The Mechanism of the Copper-Catalyzed Addition of Diazoalkanes to Olefins. I. Steric Effects

William R. Moser*

Contribution from Monsanto Research SA, Zurich, Switzerland.

Received September 9, 1968

Abstract: The homogeneous catalyzed addition of ethyl diazoacetate to olefins utilizing (trialkyl phosphite)copper(I) chloride complexes was studied. The systematic changes in the isomeric cyclopropane product distribution as a function of the steric bulk of the ligand on copper proves the intermediacy of a carbene–metal–olefin complex in the irreversible cyclopropane-forming step. The direction of the steric effect afforded information on the stereochemistry of the excited complex.

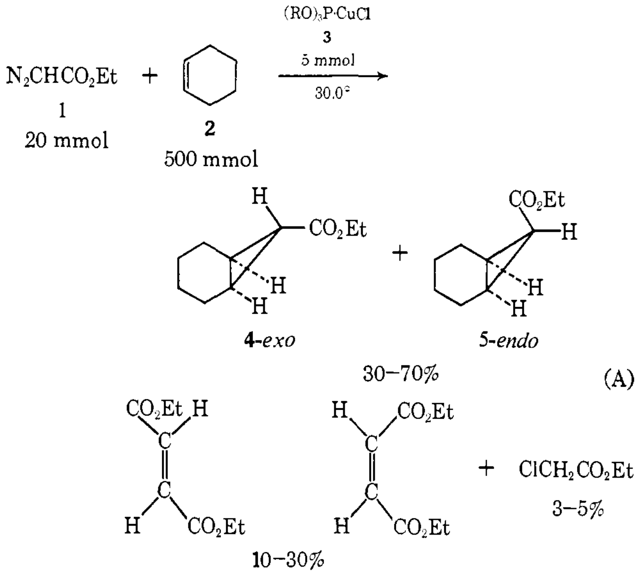
As a model system for general homogeneous metal catalysis, the soluble copper complex, catalyzed addition of diazoalkanes to olefins was studied. This investigation attempts to provide further experimental justification for the formulation of the stereochemistry[1] of reactions on metal ions. In this paper it will be shown that the steric requirements of the ligand exerts a systematic and independent influence on the course of metal-catalyzed reactions, and the subsequent paper[2] will treat the nature of the electronic interactions of the central metal ion. The combined studies provide evidence that the diazoalkane + olefin → cyclopropane reaction proceeds through a soluble metal–carbene complex.

The metal-catalyzed decomposition of diazoalkanes is an old[3] reaction which has been the subject of several recent investigations.[4] Past studies on the cyclopropanation mechanism[5] tends to support Yates' original proposal[6] that the general copper-catalyzed addition of diazoalkanes to organic substrates proceeds through a carbene–metal complex. This formulation assumes that the carbene is bound to the metal surface; thus, the valence electrons of copper complete the methine carbons octet. Due to some discrepancies in the literature which we uncovered, it was felt that this carbene–metal intermediate should be subjected to further experimental proof.

Description of Systems Studied

The selection of the (trialkyl and triaryl phosphite)-copper(I) chloride catalysts **3**[7] over the other complexes which we examined[8] afforded the possibility to study the steric and electronic effects of the ligand independently. The steric or electronic composition of one ligand at a time could be systematically altered by changing either the size of the carbon moiety of the phosphite or its electron-donating or -withdrawing ability, respectively. A large number of *n*-alkyl, branched alkyl, aromatic, and optically active phosphite copper catalysts of type **3** were synthesized. These catalysts were soluble in hydrocarbon solvents and throughout the reactions reported here. The change in the ratios of the cyclopropane products was measured when the different catalysts were utilized to decompose ethyl diazoacetate in the presence of olefins.

This study using soluble complexes, like Nozaki and coworkers' unique optical induction studies,[5b] attempts to avoid the uncertainties of heterogeneous surfaces. The model system which was selected for this study of homogeneous catalysis is shown in eq A. In this



(A)

---

[*] Address inquiries to: Corporate Research Laboratories, Esso Research and Engineering Co., Linden, N. J.

(1) (a) C. W. Bird, "Transition Metal Intermediates in Organic Synthesis," Academic Press, New York, N. Y., 1967; (b) F. Basolo and R. Johnson, "Coordination Chemistry," W. A. Benjamin, Inc., New York, N. Y., 1964, Chapter 6; (c) J. P. Collman in "Transition Metal Chemistry," Vol. 2, R. L. Carlin, Ed., Marcel Dekker, Inc., New York, N. Y., 1966, p 1; (d) G. N. Schrauzer, P. Glockner, and S. Eichler, *Angew. Chem.*, **76**, 28 (1964).

(2) W. R. Moser, *J. Am. Chem. Soc.*, **91**, 1141 (1969).

