

Correlations between Catalytic Reactions of Diazo Compounds and Stoichiometric Reactions of Transition-Metal Carbenes with Alkenes. Mechanism of the Cyclopropanation Reaction

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Relative reactivities and stereoselectivities are reported for $\text{Rh}_2(\text{OAc})_4$ catalyzed reactions of ethyl diazoacetate and phenyldiazomethane and for stoichiometric reactions of $(\text{CO})_5\text{WCHC}_6\text{H}_5$ with alkenes. Linear correlations are observed in relative reactivities for cyclopropane formation from $(\text{CO})_5\text{WCHPh}$ with those from $\text{Rh}_2(\text{OAc})_4$ catalyzed reactions of either phenyldiazomethane or ethyl diazoacetate. Predominant cis (syn) stereoselectivity is observed in cyclopropane formation for reactions of phenyldiazomethane, catalyzed by $\text{Rh}_2(\text{OAc})_4$, and a linear relationship exists between cyclopropanation stereoselectivities from reactions of $(\text{CO})_5\text{WCHC}_6\text{H}_5$ and $\text{C}_6\text{H}_5\text{CHN}_2/\text{Rh}_2(\text{OAc})_4$ with alkenes. Correspondence of relative reactivities with Taft σ^* values is observed with $(\text{CO})_5\text{WCHC}_6\text{H}_5$ ($\rho^* = -3.7$) and with $\text{C}_6\text{H}_5\text{CHN}_2/\text{Rh}_2(\text{OAc})_4$ ($\rho^* = -1.0$), and the ratio of these ρ^* values is nearly identical with the slope of the log-log plot of relative reactivities for the stoichiometric and catalytic cyclopropanation reactions (3.8). These results are presented within the context of a unified mechanism for cyclopropane formation in which association of the olefin with the electrophilic center of the metal carbene precedes bond formation that results in cyclopropane production. Cyclopropane stereochemistry is determined by interactions in the π complex and at the cyclopropane forming stage. Predominant cis (syn) stereoselectivity is predicted for alkylidene transfer to alkenes, and the predominant trans (anti) selectivity of α -carbonylcarbenoid intermediates is consistent with the proposed model. The origin of dihydrofuran and apparent allylic C-H insertion products from reactions of α -carbonylcarbenoid intermediates with vinyl ethers is explained.

In the accompanying paper stereoselectivities for transition-metal catalyzed cyclopropanation reactions of ethyl diazoacetate with olefins were reported to correlate linearly with stereoselectivities derived from a reference catalyst, $\text{Rh}_2(\text{OAc})_4$.¹ The relative order of catalyst-derived stereoselectivities, $\text{Cu} > \text{Rh} > \text{Pd}$, was expressly different from the previously determined order of relative reactivities for these same catalysts.² Inference was made that the electronic and/or steric influences that govern relative reactivities were different from those that affect cyclopropanation stereoselectivity¹ or regioselectivity in reactions with conjugated dienes.³ This hypothesis infers that relative reactivities for cyclopropanation reactions should be independent of the stereochemical outcome of the reaction and that, in the absence of complicating factors such as differential steric dependence on olefin coordination with the transition metal,⁴ relative reactivities for stereochemically divergent cyclopropanation reactions should correlate linearly. To test this hypothesis, we have examined relative reactivities and stereoselectivities from reactions of $(\text{CO})_5\text{WCHC}_6\text{H}_5$ with alkenes and those from $\text{Rh}_2(\text{OAc})_4$ catalyzed reactions of phenyldiazomethane and ethyl diazoacetate with the same set of alkenes.

The metal carbene $(\text{CO})_5\text{WCHC}_6\text{H}_5$ has been reported to undergo electrophilic attack on alkenes to produce cyclopropane products with an unexpected preference for the thermodynamically less stable cis isomer.⁵ This carbene system has become a model for subsequently discovered reactive transition-metal phenylcarbene systems,⁶ and in-

ferences drawn from these studies have been applied to analogous transition-metal alkylcarbene complexes.⁷⁻⁹ Metal carbene intermediates have also been inferred in catalytic reactions with diazo compounds.^{2,4,10,11} However, catalytic cyclopropanation reactions with phenyldiazomethane or diazoalkanes that would offer direct analogy with the recently developed "stable" transition-metal carbenes have not been previously described. We now report that relative reactivities and stereoselectivities for catalytic cyclopropanation reactions of phenyldiazomethane with alkenes correlate directly with stereoselectivities and relative reactivities for cyclopropanation of alkenes by $(\text{CO})_5\text{WCHPh}$.

Results

Relative Reactivities: Rhodium(II) Acetate Catalyzed Reactions of Ethyl Diazoacetate with Alkenes. Competitive cyclopropanation of two olefins by diazo compounds in the presence of metal catalysts has been employed to characterize the relative reactivities of intermediate metal carbene species with alkenes,^{2,4} and inferences have been drawn from these investigations on the nature of the reactive carbene species and on the mechanism of the cyclopropanation transformation. These data have ordinarily been obtained from experiments in which

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Table I. Relative Reactivities and Stereoselectivities for $Rh_2(OAc)_4$ Catalyzed Reactions of Ethyl Diazoacetate with Representative Alkenes^a

alkene	rel reactivity	cyclopropane trans/cis	alkene	rel reactivity	cyclopropane trans/cis
2-methoxypropene	14.2	1.0 ^b	cyclohexene	3.7	3.8 ^c
<i>n</i> -butyl vinyl ether	12.9	1.7	2,5-dimethyl-2,4-hexadiene	3.2	1.8
ethyl vinyl ether	12.5	1.7	2-methyl-2-butene	2.2	1.5
dihydropyran	11.2	6.5	vinyl acetate	1.7	1.6
phenyl vinyl ether	5.8	1.4	1-hexene	1.5	1.5
styrene	5.3	1.6	3-methyl-1-butene	1.3	2.0
cyclopentene	4.2	2.1 ^c	3,3-dimethyl-1-butene	1.00	4.2

^a Reactions performed at 25 °C. ^b *E/Z* cyclopropane isomer ratio. ^c Anti/syn cyclopropane isomer ratio.

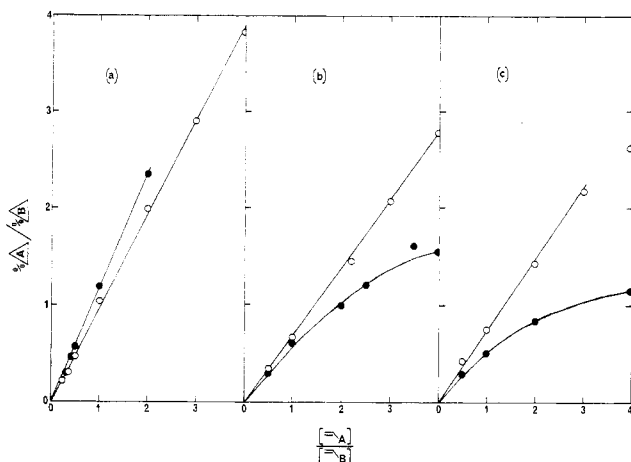


Figure 1. Plots of molar ratios of cyclopropane products vs. molar ratios of reactant alkenes from reactions of ethyl diazoacetate with (a) *n*-butyl vinyl ether/ethyl vinyl ether, (b) 2,5-dimethyl-2,4-hexadiene-styrene, and (c) cyclohexene/styrene combinations, catalyzed by $Rh_2(OAc)_4$ (○) and by $Cu(OTf)_2$ (●).

initial concentrations of the two olefins undergoing competitive cyclopropanation are identical. However, relative reactivities in cyclopropanation reactions using transition-metal compounds that form complexes with alkenes can be expected to be influenced by the coordinated olefin. In such cases relative reactivities are accurate only under the conditions employed for their determination.

