Stereoselectivity of Catalytic Cyclopropanation Reactions. Catalyst Dependence in Reactions of Ethyl Diazoacetate with Alkenes

Michael P. Doyle,* Roberta L. Dorow, William E. Buhro, John H. Griffin, William H. Tamblyn, and Mark L. Trudell

Department of Chemistry, Hope College, Holland, Michigan 49423

Received July 26, 1983

Product yields and stereoselectivities for $Rh_2(OAc)_4$ catalyzed cyclopropanation reactions of ethyl diazoacetate with vinyl ethers, dienes, and simple alkenes are reported and compared with stereoselectivities for cyclopropane formation in reactions that employ $CuCl{\cdot}P(O\text{-}i\text{-}Pr)_3$, $Rh_6(CO)_{16}$, and $PdCl_2{\cdot}2PhCN$ as catalysts. Linear correlations are observed when product stereoisomer ratios from reactions with 22 alkenes, which range from 0.6 to 6.8, are plotted against those from $Rh_2(OAc)_4$ catalyzed reactions. Values for the slopes of these lines, which define relative catalyst-dependent stereoselectivities, are 1.74 for $CuCl{\cdot}P(O\text{-}i\text{-}Pr)_3$, 1.04 for $Rh_6(CO)_{16}$, and 0.59 for $PdCl_2{\cdot}2PhCN$. However, investigations of these reactions with five copper catalysts show substantial uniformity in selectivity despite significant differences in the initial oxidation state and associated ligands of the catalyst employed, and similar uniformity is observed among rhodium and among palladium catalysts. These results specify that electronic influences derived from the transition metal provide major stereochemical and regiochemical control in catalytic cyclopropanation reactions.

Considerable attention has been directed toward recent developments in catalytic cyclopropanation reactions as a result of their extensive utilization in organic syntheses[1-9] and disclosures of new, highly effective catalysts and catalytic methods for these transformations.[10-12] Surprisingly little attention has been devoted to selectivity in catalytic transformations. With the exception of specific studies with alkenes such as cyclohexene and styrene, stereoselectivities in catalytic cyclopropanation reactions are generally unknown.[13-17] Since Moser's report that alteration of the steric and electronic identity of phosphite ligands for soluble copper(I) catalysts causes a decrease in the exo/endo ratio for cyclopropane products formed from cyclohexene and ethyl diazoacetate,[18] the limited efforts to modify cyclopropane stereoselectivity have utilized this approach and moderate successes have been achieved.[19-22] However, few reports have detailed the effect of variation in the diazo compound on product selectivity,[21,23] and none have taken a systematic approach to the effect of olefin structure on stereoselectivity.

Data that are currently available indicate that catalytic cyclopropanation reactions are relatively unselective in their production of geometrical isomers. With diazoacetates only minor changes in stereoselectivity are observed with substantial increases in the steric bulk of the ester alcohol.[13,21] Alterations in the electronic and steric influences of ligand associated with the metal species employed for these catalytic reactions do not appear to dramatically influence cyclopropanation stereoselectivity.[18,21,22] The nature of the central metal of the catalyst has been described as significant for the production of cyclopropane compounds,[20,24] but its influence on product stereochemistry has not been reported.

We have recently discovered that the metal complexes employed for catalytic cyclopropanation reactions with ethyl diazoacetate influence regioselectivities in reactions with conjugated dienes.[25] Regioselectivities from $CuCl{\cdot}P(O\text{-}i\text{-}Pr)_3$, $Rh_6(CO)_{16}$, and $PdCl_2{\cdot}2PhCN$ catalyzed reactions were observed to vary by a factor of 3 with individual dienes and to correlate linearly with regioselectivities from $Rh_2(OAc)_4$ catalyzed reactions. These results, with catalysts commonly used in cyclopropanation reactions, confirm implications drawn from investigations of asymmetric induction with chiral catalysts[23,26] that the transition metal is directly involved in the product-forming step. We now report a parallel systematic investigation of stereoselectivity in catalytic cyclopropanation reactions that affords a similar index for evaluation of the effect of the reaction catalyst and provides detailed information concerning the relative influence of the transition metal,