(3) (a) A. Loose, *J. Prakt. Chem.*, **79**, 507 (1909); (b) L. Wolff, *Ann.*, **394**, 23 (1912); (c) F. Ebel, R. Brunner, and P. Mangelli, *Helv. Chim. Acta*, **12**, 19 (1929); (d) C. Grundmann, *Ann.*, **536**, 29 (1938).

(4) (a) E. Müller, B. Zeeh, and H. Kessler, *Fortschr. Chem. Forsch.*, 7, 128 (1966); (b) W. Kirmse and K. Horn, *Ber.*, **100**, 2698 (1967); (c) D. Seyferth, *Chem. Rev.*, **55**, 1155 (1955); (d) A. G. Witenberg, I. A. D'yakonov, and A. Zindel, *Zh. Org. Khim.*, **2**, 1532 (1966); (e) R. Huisgen, *et al.*, *Angew. Chem.*, **73**, 368 (1961); **67**, 439 (1955); (f) C. Rüchardt and G. N. Schrauzer, *Ber.*, **93**, 1840 (1960); (g) W. von E. Doering and L. Knox, *J. Am. Chem. Soc.*, **78**, 4947 (1956); (h) D. D. Phillips, *ibid.*, **76**, 5385 (1954).

(5) (a) P. S. Skell and R. M. Etter, *Chem. Ind.* (London), 624 (1958); *Proc. Chem. Soc.*, 443 (1961); (b) H. Nozaki, S. Moriuti, M. Yamabe, and R. Noyori, *Tetrahedron Letters*, 59 (1966); H. Nozaki, S. Moriuti, H. Takaya, and R. Noyori, *Tetrahedron*, **24**, 3655 (1968).

(6) P. Yates, *J. Am. Chem. Soc.*, **74**, 5376 (1952).

(7) (a) A. Arbuzov, *Ber.*, **38**, 1171 (1905); (b) Y. Nishizawa, *Bull. Chem. Soc. Japan*, **34**, 1170 (1961).

(8) To be published elsewhere.

study we were concerned only with the changes in the cyclopropane products **4**-*exo* and **5**-*endo*. This model allows one to study homogeneous catalysis at low temperatures where the products are primary ones.

The *exo* and *endo* isomers are not isomerized under the reaction conditions, and are extremely slow to isomerize under equilibrating conditions. Sodium ethoxide in ethanol (0.1 *N*) afforded very slow isomerization[8] even at 60°. The structure of the products was identified by comparison to products from independent synthesis. The olefins and diazoalkane were chemically inert at 30°, but reacted very slowly above 80°. The cyclopropane isomers were not changed by ethyl diazoacetate, the copper catalysts, or free phosphite.[8] Metallic copper had no catalytic effect at 30°, but afforded smooth, rapid decompositions in refluxing cyclohexene. Using the soluble catalysts at 30° the rate of evolution of nitrogen was very fast after *ca.* 1-min induction period, and it was independent of the nature of the solvent. All decompositions were carried out at 30.0 ± 0.05° under identical conditions, distilled, and analyzed by glpc methods. A tenfold change in the amount of catalyst employed afforded only a 2% change in the observed ratios of the *exo*/*endo* products. An X-ray molecular weight determination showed the (triisopropyl phosphite) copper(I) chloride to be a tetramer.[8] From the beginning it must be pointed out that the absolute magnitude of differences in observed isomer ratios as a function of the applied catalyst were not large. Therefore, any interpretation of data must be viewed within this restriction. Nevertheless, all of the differences lie significantly outside of the error limits of 0.5% of the observed value and one considers them meaningful. This degree of accuracy could be obtained by the measurement of very similar isomers, at large retention times and integrator counts (see Experimental Section).

The best evidence in the literature for the intermediacy of a carbene–metal complex is taken from Skell and Etters' work[5a] where they compared the ratio of the products **4** and **5** from the photochemical and copper metal catalyzed decomposition of ethyl diazoacetate in cyclohexene (see Table I). These reactions were repeated due to discrepancies in the isomer ratios in the literature, and the above data are our own.[8] Skell and Etter compared the products of the photochemical reaction (high insertion and low *exo*/*endo* ratio) with the products of the copper metal decomposition (low insertion and high *exo*/*endo* ratio). They reasoned that the photolytic reaction probably proceeded through a free carbene. Since the products of the metal-catalyzed reaction were quite different, they proposed that this is evidence for the absence of a free carbene in the latter reaction and support for a carbene–metal-complexed intermediate. However no comparison was made to the isomer ratio produced from the purely thermal reaction, which was evidently unknown in the literature. If one now compares our data from the thermal reaction (low insertion and high *exo*/*endo* ratio) to the other two reactions, it is evident that this reaction is *more similar* to the metal-catalyzed reaction than the free carbene (photolytic) reaction. The thermal reaction, obviously, cannot proceed through a metal-complexed intermediate. Therefore, the dissimilarity in product ratios of the photolytic and metal-catalyzed reaction cannot be used as a proof for a carbene–metal-complexed intermediate in the latter case.