Rhodium(II) acetate, in contrast to copper(I) triflate¹² or palladium(II) chloride,¹³ does not form complexes with olefins to any measureable degree.¹⁴ As a result, relative reactivities in competitive cyclopropanation reactions using $Rh_2(OAc)_4$ as the catalyst were anticipated to be uniform throughout a wide range of alkene pair molar ratios. This expectation was confirmed. Figure 1 describes results from comparative examination of three pairs of alkenes in competitive cyclopropanation reactions with ethyl diazoacetate. The molar ratio of cyclopropane products is linearly related to the molar ratio of reactant alkenes with $Rh_2(OAc)_4$ catalysis. A higher order dependence on the molar ratio of reactant alkenes is observed with $Cu(OTf)_2$ catalysis. Vinyl ether comparisons (Figure 1a) represent the exception with $Cu(OTf)_2$. As a consequence, $Rh_2(OAc)_4$ is an appropriate choice of catalyst for comparisons of relative reactivities with those derived from other similarly

Table II. $Rh_2(OAc)_4$ Catalyzed Reactions of Phenyl diazomethane with Representative Alkenes^a

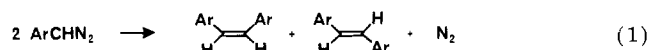
alkene	cyclopropane yield, %	cis/trans (Z/E) ^b	rel reactivity
α -methoxystyrene	98	0.67	48
2-methoxypropene	82	1.2	25
3,3-dimethyl-2-methoxy-1-butene	92	0.15	8.8
<i>n</i> -butyl vinyl ether	92	2.5	4.6
ethyl vinyl ether	54	3.0	4.1
styrene	38	3.3	1.00
2-methyl-2-butene	23	12	0.33
vinyl acetate	7	3.8	
1-hexene	6	0.90	
cyclopentene	6	1.6 ^c	
3-methyl-1-butene	4	0.56	

^a Reactions performed in ether at 25 °C. ^b For 1,1-disubstituted ethylenes. ^c Syn/anti cyclopropane isomer ratio.

behaved carbenoid systems. The activity of $Cu(OTf)_2$ is more complex, probably related to olefin coordination with the catalytically active species,⁴ and deserving of further investigation.

To achieve a higher level of accuracy and a wider representation of alkenes in relative reactivity values than has been previously reported,² we examined multiple pairs of alkenes by the methodology exemplified in Figure 1. Multiple comparisons of a single alkene with two or more reference alkenes confirmed the uniformity of these relative reactivity determinations. Table I presents these alkene reactivities, relative to 3,3-dimethyl-1-butene, ordered according to their calculated values. Stereoselectivities derived from these alkenes in cyclopropane formation¹ are also reported. Of particular interest are the observations that cyclopentene is more reactive than cyclohexene and that these cyclopropanation reactivities follow the order styrene \gg 1-hexene $>$ 3-methyl-1-butene $>$ 3,3-dimethyl-1-butene. These same orders of relative reactivity characterize electrophilic addition reactions.¹⁵

Rhodium(II) Acetate Catalyzed Reactions of Phenyl diazomethane with Alkenes. The decomposition of aryl diazomethanes to the corresponding stilbenes (eq 1)



by copper(II) salts,¹⁶ rhodium(II) acetate,¹⁷ and iodorrhodium(III) tetraphenylporphyrin¹⁷ has recently been investigated. With $Rh_2(OAc)_4$ these reactions are rapid, efficient, and selective for the formation of the *cis*-stilbene

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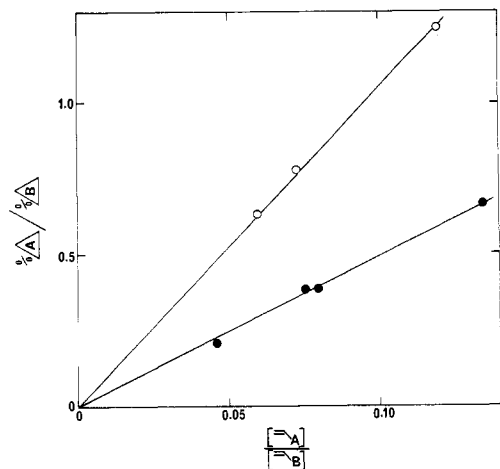
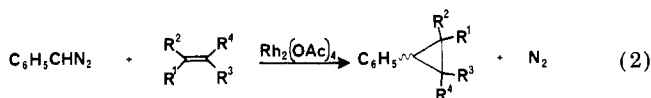


Figure 2. Plot of molar ratios of cyclopropane products vs. molar ratios of reactant alkenes from $\text{Rh}_2(\text{OAc})_4$ catalyzed reactions of phenyldiazomethane with α -methoxystyrene/*n*-butyl vinyl ether (O) and 2-methoxypropene/*n*-butyl vinyl ether (●) combinations.

isomer. Anticipating that cyclopropanation of alkenes (eq 2) would be competitive with this transformation, we have



investigated the characteristics of olefin cyclopropanation in $\text{Rh}_2(\text{OAc})_4$ catalyzed reactions with phenyldiazomethane for comparison with results from reactions of $(\text{CO})_5\text{WCHPh}$ with olefins.^{5a} These reactions were performed in ethyl ether by using a 20- to 40-fold excess of the olefin, and the phenyldiazomethane solution was added over a 4- to 8-h period to minimize formation of *cis*- and *trans*-stilbene. Product yields and stereoselectivities are reported in Table II.

The catalytic route to phenylcyclopropane formation is exceptionally sensitive to the nucleophilic reactivity of the olefin employed. Among the olefins that were examined, only the vinyl ethers underwent cyclopropanation in synthetically meaningful yields. The stilbenes were the major byproducts of these reactions, and their isomeric ratio (*c/t* = 4) was identical with that previously reported.¹⁷ Benzalazine, formed as a minor product but in variable yields, inhibited $\text{Rh}_2(\text{OAc})_4$ catalysis of olefin cyclopropanation by phenyldiazomethane; as a consequence, $\text{Rh}_2(\text{OAc})_4$ was employed at 4 mol % based on phenyldiazomethane.

The stereochemical preference for the *cis* (or *syn*) cyclopropane isomer (Table II) contrasts with the stereochemical preference for the *trans* (or *anti*) cyclopropane isomer in comparable reactions that employ ethyl diazoacetate (Table I).¹ In addition, these selectivities are temperature dependent; the *cis/trans* ratio for cyclopropanes derived from phenyldiazomethane and ethyl vinyl ether increases from 3.0 (25 °C) to 3.8 (8 °C) to 4.2 (0 °C).¹⁸ Stereochemical results were reproducible to within $\pm 5\%$ of the reported values.

Relative reactivities of alkenes employed in competitive cyclopropanation reactions with phenyldiazomethane using $\text{Rh}_2(\text{OAc})_4$ as the catalyst were determined as previously reported for catalytic reactions involving ethyl diazoacetate (Table II). Figure 2 describes the uniformity obtained

(18) Reaction temperatures lower than that reported in Table II did not offer any apparent yield advantage for cyclopropane formation. However, the temperature effect on cyclopropanation stereoselectivity is substantial. Extrapolation of this data to -78 °C suggests production of an isomer ratio (*c/t*) of 7.1.

Table III. Reactions of $(\text{CO})_5\text{WCHC}_6\text{H}_5$ with Representative Alkenes^a

alkene	cyclopropane		rel reactivity ^c
	yield, %	<i>cis/trans</i> (Z/E) ^b	
α -methoxystyrene	89	0.55	104×10^4 (2.5×10^3)
2-methoxypropene	98	1.4	38×10^4 (9.4×10^2)
3,3-dimethyl-2-methoxy-1-butene	96	0.011	4.4×10^4 (108)
<i>n</i> -butyl vinyl ether	96	5.8	2.2×10^4 (54)
ethyl vinyl ether	89	7.6	1.7×10^4 (41)
styrene ^d	39	9.7	410 (1.0)
2-methyl-2-butene ^d	81	94	820 (2.0)
vinyl acetate	85	10.5	9.4
cyclopentene ^d	40	2.6 ^e	6.0
1-hexene	37	0.84	4.7
3-methyl-1-butene ^d	72	0.36	2.4
3,3-dimethyl-1-butene ^d	69	0.01	1.0

^a Reactions performed in dichloromethane at -78 °C.

