertation of R. S. McDaniel, University of Missouri-Rolla (1974); [b] Taken in part from the Ph.D. Dissertation of B. W. Peace, University of Missouri-Rolla (1971).

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