Table I

	Relative ratios		
	eudo-**5**	*exo*-**4**	Insertion
Photolytic (25°)	(1.00)	1.89	2.36
Thermal (reflux, very slow)	(1.00)	7.14	0.25
Copper metal (reflux, fast)	(1.00)	9.66	0.05

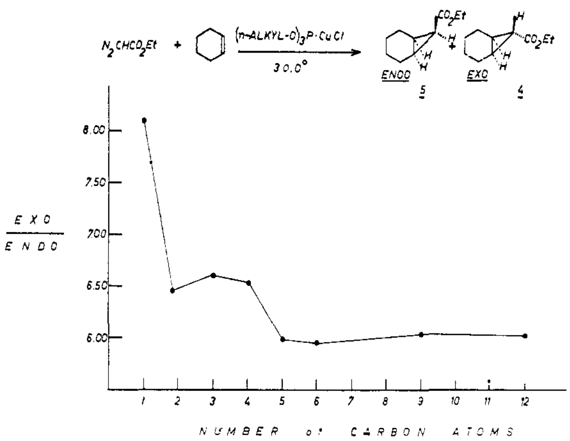


Figure 1.

Examining eq A, the method of proof utilized here will be the following. If one (1) observes systematic, predictable changes in the *exo*/*endo* isomer ratio when (2) the electrical or steric component, only, of the ligand on the metal is systematically changed when (3) the diazoalkane reacts with the olefin, (4) this is good proof that (5) the metal, olefin, and at least the carbon moiety of the diazoalkane **1** are all in the final transition state leading to the products **4** and **5**. This could mean a unimolecular decomposition of an intermediate carbene–metal–olefin complex irreversibly in two directions or a bimolecular reaction of an olefin–metal complex with the diazoalkane to form **4** and **5**.

n-Alkyl Effect on Reactivity

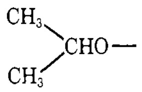
The solution of the problem of the effect of steric bulk on the course of catalytic reactions was first examined by the effect of (tris(*n*-alkyl) phosphite) copper(I) halides on the *exo*/*endo* isomer ratios. These catalysts were prepared with chain lengths from 1 to 12 carbon atoms, and each were used to decompose ethyl diazoacetate as shown in eq A. The resultant changes observed in the *exo*/*endo* cyclopropane ratios are demonstrated graphically in Figure 1.

As the length of the *n*-alkyl chain was increased from methyl to *n*-amyl, significant changes were observed in the *exo*/*endo* ratio. However, after *n*-amyl, the effective bulk at the reaction center where the carbethoxy group is combining with the olefin does not further increase through *n*-dodecyl. Substitution on methyl seems to make the greatest difference. Most importantly, an increase in the size of the *n*-alkyl group afforded a *decrease* in the *exo*/*endo* ratio. The zig-zag course of the *n*-alkyl effect of methyl through *n*-butyl is probably due to a combination of the slight differences in the group electronic contributions but more importantly through conformational changes of the *n*-alkyl chains. It is interesting that the same kind of zig-zag reactivity was observed in Schrauzer and Eichler's study[9] of the *n*-alkyl ligand effect in the nickel-catalyzed cyclization of acetylenes to cyclooctatetraene. This comparison of these two reactions is interesting because the latter must proceed through a metal complex.

Branched Alkyl Effect on Reactivity

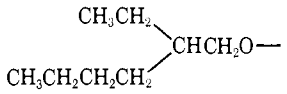
A series of (trialkyl phosphite)copper(I) chlorides were synthesized where the carbon part of the phosphites were highly branched. The *exo*/*endo* isomer ratios produced by each of these catalysts in the model reaction, eq A, were measured. The differences which were measured were relatively small but considerably outside the error limits (0.5%). These results are found in Chart I.

Chart I



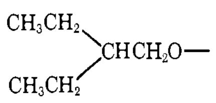
$(CH_3)_2CHO-$

6, 6.84



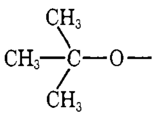
$(CH_3CH_2)(CH_3CH_2CH_2CH_2)CHCH_2O-$

9, 5.98



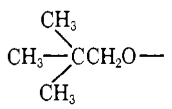
$(CH_3CH_2)_2CHCH_2O-$

7, 6.32



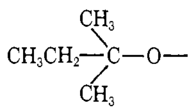
$(CH_3)_3C-O-$

10, 5.72



$(CH_3)_3CCH_2O-$

8, 6.25



$CH_3CH_2C(CH_3)_2-O-$

11, 5.52

A comparison of the ratios produced by complexes using the groups **6** and **10** in this diagram shows the effect of α substitution. A moderate decrease in the *exo*/*endo* ratio was observed when H was substituted by CH_3. In complexes using **10** and **11** as well as **7** and **8** the β effect is shown by the observation of a decrease in the *exo*/*endo* ratio when H was replaced by a larger alkyl group. The δ branching effect was obtained from the decrease in the *exo*/*endo* ratio when the H in **7** was replaced by an ethyl group as in **9**.