^b For 1,1-disubstituted ethylenes. ^c Numbers in parentheses are reactivities relative to styrene. ^d From ref 5a.

^e *Syn/anti* cyclopropane isomer ratio.

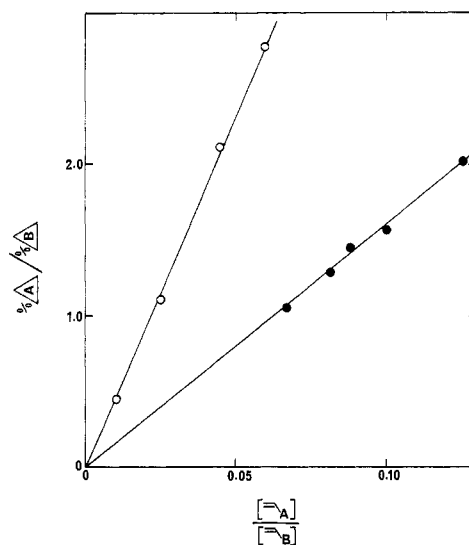


Figure 3. Plot of molar ratios of cyclopropane products vs. molar ratios of reactant alkenes from reactions of $(\text{CO})_5\text{WCHC}_6\text{H}_5$ with α -methoxystyrene/*n*-butyl vinyl ether (O) and 2-methoxypropene/*n*-butyl vinyl ether (●) combinations.

from plots of the corresponding product ratios vs. mole ratio of reactant alkenes. Because of low product yields, relative reactivity values for vinyl acetate, 1-hexene, cyclopentene, and 3-methyl-1-butene were not determined. Product stereoselectivities from competitive cyclopropanation reactions showed little variance from the values reported in Table II.

Reactions of $(\text{CO})_5\text{WCHPh}$ with Alkenes. The reactive $(\text{CO})_5\text{WCHC}_6\text{H}_5$ was prepared in the manner previously described,^{5a,19} and reactions were carried out in methylene chloride at -78 °C by using a 50-fold molar excess of the reactant olefin. The composite data for these and previously reported reactions of $(\text{CO})_5\text{WCHPh}$ with alkenes are listed in Table III. Figure 3 exemplifies the uniformity obtained from plots of cyclopropane product ratios vs. mole ratio of reactant alkenes in relative reactivity determinations. This uniformity suggests that differential olefin coordination to a coordinatively unsat-

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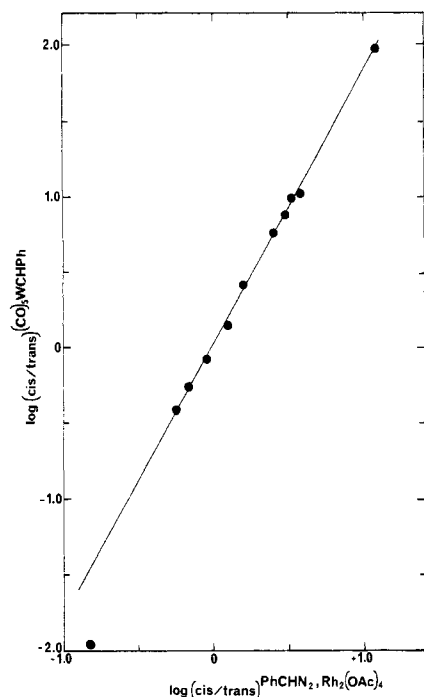
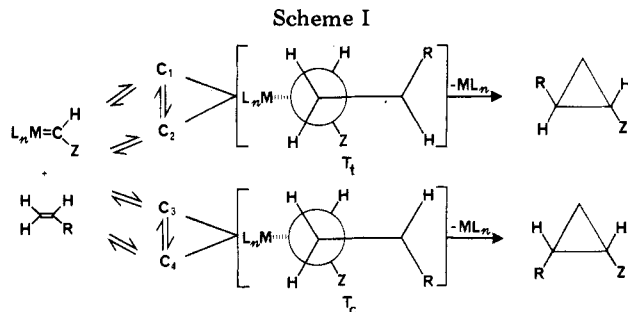


Figure 6. Plot of $\log(\text{cis}/\text{trans})$ or $\log(Z/E)$ for cyclopropanation of alkenes with $(\text{CO})_5\text{WCHC}_6\text{H}_5$ at -78°C vs. those with phenyldiazomethane catalyzed by $\text{Rh}_2(\text{OAc})_4$ at 25°C .

coefficient 0.99), and for $\text{Rh}_2(\text{OAc})_4$ catalyzed reactions a similar correspondence is evident ($\rho^* = -1.0$; correlation coefficient 0.98). Although these data are limited, it is noteworthy that the ratio of ρ^* values (3.7) is nearly identical with the slope of the line in Figure 4 (3.8). This correspondence further defines the remarkable relationship of $\text{Rh}_2(\text{OAc})_4$ catalyzed reactions of diazo compounds with reactions of $(\text{CO})_5\text{WCHC}_6\text{H}_5$ with alkenes and suggests that the reactive intermediate in both transformations is an electrophilic metal carbene.

That metal carbenes are distinctive intermediates in transition-metal-catalyzed reactions of diazo compounds is not surprising. The influence of the transition metal on stereo- and regioselectivities in catalytic cyclopropanation reactions^{1,3} demands involvement of the transition metal in the product-determining step. Similarly, asymmetric induction in catalytic cyclopropanation reactions with the use of chiral catalysts^{25,26} infers that the chiral ligand of the transition metal controls effective approach of the olefin to the carbenic center. That relative reactivities for catalytic cyclopropanation reactions involving $\text{Rh}_2(\text{OAc})_4$ correlate directly with those for stoichiometric reactions of $(\text{CO})_5\text{WCHC}_6\text{H}_5$ now affords direct analogy of the transition-metal-catalyzed reactions with the reaction characteristics of known transition-metal carbenes.

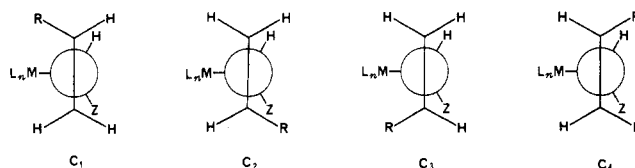
Stereoselectivity Correlation. There is no obvious relationship for cyclopropanation stereoselectivities between ethyl diazoacetate and phenyldiazomethane in $\text{Rh}_2(\text{OAc})_4$ catalyzed reactions but, as seen in Figure 6, a linear relationship exists between $\text{Rh}_2(\text{OAc})_4$ catalyzed reactions of phenyldiazomethane and stoichiometric reactions of $(\text{CO})_5\text{WCHC}_6\text{H}_5$. With the exception of 3,3-dimethyl-2-methoxy-1-butene, data points for all olefins compared (Tables II and III) fall on a straight line having



a slope of 1.78 in this log-log plot.²⁷ This remarkable uniformity demands that those factors that govern the product-determining step in each of these cyclopropanation reactions are identical. The diverse stereochemical results obtained for transition-metal phenylcarbene and carboethoxycarbene intermediates suggests that the phenyl or carboethoxy carbene substituent determines the stereochemical preference of these reactions.

Mechanism of the Cyclopropanation Reaction.