It is clear that any conclusion based on the small differences observed between a single set of the above data would be dubious. However, one should consider the data as a whole. In every case where an element of higher substitution was introduced on the ligand, a resultant decrease in the *exo*/*endo* isomer ratio was observed. One feels that the combination of these data independently support the stereochemical consequence of the steric effect which was observed in the *n*-alkyl case.

It will be shown in the subsequent paper[2] that the effect of electron donation *via* the ligand causes an increase in the *exo*/*endo* ratio, *i.e.*, as the normal Hammett σ constant of the substituent becomes more negative, the isomer ratio increases. Using this fact, one can show that the ratio changes observed above resulted from a pure bulk effect and not an electronic effect. In the branched alkyl case, the group polar substituent constants, σ^*[10] predicts that a pure electronic effect would result in an increase in the *exo*/*endo* ratio as the substituent is changed from isopropyl ($\sigma^* = -0.19$) to *t*-butyl (-0.30). Likewise in the *n*-alkyl case, the electronic effects predict an increase instead of the observed decrease as the length of the alkyl chain grows from methyl (0.00) to *n*-butyl (-0.13). Therefore, the steric effect predominates over any electrical effect in these two studies.

ortho-Substituted Aromatic Ligand Effect

It is widely recognized in organic reactivity that the steric effects of *ortho*-substituted aromatics results in a failure of the electronic properties of these substituents to correlate with their relative reactivities. In this work this normally undesirable case was put to advantage. If one obtains a Hammett correlation using the *para* and *meta* substituents, the *ortho* groups can be utilized to determine the direction of the steric effect on reactivity. Although we will comment in the subsequent paper on the correlation[2] which was obtained for the reactivity of the *para*- and *meta*-substituted aromatic phosphite copper(I) chlorides and the Hammett σ constants, these data will only be briefly mentioned here. The importance of this fit, as well as the meaning of the slope of the line will be discussed later. In reference to the steric problem, one should compare the observed value of the *exo*/*endo* isomer ratio (4.5) obtained from the *o*-methyl catalyst appearing at -0.170σ in Figure 1 of the subsequent paper[2] with the calculated value (5.3). Also the very bulky *o*-*t*-butyl-*p*-methyl catalyst appearing at -0.367σ afforded a ratio of 3.9 whereas the calculated value was 5.7. In the latter case the minimum electronic group contribution was taken from the summation of the *p*-σ constants of the *t*-butyl and methyl groups. In both cases the resultant of increased steric requirements of the ligand was a decrease in the *exo*/*endo* isomer ratio. We feel that this comparison is one of the better experimental proofs for the direction of the steric effects of the ligand on this reaction, because the electronic effects are under good control. This tight electronic control was not possible in the other reactions studied, *i.e.*, *n*-alkyl and branched alkyl phosphite catalysts.

Optically Active Catalyst.

((−)-Tribornyl phosphite)copper(I) chloride was synthesized with an optical rotation of $[\alpha]^{25.5}\mathrm{D}$ $-47.8°$. When this catalyst was utilized to decompose ethyl diazoacetate in styrene, shown in Scheme I, both of the cyclopropane products were optically active. After glpc separation of the *cis* and *trans* isomers, **15** and **14**, measurement of their rotations afforded 3.2 and 2.6% optical yields, respectively. This result is comparable to Nozaki and coworkers' recently observed 6% optical yield utilizing a copper(II) catalyst,[11] also shown

---

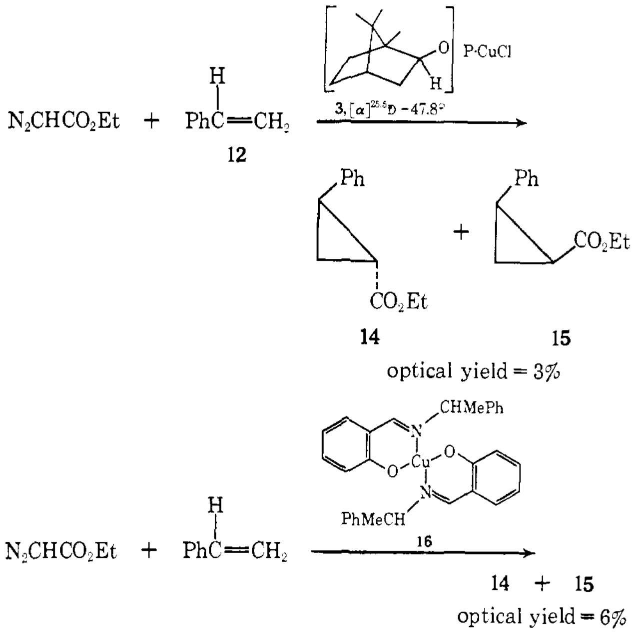
(9) G. N. Schrauzer and S. Eichler, *Ber.*, **95**, 550 (1962).

(10) (a) R. W. Taft, *J. Am. Chem. Soc.*, **74**, 2729 (1952); (b) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley & Sons, Inc., New York, N. Y., 1963, p 226.

(11) H. Nozaki, S. Moriuti, H. Takaya, and R. Nozori, *Tetrahedron Letters*, 5239 (1966).

in Scheme I. The higher optical yield in the copper(II) case most likely results from the fact that the center of optical activity is two atoms away from the reaction center whereas it was three atoms away in this study. In any case the magnitude of induction is reasonable for a reaction of this sort and this represents independent proof that this system proceeds through an olefin–metal–carbene complex.

Scheme I



Temperature Dependence of Reaction

In Figure 2, one finds the Arrhenius plot of the reaction of ethyl diazoacetate with cyclohexene using the (triisopropyl phosphite)copper(I) chloride catalyst. The variation in temperature was between 30 and 70° and the thermochemical data calculated from the plot were

$$E_a(endo) - E_a(exo) = 740 \pm 21 \text{ cal/mol}$$

$$\Delta S(exo) - \Delta S(endo) = 1.37 \pm 0.26 \text{ cal/(deg mol)}$$

There are several interesting features about this plot. (a) The fact that one obtained a good fit is convincing evidence that each of the cyclopropane isomers are produced *via* a single mechanism as opposed to several different routes. One of the principle reasons that a reaction fails to fit an Arrhenius plot lies in the fact that the process proceeds *via* multiple mechanisms.[12] Since a good fit was obtained the reaction does not proceed through a mixed homogeneous and heterogeneous mechanism.[13] Due to the fit of these data as well as the general reproducibility of the *exo/endo* isomer ratios, discussed in a latter section, a pure heterogeneous mechanism is unlikely. (b) Since $1/T$ was plotted against the log of the relative rates, instead of absolute rates, a fit to the data would be obtained from either a unimolecular or bimolecular reaction as well as a definite preequilibrium step in the scheme. Although the mechanism of this reaction will be discussed later in more detail, we feel that our data disfavors a bimolecular step. Rather, a rapid bimolecular combination of an intermediate complex and ethyl diazoacetate followed by a relatively slower, stereochemical-determining, unimolecular step is favored.

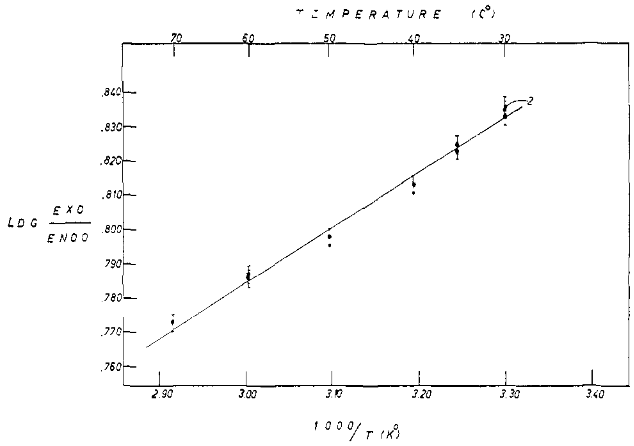


Figure 2.

A legitimate assignment of the cause of the change in the *exo/endo* isomer ratios to either an entropy or an activation energy difference could be obtained only through a comparison of the thermochemical data derived from two separate Arrhenius plots utilizing a nonbulky and a bulky catalyst. Although we feel that the measured entropy value is a bit low, as would be expected, the difference is not so extreme to be convincing.

Other Olefinic Systems

The testing of other olefinic systems for the direction of the steric effect proved to be consistent with the results of the cyclohexene system. When ethyl diazoacetate was decomposed in pure 1-heptene using the (tris(*o-t*-butyl-*p*-methyl) and triethyl phosphite)copper(I) chloride catalysts, the resulting *trans/cis* isomer ratios were 1.0 and 1.6. Similarly, when the triethyl, tribornyl, and tris(*p*-chlorphenyl) catalysts were utilized for the same decomposition in styrene, the respective *trans/cis* ratios were 1.8, 1.6, and 1.6. Thus, comparing the same catalysts, a higher percentage change was observed in the 1-heptene case than in the cyclohexene system, while a lower change was observed for the styrene reaction. Importantly, the less stable *cis* isomer, or *endo* isomer, was favored in each case as the steric size of the ligand was increased.