Previously, relative reactivities of alkenes toward $(\text{CO})_5\text{WCHC}_6\text{H}_5$ have been understood in terms of an interaction between the electrophilic carbene carbon and one terminus of the reacting alkene.^{5a,6a} However, an alternate explanation, that the initial interaction between the electrophilic carbon center and the olefin is that of a π complex, is also in accord with available data. If such a π complex has independent existence, a condition that can only be inferred at this time, four orientations can be used to form the basis set of stable conformations.²⁸ For the set of π complex orientations involving monosubstituted olefins (C_1 – C_4), C_1 and C_3 are of higher energy than C_2 and C_4 as



a result of interactions of the olefin substituent with metal ligands, and C_4 can be anticipated to be favored over C_2 on steric grounds. In the second stage of reaction, the olefin rotates around the electrophilic center to an orientation that places the carbon-carbon bond of the olefin parallel to the metal-carbon bond so that the more substituted carbon of the olefin is anti to the ligated metal (Scheme I). In this operation C_1 and C_2 are both transformed to T_t , and C_3 and C_4 are both transformed to T_c . Crossover between C_1/C_2 and C_3/C_4 occurs only when olefin dissociation from the π complex returns the reactants to their initial states. For this second stage T_t and T_c can be viewed as transition states through which cyclopropane formation results from dissociation of ML_n . An analogous transition state characterizes the solvolysis of $\gamma\text{-SnR}_3$ derivatives in which cyclopropane formation occurs

(27) Stereochemical results for the formation of phenylcyclopropanes by reactions of $\eta^5\text{-C}_5\text{H}_5(\text{CO})_2\text{FeCHC}_6\text{H}_5^+$ with alkenes have been reported.^{6a} Although only three data points, those for reactions with propene, 1-butene, and 3-methyl-1-butene, are available for comparison with results from $(\text{CO})_5\text{WCHC}_6\text{H}_5$, a plot of $\log(c/t)$ for $\eta^5\text{-C}_5\text{H}_5(\text{CO})_2\text{FeCHC}_6\text{H}_5^+$ vs. $\log(c/t)$ for $(\text{CO})_5\text{WCHC}_6\text{H}_5$ suggests a linear relationship with a slope of 2.4.

(28) Independent existence of four orientations is based on the assumption that there is a barrier to rotation for the interconversion of C_1 with C_2 and of C_3 with C_4 .

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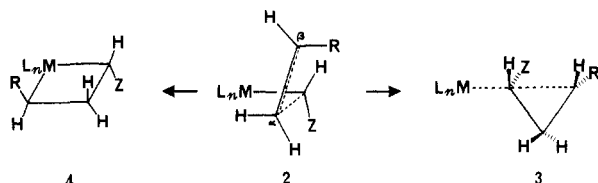
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with backside displacement of R_3Sn^+ by the developing carbenium ion.²⁷

Previous interpretation that the initial interaction between the electrophilic metal carbene and the alkene occurred at one terminus of the reactant alkene was based solely on the reactivity pattern of methyl-substituted ethylenes.^{5a} However, relative rates for electrophilic addition by reagents that are known to form transitory π complexes and/or three-membered cyclic activated complexes exhibit similar olefin substituent effects.¹⁵ These reactivities are determined by a complex set of steric and electronic influences that in the specific case of olefin cyclopropanation represent a composite of factors that govern formation of each π complex and its collapse to products or reactants. Data reported in Tables I-III for relative reactivities and a comparative analysis with equilibrium constants for complex formation between transition metals and these same olefins³⁰ suggest that collapse of these π complexes to products is the dominant contributor to olefin reactivity.

High *cis* stereoselectivities in benzylidene transfer from $(CO)_5WCHC_6H_5$ and $Cp(CO)_2FeCHC_6H_5^+$ to alkenes have been attributed to a stabilizing interaction between the developing electrophilic center of the reacting alkene and the aryl group.^{5a,6a} However, ethylidene transfer reactions of $Cp(CO)_2FeCH(OCH_3)CH_3$, for which such a stabilizing interaction is not possible, also exhibit a pronounced preference for formation of the *cis*-cyclopropane isomer.^{7b} As a consequence of this development, transition-state model 2 (e.g., $L_nM = (CO)_5W$, $Cp(CO)_2Fe^+$) has been invoked to explain *cis* stereoselectivity.^{7b} According to this model, the developing electrophilic center at C_β may displace ML_n with synchronous $C_{\text{carbene}}-C_\beta$ bond formation (3 \rightarrow *cis*-cyclopropane product), or a discrete metalocycle (4 \rightarrow *trans*-cyclopropane product) may be formed. Al-



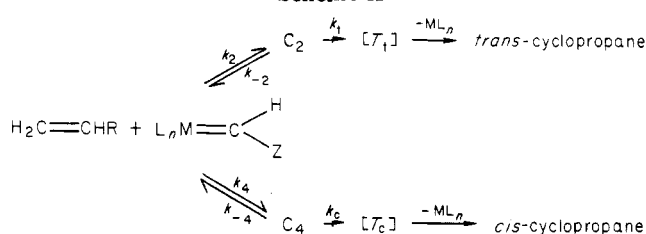
though this model is consistent with observations that substituents at C_β have little effect on stereoselectivity whereas substituents at C_α strongly control stereoselectivity, the influence of increasing size of a single substituent (e.g., R = Me, Et, *i*-Pr, *t*-Bu) demands a partitioning of 2 to 3 and 4.

Scheme I affords a mechanism that provides uniformity and predictability to this diverse stereochemical data. Using a simplified version of Scheme I in which C_1 and C_3 are not included (Scheme II), stereoselectivities are represented by $[c]/[t] = K_4k_c/K_2k_t$ if $k_{-2} \gg k_t$ and $k_{-4} \gg k_c$. Relative reactivity is related to stereoisomer ratios and values of K_4 and K_2 by the equation

$$\text{relative reactivity} = \frac{k_c^A [1 + ([t]K_4/[c]K_2)]^A}{k_c^B [1 + ([t]K_4/[c]K_2)]^B}$$

where A and B denote olefins A and B. When $[c] \gg [t]$ for both A and B, relative reactivity is equal to k_c^A/k_c^B only if $([t]K_4/[c]K_2) \ll 1$ for both A and B. A similar statement can be made for k_t^A/k_t^B when $[t] \gg [c]$. Relative reactivity correlations between electronically different carbenoid intermediates (Figures 4 and 5) are possible because values for $([t]K_4/[c]K_2)$ can be expected to reflect

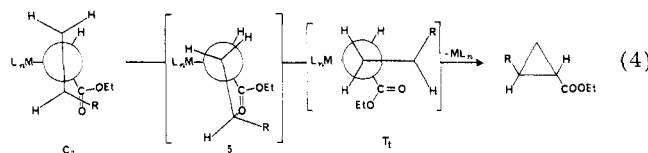
Scheme II



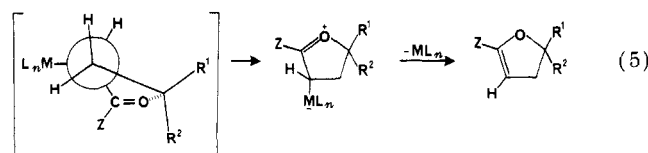
proportional dependence on olefin structure.

Steric interactions between R and Z in the π complex provide preference for C_4 over C_2 . In the absence of pronounced steric interaction between R and Z in transition state T_c , $k_c \approx k_t$ and the *cis*-cyclopropane product will dominate. Steric interaction between R and Z in T_c increases k_t relative to k_c , but the R group giving rise to such steric interaction will also cause a decrease in K_2 relative to K_4 . With bulky R groups steric interactions can be expected to be less important in C_2 than in T_c , and, consequently, Scheme II also accounts for the effect of increasing size of R on stereoselectivity. For *gem*-disubstituted olefins, the weakened influence of individual substituents on stereoselectivity is due to the counterbalance of steric influences from the π complex with those from the transition state for cyclopropane formation. Similarly, *cis*-disubstituted olefins are predicted by this model to produce cyclopropane products with a high degree of *cis* (syn) stereoselectivity.

Stereochemical preference for the *trans*-cyclopropane isomer in reactions involving transition-metal-catalyzed decomposition of ethyl diazoacetate¹ and related diazo-carbonyl compounds appears to be the exception to this model. However, examination of the specific influence of the carbonyl group on the conversion of the intermediate π complex to cyclopropane products explains this apparent discrepancy. In passing from C_2' to T_t' the developing electrophilic C_β of the original alkene must pass over the carbonyl oxygen (5) resulting in stabilization of the tran-



sition state leading to the *trans*-cyclopropane. The transition leading to the *cis*-cyclopropane product does not offer similar stabilization. Increasing the nucleophilicity of the carbonyl oxygen and/or the electrophilicity of C_β in 5 can be expected to alter the reaction course by forming dihydrofuran products (eq 5). These transformations are,



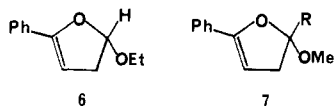
in fact, well documented in copper-catalyzed reactions of diazomalones, 2-diazo-3-oxybutyrates and 3-diazo-2,4-pentanedione with vinyl ethers.^{31,32} Similar results were

(31) (a) Wenkert, E. *Acc. Chem. Res.* 1980, 13, 27. (b) Wenkert, E. *Heterocycles* 1980, 14, 1703.

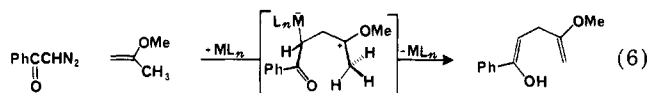
(32) (a) Wenkert, E.; Alonso, M. E.; Buckwalter, B. L.; Sanchez, E. L. *J. Am. Chem. Soc.* 1983, 105, 2021. (b) Wenkert, E.; Arrhenius, T. S. *Ibid.* 1983, 105, 2030. (c) Alonso, M. E.; Morales, A.; Chitty, A. W. *J. Org. Chem.* 1982, 47, 3747. (d) Wenkert, E.; Alonso, M. E.; Buckwalter, B. L.; Chow, J. K. *J. Am. Chem. Soc.* 1977, 99, 4778.

(30) Hartley, F. R. *Chem. Rev.* 1973, 73, 163.

obtained with dimethyl diazomalonate or α -diazoacetophenone in reactions catalyzed by either $\text{Rh}_2(\text{OAc})_4$ or $\text{PdCl}_2 \cdot 2\text{PhCN}$: dihydrofuran **6** was formed as a minor



product in reactions with ethyl vinyl ether whereas **7** was a major product in reactions with either 2-methoxypropene ($\text{R} = \text{Me}$) or α -methoxystyrene ($\text{R} = \text{Ph}$).³³ Competitive elimination, which we observe in $\text{Rh}_2(\text{OAc})_4$ catalyzed reactions of α -diazoacetophenone with 2-methoxypropene (eq 6), has been previously reported for reactions of various



α -diazocarbonyl compounds with vinyl ethers bearing a hydrogen on an α -alkyl substituent^{31,32} and with certain simple alkenes.³⁴ This transformation is also in accord with the directive influence of the carbene carbonyl substituent.

With this electronic stabilization of the transition state leading to the *trans*-cyclopropane product, the relative ordering of stereoselectivities in transition-metal-catalyzed reactions with diazocarbonyl compounds now becomes understandable. With monosubstituted olefins, increasing the electrophilicity of C_β in **5** results in increased interaction of the developing carbocation with the carbonyl oxygen and increased preference for production of the *trans*-cyclopropane isomer. Increasing the nucleophilicity of the carbonyl oxygen also results in an increase in the stereochemical preference for the *trans*-cyclopropane isomer.³⁵ Notably, decreasing the electrophilicity of the carbene carbon in transition-metal-catalyzed reactions with ethyl diazoacetate increases the stereochemical preference for the *cis*-cyclopropane isomer.^{1,26,36} With an alkene such as cyclopentene, whose orientation in the π complex is symmetrical with respect to the metal, electronic stabilization by the carbonyl group proves to be sufficiently strong to preferentially direct cyclopropane formation to the anti isomer (Table I). The syn isomer is dominant when the carbonyl substituent is replaced by a phenyl group (Tables II and III).

Summary. Stereoselectivity and relative reactivity correlations between $\text{Rh}_2(\text{OAc})_4$ catalyzed reactions of diazo compounds with alkenes and stoichiometric reactions of $(\text{CO})_5\text{WCHPh}$ with these same alkenes define metal carbene involvement in $\text{Rh}_2(\text{OAc})_4$ catalyzed reactions. Correlations in regioselectivity³ and stereoselectivity¹ for cyclopropane formation between $\text{Rh}_2(\text{OAc})_4$ catalyzed reactions and those from representative copper-, rhodium-, and palladium-catalyzed transformations provide their interlink to the involvement of electrophilic metal carbene intermediates in cyclopropane forming reactions. Linear correspondence between relative reactivities in $\text{Rh}_2(\text{OAc})_4$ catalyzed reactions of ethyl diazoacetate and of phenyl-diazomethane with monosubstituted alkenes and stoi-

chiometric reactions of $(\text{CO})_5\text{WCHC}_6\text{H}_5$ suggests a unified mechanism for cyclopropane formation in which association of the olefin with the electrophilic center of the metal carbene precedes σ bond formation that results in cyclopropane production. Cyclopropane stereochemistry is determined by a combination of steric and/or electronic interactions at the π complex and cyclopropane-forming stages. In the absence of prominent steric influences in the cyclopropane-forming stage, predominant *cis* stereoselectivity is predicted and observed for reactions of monosubstituted alkenes with metal carbenes possessing alkyl or aryl substituents. Electronic stabilization of the transition state leading to *trans*-cyclopropane products by interaction of the developing electrophilic carbon of the original alkene with an α -carbonyl substituent of the metal carbene accounts for the predominant *trans* stereoselectivity observed in transition-metal-catalyzed reactions of alkenes with α -diazocarbonyl compounds. This mechanistic model offers a predictive format for regioselectivity and stereoselectivity in cyclopropane-forming reactions of electrophilic metal carbenes, either stoichiometric reagents or catalytically generated. The influence of carbene substituents in altering the pathway for product formation from cyclopropane formation, which with an α -carbonyl substituent can result in dihydrofuran formation or apparent allylic C-H insertion of the carbene in reactions with alkenes, can now also be understood within the context of metal carbene electrophilicity and alkene nucleophilicity.

Experimental Section

Competitive Reactions of Ethyl Diazoacetate. Ethyl diazoacetate (1.00 mmol) was added at a controlled rate over a 4–8-h period to a stirred mixture of the two alkenes (minimum amount of each olefin: 10.0 mmol) and either rhodium(II) acetate or copper(II) trifluoromethanesulfonate³⁷ (0.010 mmol) under nitrogen at 25 °C.³⁸ Alkenes were usually purified by distillation prior to their use. After reaction was complete, dibenzyl ether was added to the reaction solution as the internal standard followed by 50 mL of ethyl ether. The resulting ether solution was washed twice with 50-mL portions of aqueous sodium bicarbonate and dried over anhydrous magnesium sulfate, and the ether and excess olefin were distilled under reduced pressure. The product mixture was then subjected to GC analysis, ordinarily with 4-m 20% Carbowax 20 M columns. Product isomer ratios in $\text{Rh}_2(\text{OAc})_4$ catalyzed reactions were identical with those determined from reactions with a single olefin.^{1,39} Cyclopropane product yields were obtained with the use of experimentally measured relative response ratios for each cyclopropane pair and generally accounted for greater than 95% of the ethyl diazoacetate initially employed. A minimum of three olefin ratios was employed to determine each relative reactivity value. Correlation coefficients of greater than 0.99 characterized the linear relationships between cyclopropane product ratios and initial olefin concentration ratios in $\text{Rh}_2(\text{OAc})_4$ catalyzed reactions. Olefin pairs were chosen to include styrene or ethyl vinyl ether, and relative reactivity values for one olefin vs. styrene and for that same olefin vs. ethyl vinyl ether were observed to provide the same relative reactivity value as obtained directly from the styrene/ethyl vinyl ether combination.

(37) Salomon, R. G.; Salomon, M. F.; Heyne, T. R. *J. Org. Chem.* **1975**, *40*, 756.

(38) Reactions that employed 3-methyl-1-butene were performed at 9 °C to avoid differential loss of this olefin in competitive cyclopropanation reactions.

(39) Isomer ratios were dependent on the molar ratio of reactant alkenes in copper triflate catalyzed reactions. For example, the t/c ratio of ethyl 2-phenylcyclopropanecarboxylate increased from 1.5 to 1.7 in reactions performed with styrene in combination with 2,5-dimethyl-2,4-hexadiene where the lowest t/c value is associated with the lowest molar ratio of styrene to 2,5-dimethyl-2,4-dexadiene. For reactions with styrene in combination with cyclohexene, the t/c ratio of ethyl 2-phenylcyclopropanecarboxylate was 2.1–2.2.