In another series of experiments the *exo/endo* cyclopropane product ratios were determined when ethyl diazoacetate was allowed to decompose in a series of cyclic olefins while keeping the applied catalyst constant. The results of these experiments are found in Table II, and can be interpreted mainly on the basis of an I strain[14] picture. The relative rates so obtained

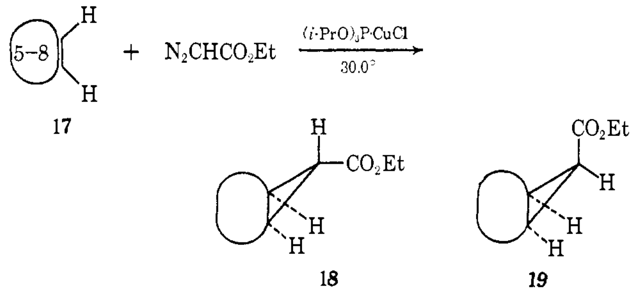
---

(12) S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, p 67.

(13) A. F. Frost and R. G. Pearson, "Kinetics and Mechanisms," John Wiley & Sons, Inc., New York, N. Y., 1953, p 25.

(14) (a) H. C. Brown, R. S. Fletcher, and R. B. Johannesen, *J. Am. Chem. Soc.*, 73, 212 (1951); (b) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 265; (c) M. L. H. Green in "Organometallic Compounds," G. E. Coates, M. L. H. Green, and K. Wade, Ed., Methuen Publishers, Ltd., London, 1968, p 21; (d) J. C. Traynham and J. R. Olechawski, *J. Am. Chem. Soc.*, **81**, 571 (1959).

parallel the relative reactivities of other cyclic systems in which there was a sp^2–sp^3 rehybridization in the transition state. The comparison of these I strain data with the *exo*/*endo* ratios obtained in these studies are likewise shown in Table II.



17

18 **19**

Table II

Olefin	*exo*/ *endo* ratio **18/19**	Predicted[14] relative rates for $sp^2 \rightarrow sp^3$	Reaction[a] A	Reaction[b] B
Cyclopentene	3.5	Difficult	3.33	15.4
Cyclohexene	6.9	Facile	70	355
Cycloheptene	3.3	Difficult	0.54	2.25
Cyclooctene	2.1	Difficult	0.081	0.172

[a] Reaction A: $K_{(eq)}$ for addition of HCN to ketones to give cyanohydrins (V. Prelog and M. Koblet, *Helv. Chim. Acta*, **32**, 1187 (1949)). [b] Reaction B: relative rates of reduction of ketones with sodium borohydride (H. C. Brown and K. Ichikawa, *Tetrahedron*, **1**, 221 (1957)).

The equilibrium constants for the formation of olefin–metal complexes of cyclic olefins should roughly parallel I strain[14c,d] data since two sp^2 carbons are being converted into sp^3 carbons accompanying a release of strain. Therefore, olefins with higher internal strain due to the olefinic linkage should form strong complexes, *i.e.*, shorter metal–carbon bonds than those with less internal strain.

Our working model for the transition state for the diazoalkane reaction predicts that any shortening of the olefin–metal bond length should result in a lowering of the *exo*/*endo* isomer ratio (discussed later).[2] In this way a reasonable rational is met for the correlation of this kind of metal-catalyzed reaction, using cyclic olefins, with I strain.

Investigation of Tyndall Effect

Although the magnified reaction solutions appeared to be homogeneous in all respects they were examined for a Tyndall effect. A narrow beam of light was passed through the reaction solution, a starch solution, and cyclohexene. The path of light could be traced only in the starch solution indicating that the reaction solution contained no particle larger than 10 Å.[15]

The error limits in the measurement of the *exo*/*endo* isomers **4**/**5** were determined utilizing ten different runs (see Experimental Section) and could be set at ±0.5% of the measured value.

Interpretation of Data

The systematic change which was observed in the *exo*- and *endo*-cyclopropanes **4** and **5** when the steric requirements of the ligand on metal were increased is good proof that the metal, olefin, and the carbon moiety of the diazoalkane are all in the final transition state leading to products. Thus the reaction proceeds through a carbene–metal–olefin complex.

Stereochemistry of the Transition State

From the data presented above any transition state postulated for this reaction must be able to account for the following facts. (a) The excited complex must contain olefin, metal, and the carbon part of the diazoalkane. (b) The complex must be asymmetric. (c) An increase in the size of the phosphite ligand must disfavor the *exo* isomer **4** in respect to the *endo* isomer **5**. (d) The products must be obtained through a unimolecular decomposition of an intermediate. (e) The intermediate would be expected to have a tetrahedral configuration since the metal atom is copper(I). (f) The transition state must involve a dissolved complex as opposed to a surface-absorbed ring closure.