(33) Neither **6** nor **7** was transformed to cyclopropane products, and 1-benzoyl-2-ethoxycyclopropane was not converted to **6** under these catalytic reaction conditions.

(34) Alonso, M. E.; Gomez, M. *Tetrahedron Lett.* **1979**, 2763.

(35) In reactions with ethyl vinyl ether catalyzed by $\text{Rh}_2(\text{OAc})_4$, the t/c ratio increases from 1.7 for reactions with ethyl diazoacetate to 2.0 for reactions with α -diazoacetophenone.

(36) Callot, H. J.; Piechocki, C. *Tetrahedron Lett.* **1980**, *21*, 3489.

Cyclopropanation Reactions of Phenyl diazomethane. Phenyl diazomethane⁴⁰ (0.50 mmol) in 3.0 mL of anhydrous ethyl ether was added through a 5-mL syringe at a controlled rate over a 4–8-h period to a stirred solution of the alkene (usually minimum 10-fold molar excess) and rhodium(II) acetate (0.020 mmol) under nitrogen and ordinarily in the dark at 25 °C. Reactions with α -methoxystyrene were performed with only a 2.6 molar excess of olefin. Attempts to increase product yields from reactions with aliphatic olefins and vinyl acetate by performing these reactions with as much as a 200-fold molar excess of olefin relative to diazo compound and by employing phenyl diazomethane with even higher ether dilution were only moderately successful (less than 50% increase in reported yield) and, consequently, yields reported in Table II are from those experiments in which a 20- and 40-fold excess of alkene was used. Gas evolution occurred immediately upon addition of phenyl diazomethane. After addition was complete, dibenzyl ether or diphenylmethane was added as the internal standard, and products were isolated as previously described.¹ The product mixture was subjected to NMR and GC analyses. Product yields were determined by GC through the use of experimentally measured response ratios obtained from GC collected cyclopropanes, in the case of vinyl ethers, or from cyclopropane products produced in the reaction of benzal bromide with methyl lithium performed in the presence of an alkene.⁴¹ Duplicate experiments were minimally performed for each reported reaction. Isomer ratios were determined by GC and, when applicable, NMR analyses. Mass spectral analyses of reaction mixture were employed to confirm product identity, particularly for those reactions that resulted in low product yields. Spectral information for cyclopropane products formed from styrene, 2-methyl-2-butene, 3-methyl-1-butene, and cyclopentene have previously been reported.^{5a}

1,2-Diphenyl-1-methoxycyclopropane. ¹H NMR (CDCl₃): for *Z* isomer, δ 7.50–7.10 (m, 10 H), 3.09 (s, OCH₃), 2.43 (d of d, *J* = 9.5, 7.7 Hz, CHPh), 1.66–1.50 (m, 2 H); for *E* isomer, δ 7.40–6.80 (m, 10 H), 3.21 (s, OCH₃), 2.72 (d of d, *J* = 8.6, 8.5 Hz, CHPh), 1.63–1.50 (m, 2 H).

1-Methoxy-1-methyl-2-phenylcyclopropane. ¹H NMR (CDCl₃): for *Z* isomer, δ 7.32–7.18 (m, 5 H), 3.05 (s, OCH₃), 1.92 (d of d, *J* = 9.5, 6.7 Hz, CHPh), 1.58 (s, CH₃), 1.25 (d of d, *J* = 6.7, 5.8 Hz, 1 H), 1.00 (d of d, *J* = 9.5, 5.8 Hz, 1 H); for *E* isomer, δ 7.32–7.08 (m, 5 H), 3.36 (s, OCH₃), 2.31 (d of d, *J* = 10.1, 7.1 Hz, CHPh), 1.25 (d of d of q, *J* = 10.1, 5.7, 0.6 Hz, 1 H), 1.10 (d, *J* = 0.6 Hz, CH₃), 0.91 (d of d, *J* = 7.1, 5.7 Hz, 1 H).

1-tert-Butyl-1-methoxy-2-phenylcyclopropane. ¹H NMR (CDCl₃): for *Z* isomer, δ 7.30–7.15 (m, 5 H), 3.22 (s, OCH₃), 2.18 (d of d, *J* = 9.8, 7.2 Hz, CHPh), 1.21 (d of d, *J* = 9.8, 4.6 Hz, 1 H), 1.17 (d of d, *J* = 7.2, 4.6 Hz, 1 H), 1.02 (s, *t*-Bu); for *E* isomer, δ 7.35–7.05 (m, 5 H), 3.45 (s, OCH₃), 2.49 (d of d, *J* = 10.1, 7.5 Hz, CHPh), 0.79 (s, *t*-Bu).

1-*n*-Butoxy-2-phenylcyclopropane. ¹H NMR (CDCl₃): for *cis* isomer, δ 7.22 (s, 5 H), 3.58–3.03 (m, 3 H), 1.95 (d of d of d, *J* = 8.6, 8.2, 6.2 Hz, CHPh), 1.5–1.0 (m, 6 H), 0.76 (t, *J* = 6.2 Hz, CH₃); for *trans* isomer, δ 7.35–6.94 (m, 5 H), 3.55 (t, *J* = 6.2 Hz, CH₂O), 3.34 (d of d of d, *J* = 8.6, 3.7, 2.6 Hz, CHOBu), 2.04 (d of d of d, *J* = 8.1, 3.9, 2.6 Hz, CHPh), 1.6–0.75 (m, 6 H), 0.92 (t, *J* = 6.2 Hz, CH₃).

1-Ethoxy-2-phenylcyclopropane. ¹H NMR (CDCl₃): for *cis* isomer, δ 7.23 (s, 5 H), 3.6–3.0 (m, 3 H), 1.97 (d of d of d, *J* = 8.6, 8.2, 6.2 Hz, CHPh), 1.3–1.0 (m, 2 H), 0.98 (t, *J* = 7.1 Hz, CH₃CH₂O); for *trans* isomer, δ 7.35–6.95 (m, 5 H), 3.62 (q, *J* = 7.1 Hz, CH₂O), 3.33 (d of d of d, *J* = 10.0, 3.8, 1.1 Hz, CHOEt), 2.07 (d of d of d, *J* = 10.1, 3.8, 2.6 Hz, CHPh), 1.38–0.88 (m, 2 H), 1.21 (t, *J* = 7.1 Hz, CH₃CH₂O).

1-Acetoxy-2-phenylcyclopropane. ¹H NMR (CDCl₃): for *cis* isomer, δ 7.22 (s, 5 H), 4.33 (d of d of d, *J* = 6.9, 5.8, 4.7 Hz, CHOAc), 2.26 (d of d of d, *J* = 8.6, 8.5, 6.9 Hz, CHPh), 1.79 (s, CH₃COO), 1.36–1.18 (m, 2 H); for *trans* isomer, δ 7.55–7.10 (m, 5 H), 3.80–3.55 (m, CHOAc), 2.2–2.0 (m, CHPh), 2.06 (s, CH₃COO), 1.35–0.85 (m, 2 H).

1-*n*-Butyl-2-phenylcyclopropane. ¹H NMR (CDCl₃): for *cis* isomer, δ 7.20 (m, 5 H), 2.30–1.95 (m, CHPh), 1.4–0.5 with t centered at 0.77 (m, 12 H); for *trans* isomer, δ 7.45–6.95 (m, 5 H), 1.7–0.6 with t centered at 0.89 (m, 13 H).

Cyclopropanation Reactions with (CO)₅WCHC₆H₅. The procedure employed for these reactions was adapted from that previously reported.^{5a} To a stirred degassed solution of Et₄N⁺[(CO)₅WCH(OCH₃)C₆H₅]⁻ (0.210 g, 0.365 mmol)¹⁹ and the reactant olefin (18.2 mmol) dissolved in 10 mL of freshly distilled anhydrous dichloromethane and cooled to -78 °C was added 80 μ L of trifluoroacetic acid (1.03 mmol) in an equal volume of dichloromethane. The initial yellow solution became deep red upon addition of trifluoroacetic acid, and disappearance of this red color served as a monitor of the progress of the reaction. With vinyl ethers the red color faded within minutes, whereas with simple olefins the red color persisted for as long as 2–3 h. Within 1 h after the reaction was complete, 1.0 g of solid sodium carbonate was added to the reaction solution which was then allowed to warm to room temperature. Internal standard, dibenzyl ether or diphenylmethane, was added to the resulting light orange solution, and the solvent and excess olefin were removed under reduced pressure at or below room temperature. Reaction products were extracted with pentane, and their analysis has been previously described. Reactions performed with vinyl ethers gave no evidence for stilbene formation or, generally, for the production of any other identifiable byproduct. Detection of styrene (0.3%) from reactions of (CO)₅WCHC₆H₅ with α -methoxystyrene was conducted by GC and GC/mass spectral analyses.

Competitive Reactions of Phenylcarbene Systems. Reactions were performed as previously described for phenyl diazomethane/Rh₂(OAc)₄ and (CO)₅WCHC₆H₅. With either system the minimum amount of each of the two olefins employed was a 20-fold molar excess relative to reactant carbene source. A minimum of three olefin ratios was employed to determine each relative reactivity value. Correlation coefficients of greater than 0.99 characterized the linear relationships between cyclopropane product ratios and initial olefin concentration ratios. Olefin pairs were chosen to include styrene or *n*-butyl vinyl ether, and relative reactivity values for one olefin vs. styrene and for that same olefin vs. *n*-butyl vinyl ether were observed to provide the same relative reactivity value as obtained directly from the styrene/*n*-butyl vinyl ether combination. Product isomer ratios were identical within experimental error to those determined from reactions with a single olefin (\pm 6% of reported values).

Catalytic Cyclopropanation of Ethyl Vinyl Ether with α -Diazoacetophenone. α -Diazoacetophenone⁴² (1.46 g, 10.0 mmol) in 9.0 mL of anhydrous ethyl ether was added at a controlled rate over a 10-h period to a stirred mixture of ethyl vinyl ether (3.1 g, 50 mmol) and Rh₂(OAc)₄ (0.10 mmol) in 20 mL of ethyl ether at 25 °C. Products were isolated in the manner previously described for reactions with ethyl diazoacetate to give 1.57 g (83% yield) of a liquid composed of *cis*- and *trans*-1-benzoyl-2-ethoxycyclopropane (92%, *t/c* = 2.0) and 2-ethoxy-5-phenyl-2,3-dihydrofuran (8%). In reactions catalyzed by PdCl₂·2PhCN, the relative yield of 2-ethoxy-5-phenyl-2,3-dihydrofuran was 18%.

1-Benzoyl-2-ethoxycyclopropane. ¹H NMR (CDCl₃): for *trans* isomer, δ 8.20–7.85 (m, 2 H), 7.70–7.10 (m, 3 H), 3.75–3.50 (m, CHOEt), 3.58 (q, *J* = 7.1 Hz, CH₂O), 2.83 (d of d of d, *J* = 9.2, 5.9, 1.9 Hz, CHCOPh), 1.61 (d of d of d, *J* = 10.9, 5.9, 5.0 Hz, 1 H), 1.43 (d of d of d, *J* = 9.2, 6.8, 5.0 Hz, 1 H), 1.16 (t, *J* = 7.1 Hz, CH₃CH₂O); for *cis* isomer, δ 8.20–7.85 (m, 2 H), 7.70–7.10 (m, 3 H), 3.85–3.60 (m, CHOEt), 3.32 (q, *J* = 7.0 Hz, CH₂O), 2.80–2.55 (m, CHCOPh), 1.95 (d of d of d, *J* = 6.8, 5.8, 4.8 Hz, 1 H), 1.30–1.05 (m, 1 H), 1.03 (t, *J* = 7.0 Hz, CH₃CH₂O). Treatment of the cyclopropane mixture at room temperature with 95% aqueous acetone containing a catalytic amount of sulfuric acid resulted in the quantitative formation of 3-benzoylpropanal. Thermal rearrangement of 1-benzoyl-2-ethoxycyclopropane occurs at temperature greater than 150 °C to produce 1-benzoyl-3-ethoxy-1-propene.

(40) Adaption of the Shechter method described by X. Creary, private communication: Kaufman, G. M.; Smith, J. A.; Vander Stouw, G. G.; Shechter, H. J. *Am. Chem. Soc.* **1965**, *87*, 935. Overberger, C. G.; Anselme, J. P. *J. Org. Chem.* **1963**, *28*, 592.

(41) Closs, G. L.; Moss, R. A. *J. Am. Chem. Soc.* **1964**, *86*, 4042.

(42) Eistert, B.; Regitz, M.; Heck, G.; Schwall, H. "Methoden der Organischen Chemie" (Houben-Weyl-Müller), 4th ed.; Georg Thieme Verlag: Stuttgart, 1968; Vol. 4, p 714.

2-Ethoxy-5-phenyl-2,3-dihydrofuran. ^1H NMR (CDCl_3): δ 7.5–7.1 (m, 5 H), 5.68 (d of d, $J = 6.7, 2.8$ Hz, CHOEt), 5.36 (d of d, $J = 2.9, 2.6$ Hz, $=\text{CH}$), 3.68 (q, $J = 7.1$ Hz, CH_2O), 2.92 (d of d, $J = 6.7, 2.6$ Hz, 1 H), 2.73 (t, $J = 2.9$ Hz, 1 H), 1.26 (t, $J = 7.1$ Hz, $\text{CH}_3\text{CH}_2\text{O}$).

The ratio of dihydrofuran to cyclopropane was constant, independent of the amount of catalyst employed (0.5–2.0 mol %) and the reaction time (1–10 h). Subsequent treatment of the isolated reaction products with $\text{Rh}_2(\text{OAc})_4$ did not cause conversion of cyclopropanes to the dihydrofuran, even at 50 °C, but did result in the loss of 2-ethoxy-5-phenyl-2,3-dihydrofuran.

Catalytic Cyclopropanation of *n*-Butyl Vinyl Ether with Dimethyl Diazomalonate. Dimethyl diazomalonate⁴³ (0.792 g, 5.05 mmol) in 4.0 mL of anhydrous ethyl ether was added at a controlled rate over a 5-h period to a stirred mixture of *n*-butyl vinyl ether (2.5 g, 25 mmol) and $\text{Rh}_2(\text{OAc})_4$ (0.022 g, 0.05 mmol) in 10 mL of ethyl ether at 35 °C. After addition was complete, the mixture was stirred for an additional hour. Products were isolated in the manner previously described to give 0.88 g (77% yield) of a liquid composed of dimethyl 2-*n*-butoxy-1,1-cyclopropanedicarboxylate (65%) and 2-*n*-butoxy-4-carbomethoxy-5-methoxy-2,3-dihydrofuran (35%).

Dimethyl 2-*n*-Butoxy-1,1-cyclopropanedicarboxylate. ^1H NMR (CDCl_3): δ 4.02 (d of d, $J = 6.2, 2.1$ Hz, CHOBu), 3.76 (s, OCH_3), 3.66 (s, OCH_3), 3.52 (t, $J = 7.2$ Hz, CH_2O), 2.02 (d of d, $J = 6.2, 5.2$ Hz, 1 H), 1.85–1.10 (m, 5 H), 0.92 (t, $J = 5.9$ Hz, CH_3).

2-*n*-Butoxy-4-carbomethoxy-5-methoxy-2,3-dihydrofuran. ^1H NMR (CDCl_3): δ 5.55 (d of d, $J = 7.0, 3.4$ Hz, CHOBu), 3.93 (s, OCH_3), 3.72 (s, COOCH_3), 3.61 (t, $J = 7.0$ Hz, CH_2O), 3.01 (d, $J = 7.0$ Hz, 1 H), 2.84 (d, $J = 3.4$ Hz, 1 H), 1.85–1.10 (m, 4 H), 0.89 (t, $J = 6.7$ Hz, CH_3).