Several different stereochemical arrangements for the transition state for this reaction can be conceived, and some of these will be discussed in the subsequent paper[2] on the electronic contribution to this reaction. In regard to the effect of steric bulk, the transition state which best explains the results here is the one depicted in Scheme II of the subsequent paper.[2]

The composition and stereochemical arrangement of this model meets each of the above-stated requirements. Inspection of the model in that diagram shows the compatibility of the direction of the steric effect. As one visualizes this reaction, the main factor which determines the stereochemistry of the products is the interaction of the carbethoxy group with either two *cis*-hydrogens as in **13**, to form the *exo* product or the interaction with the backbone of the cyclohexene ring as in **14** to form the *endo* isomer. Naturally, the *exo* isomer will be favored based on these considerations alone. The effect of the bulk of the phosphite ligand is to introduce a second perturbing force which will cause slight changes in the stabilities of the two transition states and thus the *exo*/*endo* isomer ratio. An inspection of the model **13** leading to *exo* product shows that an increase in the size of the phosphite ligand causes an increase in the interaction with the backbone of the six-membered ring. The effect is to destabilize this complex, which results in a disfavoring of the *exo*-isomer production. However, in the case of the excited complex **14**, leading to the *endo* isomer, an increase in the steric bulk of the ligand results in no increase in steric crowding since the phosphite ligand is *syn* to two hydrogens. The net predicted result would be a decrease in the *exo*/*endo* isomer ratio as the bulk of the phosphite ligand increases.

The experimentally determined direction of the steric effect, as shown in several ways above, was a decrease in the *exo*/*endo* ratio, as the bulk of the phosphite ligand was increased, thus consistent with the predicted change. A firmer case for this formulation of the transition state

---

(15) S. Glasstone, "The Elements of Physical Chemistry," D. Van Nostrand Co., Inc., Princeton, N. J., 1946, p 561.

will be reported in the following paper[2] on the electronic effects on this reaction. The proof that the electronic effects, in addition to the steric effects, are acting independently will also be reserved for the following paper.

Experimental Section

Materials. a. Ethyl diazoacetate was prepared by a modified procedure of Smith and McKenzie.[16] This modification afforded high yields of the diazoalkane accompanied by only traces of ethyl chloroacetate instead of the 10–18% afforded, but unreported, by the literature procedure. A solution of 279.0 g of glycine hydrochloride–ethyl ester and 1.4 g of sodium acetate was added to 550 ml of water and cooled to − 15°, and 800 ml of pentane was added to the mixture. Then 70 ml of 2 *N* H_2SO_4 was added to a solution of 220 g of sodium nitrite dissolved in 300 ml of water. This solution was cooled to +10° and added dropwise to the glycine solution as rapidly as possible without exceeding +10°. The mixture was allowed to stir for 10 min after the addition was completed. Then the pentane layer was separated and washed with water to which solid sodium bicarbonate was added until neutral. The pentane layer was twice again washed with water. The yellow pentane layer was dried with magnesium sulfate, and the solvents were removed under reduced pressure. Distillation of the residue afforded 70% yield of ethyl diazoacetate ($n^{20}\text{D}$ −1.4634, bp 34.0° (7.8 mm)) which contained 1–1.5% ethyl chloroacetate.

b. The trialkyl and triaryl phosphites were prepared by a standard procedure,[7a,17] *i.e.*, the action of phosphorus trichloride on the appropriate alcohol using dimethylaniline as base. The highly branched phosphites were prepared in the same manner but using triethylamine as the basic component.[18]

c. The (trialkyl and triaryl phosphite)copper(I) halides were prepared[7] by mixing equimolar amounts of the appropriate phosphites and solid copper(I) halide salts in either pentane or benzene. The reaction was completed when all of the solid salts were dissolved. Correct copper analyses were obtained on all catalysts utilizing the method of Wilcocks and Belcher.[19] Infrared and nmr spectra were measured on several of the catalysts.

d. All olefins were purchased from Fluka, AG, Buchs, Switzerland, and, except styrene, were distilled from sodium and passed through aluminum oxide just before use.

Analyses. The gas chromatographic analyses (glpc) were carried out on an F & M Model 720, dual-columned instrument utilizing thermal conductivity detectors. The column employed mainly for the ester separations was a 2 m × 0.64 cm copper tube filled with 10% *m*-bis(*m*-phenoxyphenoxy)benzene plus 10% Apiezon L on Chromosorb W (BPPB). Other columns utilized were: 5% polypropylene glycol adipate (PPGA) on Chromosorb W, 4 m × 0.64 cm, and 15% Carbowax 20 M, 2 m × 0.64 cm. In all cases the analyses could be obtained at temperatures less than 125°. Yields were determined utilizing internal standards and applying the appropriate response factors. Melting points were taken in sealed capillaries and are corrected.