Catalytic Reaction of 2-Methoxypropene with α -Diazoacetophenone. α -Diazoacetophenone (1.46 g, 10.0 mmol) in 8.0 mL of anhydrous ethyl ether was added at a controlled rate over a 6-h period to a stirred mixture of 2-methoxypropene (3.6 g, 50 mmol) and $\text{Rh}_2(\text{OAc})_4$ (0.044 g, 0.10 mmol) in 20 mL of ethyl ether at 25 °C. Products were isolated in the manner previously described to give 1.54 g (81% yield) of a complex mixture containing (40%) of 2-methoxy-2-methyl-5-phenyl-2,3-dihydrofuran. ^1H NMR (CDCl_3): δ 7.7–7.3 (m, 5 H), 5.30 (d of d, $J = 2.9, 2.8$ Hz, $=\text{CH}$), 3.31 (s, OCH_3), 2.92 (d, $J = 2.9$ Hz, 1 H), 2.80 (d, $J = 2.8$ Hz, 1 H), 1.63 (s, CH_3). Thermal elimination of methanol from the dihydrofuran produced 2-methyl-5-phenylfuran. A second major product (35%) was identified as 4-benzoyl-2-methoxy-1-butene. ^1H NMR (CDCl_3): δ 8.20–7.90 (m, 2 H), 7.70–7.10 (m, 3 H), 3.36 (s, $=\text{CH}_2$), 2.82–2.77 (m, CH_2CH_2). Acid-catalyzed hydrolysis of this vinyl ether in 98% aqueous acetone produced 4-benzoyl-2-butanone in quantitative yield. 4-Benzoyl-2-methoxy-2-butene was present in less than 8% relative yield. Similar results were observed in reactions with the *p*-methyl derivative of α -diazoacetophenone.

Catalytic Reaction of α -Methoxystyrene with α -Diazoacetophenone. α -Diazoacetophenone (2.92 g, 20.0 mmol) in 15 mL of anhydrous ethyl ether was added at a controlled rate over a 2-h period to a stirred mixture of α -methoxystyrene (2.68 g, 20.0 mmol) and $\text{Rh}_2(\text{OAc})_4$ (0.088 g, 0.2 mmol) in 10 mL of ethyl ether at 25 °C. Products were isolated in the manner previously described to give 4.80 g (95% yield) of a liquid composed of (*E*)- and (*Z*)-1-benzoyl-2-methoxy-2-phenylcyclopropane (70%, $Z/E = 2.1$), and 2-methoxy-2,5-diphenyl-2,3-dihydrofuran (30%).

1-Benzoyl-2-methoxy-2-phenylcyclopropane. ^1H NMR (CDCl_3): for *Z* isomer, δ 8.10–7.80 (m, 2 H), 7.80–7.10 (m, 8 H), 3.32 (d of d, $J = 9.0, 7.0$ Hz, CHCOPh), 3.16 (s, OCH_3), 2.23 (d

of d, $J = 7.0, 5.4$ Hz, 1 H), 1.56 (d of d, $J = 9.0, 5.4$ Hz, 1 H); for *E* isomer, δ 8.10–7.80 (m, 2 H), 7.80–7.10 (m, 8 H), 3.49 (d of d, $J = 8.4, 7.1$ Hz, CHCOPh), 3.13 (s, OCH_3), 2.34 (d of d, $J = 7.1, 5.8$ Hz, 1 H), 1.58 (d of d, $J = 8.4, 5.8$ Hz, 1 H). Acid-catalyzed hydrolysis of the cyclopropane products in 98% aqueous acetone produced 1,2-dibenzoyl ethane.

2-Methoxy-2,5-diphenyl-2,3-dihydrofuran. ^1H NMR (CDCl_3): δ 7.7–7.1 (m, 10 H), 5.39 (d of d, $J = 2.8, 2.6$ Hz, $=\text{CH}$), 3.25 (s, OCH_3), 3.08 (d, $J = 2.8$ Hz, 1 H), 3.00 (d, $J = 2.6$ Hz, 1 H). Mass spectrum, m/e (relative abundance): 254 (1.8, $M + 2$), 253 (15.6, $M + 1$), 252 (80, M), 237 (16), 221 (40), 220 (100), 219 (15), 191 (34), 147 (23), 131 (12), 116 (16), 115 (68), 110 (10), 105 (78), 89 (12), 78 (10), 77 (92), 63 (11), 51 (30). Thermal elimination of methanol from the dihydrofuran produced 2,5-diphenylfuran.

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Registry No. Rhodium(II) acetate, 15956-28-2; copper(II) trifluoromethanesulfonate, 34946-82-2; ethyl diazoacetate, 623-73-4; phenyldiazomethane, 766-91-6; 2-methoxypropene, 116-11-0; *n*-butyl vinyl ether, 111-34-2; ethyl vinyl ether, 109-92-2; dihydropyran, 25512-65-6; phenyl vinyl ether, 766-94-9; styrene, 100-42-5; cyclopentene, 142-29-0; 2-methoxystyrene, 4747-13-1; 3,3-dimethyl-2-methoxy-1-butene, 60693-17-6; 2-methyl-2-butene, 513-35-9; vinyl acetate, 108-05-4; 1-hexene, 592-41-6; 3-methyl-1-butene, 563-45-1; 3,3-dimethyl-1-butene, 558-37-2; 2,5-dimethyl-2,4-hexadiene, 764-13-6; cyclohexene, 110-83-8; (*Z*)-1,2-diphenyl-1-methoxycyclopropane, 87841-99-4; (*E*)-1,2-diphenyl-1-methoxycyclopropane, 87842-00-0; (*Z*)-1-methoxy-1-methyl-2-phenylcyclopropane, 52306-24-8; (*E*)-1-methoxy-1-methyl-2-phenylcyclopropane, 52306-25-9; (*Z*)-1-*tert*-butyl-1-methoxy-2-phenylcyclopropane, 87842-01-1; (*E*)-1-*tert*-butyl-1-methoxy-2-phenylcyclopropane, 87842-02-2; *cis*-1-*n*-butoxy-2-phenylcyclopropane, 87842-03-3; *trans*-1-*n*-butoxy-2-phenylcyclopropane, 87842-04-4; *cis*-1-ethoxy-2-phenylcyclopropane, 80287-85-0; *trans*-1-ethoxy-2-phenylcyclopropane, 80287-86-1; *cis*-1-acetoxy-2-phenylcyclopropane, 16526-25-3; *trans*-1-acetoxy-2-phenylcyclopropane, 16526-26-4; *cis*-1-*n*-butyl-2-phenylcyclopropane, 64286-53-9; *trans*-1-*n*-butyl-2-phenylcyclopropane, 33450-83-8; $[\text{Et}_4\text{N}^+][(\text{CO})_5\text{WCH}(\text{OCH}_3)\text{C}_6\text{H}_5]^-$, 64494-49-1; α -diazoacetophenone, 3282-32-4; *trans*-1-benzoyl-2-ethoxycyclopropane, 87842-05-5; *cis*-1-benzoyl-2-ethoxycyclopropane, 87842-06-6; 2-ethoxy-5-phenyl-2,3-dihydrofuran, 87842-07-7; dimethyl diazomalonate, 6773-29-1; dimethyl 2-*n*-butoxy-1,1-cyclopropanedicarboxylate, 87842-08-8; 2-*n*-butoxy-4-carbomethoxy-5-methoxy-2,3-dihydrofuran, 87861-44-7; 2-methoxy-2-methyl-5-phenyl-2,3-dihydrofuran, 87842-09-9; 4-benzoyl-2-methoxy-1-butene, 87842-10-2; (*Z*)-1-benzoyl-2-methoxy-2-phenylcyclopropane, 87842-11-3; (*E*)-1-benzoyl-2-methoxy-2-phenylcyclopropane, 87842-12-4; 2-methoxy-2,5-diphenyl-2,3-dihydrofuran, 87842-13-5.

Supplementary Material Available: Gas chromatographic and mass spectral data for phenylcyclopropanes (3 pages). Ordering information is given on any current masthead page.

(43) Regitz, M. *Synthesis* 1972, 351.