Catalytic Activity of Complexes. All solvents were passed through aluminum oxide and were degassed just before use; in addition, cyclohexene was distilled from sodium to remove peroxides stored at −20°.

a. General Procedure for the Cyclohexene–Ethyl Diazoacetate Reaction. The catalyst (5.0 mmol, except when otherwise stated) was dissolved in 20 ml of cyclohexene and placed in a constant-temperature bath at 30.0 ± 0.05°. Ethyl diazoacetate (20 mmol) in 20 ml of cyclohexene was added from a constant dropping funnel at a rate of five drops/min. The nitrogen evolution began within 1–2 min and was formed in quantitative amounts. The solution was dark brown after *ca.* 1 ml of the diazoalkane solution had been added; 10–15 min after the addition was completed, a sample was removed and distilled without heating under 10^{-4} mm Hg. Final traces of volatile materials were removed by a final short heating period to 150–200°. The distilled solutions were then analyzed by glpc on the BPPB column at 125° or the PPGA column at 98°. The analysis of a second sample 3–6 hr after the completion of the addition of the diazoalkane showed no change in the product ratio, thus no isomerization of the products by the catalyst was observed. The yields of the cyclopropanes varied between 30 and 70%; the balance was mainly diethyl fumarate and maleate. The unsaturated esters were identified by comparison of the infrared spectra and glpc retention times with authentic materials. The *exo*-**4** and *endo*-**5** cyclopropanes were identified by a comparison of the mixture melting points and infrared spectra of their acid derivatives with authentic material.[20]

Arrhenius Parameters. The standard method of catalytic decomposition was utilized for these experiments. (Triisopropyl phosphite)copper(I) chloride was used as catalyst in each experiment as the temperature was varied between 30 and 70°. The observed change in isomer ratios as the temperature was changed is recorded in Table III. The computed least-squares analysis[21] of these data afforded: $E_a(endo) - E_a(exo) = 740 \pm 21$ cal/mol and $\Delta S(exo) - \Delta S(endo) = 1.37 \pm 0.26$ cal/(deg mol).

Table III

Temp, °C	*exo*/*endo* ratio	Temp, °C	*exo*/*endo* ratio
30	6.86	40	6.50
30	6.86	50	6.28
30	6.84	60	6.12
30	6.81	60	6.10
35	6.68	70	5.93
35	6.65		

Optical Induction. The optically active catalyst (tri-(−)-bornyl phosphite)copper(I) chloride (mp 218° dec) was utilized to decompose ethyl diazoacetate in the presence of styrene in the usual way. The individual isomers, *cis*-**15** and *trans*-**14** carbethoxyphenylcyclopropanes were isolated by preparative glpc and their rotations measured in chloroform utilizing a Zeiss–Winkel polarimeter. A 2 ml solution of 0.2776 g of the *trans* isomer in a 2-dm tube at 25.5° afforded an observed rotation of −2.17°. The specific rotation was then $[\alpha]^{25.5}\text{D}$ −7.8°. Based on the specific rotation of the pure isomer, the optical yield was 2.6% (optical yield = $[\alpha]^{T}\text{D}$ of product/$[\alpha]^{T}\text{D}$ of pure compound × 100). Similarly, a 1 ml solution of 0.1494 g of the *cis* isomer in a 1-dl tube afforded a rotation of −0.15°. Thus the specific rotation was $[\alpha]^{25.5}\text{D}$ −1.0. The calculated optical yield was 3.2%. The polarimeter used in these experiments affords an accuracy of 0.01° in the observed rotations.

Error Limits in Measuring *exo*/*endo* Isomer Ratios. The very low error limits realized in the measurement of the products in this work were obtained by glpc analysis using high retention times and large integrator counts. Thus the error limits could be set at 0.5% utilizing the data shown in Table IV.

Table IV

Catalyst	Temp, °C	*exo*/*endo* ratio
Isopropyl	30.0	6.86
		6.84
		6.86
		6.81
	35.0	6.68
		6.65
	60.0	6.12
		6.10
Ethyl	30.0	6.48
		6.43

Acknowledgments. The author wishes to thank Mr. F. Pfyffer and Mr. W. Scherrer for carefully performing much of the experimental part of this work.

---

(16) L. I. Smith and S. McKenzie, *J. Org. Chem.*, **15**, 77 (1950).

(17) G. M. Kosolopoff, "Organophosphorus Compounds," John Wiley & Sons, Inc., New York, N. Y., 1950, p 184.

(18) V. Mark and J. R. van Wazer, *J. Org. Chem.*, **32**, 1178 (1967).

(19) C. S. Wilcox and R. Belcher in "Volumetric Analysis," Vol. III, I. M. Kolthroff and R. Belcher, Ed., Interscience Publishers, New York, N. Y., 1957, pp 350–352.

(20) Authentic samples were kindly supplied by Professor H. Musso; H. Musso and U. Biethan, *Ber.*, **97**, 2282 (1964).

(21) Dr. J. J. Daly kindly carried out these calculations using a linear regression program.