(1) Wenkert, E. *Acc. Chem. Res.* **1980**, *13*, 27.
(2) Danishefsky, S. *Acc. Chem. Res.* **1979**, *12*, 66.
(3) Burke, S. D.; Grieco, P. A. *Org. React. (N.Y.)* **1979**, *26*, 361.
(4) Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 239.
(5) Stevens, R. V. *Acc. Chem. Res.* **1977**, *10*, 193.
(6) Conia, J. M. *Pure Appl. Chem.* **1975**, *43*, 317.
(7) Reissig, H.-U. *Tetrahedron Lett.* **1981**, *22*, 2981.
(8) Wenkert, E. *Heterocycles* **1980**, *14*, 1703.
(9) Hudlicky, T.; Koszyk, F. F.; Kutchan, T. M.; Sheth, J. P. *J. Org. Chem.* **1980**, *45*, 5020.
(10) Doyle, M. P.; Tamblyn, W. H.; Buhro, W. E.; Dorow, R. L. *Tetrahedron Lett.* **1981**, *22*, 1783.
(11) Doyle, M. P.; van Leusen, D.; Tamblyn, W. H. *Synthesis* **1981**, 787.
(12) Hubert, A. J.; Noels, A. F.; Anciaux, A. J.; Teyssié, Ph. *Synthesis* **1976**, 600.
(13) Dave, V.; Warnhoff, E. W. *Org. React. (N.Y.)* **1970**, *18*, 217.
(14) Marchand, A. P.; MacBrockway, N. *Chem. Rev.* **1974**, *74*, 431.
(15) Kirmse, W. "Carbene Chemistry", 2nd ed.; Academic Press: New York, 1971.
(16) Baron, W. J.; Hedrick, M. E.; Jones, M., Jr.; Levin, R. H.; Sohn, M. E. In "Carbenes"; Jones, M., Jr.; Moss, R. A., Eds.; Wiley-Interscience: New York, 1972; Vol. 1.
(17) Wulfman, D. S.; Linstrumelle, G.; Cooper, C. F. In "The Chemistry of Diazonium and Diazo Groups"; Patai, S., Ed.; Wiley: New York, 1978; Part 2, Chapter 18.
(18) Moser, W. R. *J. Am. Chem. Soc.* **1969**, *91*, 1135, 1141.
(19) Callot, H. J.; Piechocki, C. *Tetrahedron Lett.* **1980**, *21*, 3489.
(20) Anciaux, A. J.; Hubert, A. J.; Noels, A. F.; Petiniot, N.; Teyssié, Ph. *J. Org. Chem.* **1980**, *45*, 695.
(21) Holland, D.; Milner, D. J. *J. Chem. Res., Synop.* **1979**, 317; *J. Chem. Res., Miniprint* **1979**, 3734.
(22) Aratani, T.; Yoneyoshi, Y.; Nagase, T. *Tetrahedron Lett.* **1975**, 1707.
(23) Aratani, T.; Yoneyoshi, Y.; Nagase, T. *Tetrahedron Lett.* **1977**, 2599.
(24) Salomon, R. G.; Kochi, J. K. *J. Am. Chem. Soc.* **1973**, *95*, 3300.
(25) Doyle, M. P.; Dorow, R. L.; Tamblyn, W. H.; Buhro, W. E. *Tetrahedron Lett.* **1982**, *23*, 2261.
(26) Nakamura, A.; Konishi, A.; Tsujitani, R.; Kudo, M.; Otsuka, S. *J. Am. Chem. Soc.* **1978**, *100*, 3449. Nakamura, A.; Konishi, A.; Tatsuno, Y.; Otsuka, S. *Ibid.* **1978**, *100*, 3443, 6544.

0276-7333/84/2303-0044$01.50/0

Table I. Stereoselectivities for Cyclopropane Formation from Olefins and Ethyl Diazoacetate Catalyzed by Rhodium(II) Acetate[a]

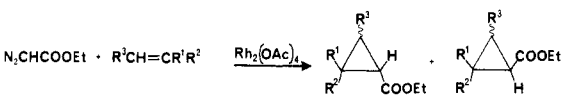
R^1	yield,[b] %	trans[c]/cis	R^1	R^2 (R^3)	yield,[b] %	trans (E)[c]/cis (Z)
Monosubstituted Olefins $H_2C=CHR^1$			Disubstituted Olefins $H_2C=CR^1R^2$			
CH_2Br	55/76[d]	1.1	Me	OMe	78	1.0
CH_2Cl	90/95[d]	1.2	Ph	OMe	88	0.96
OPh	92	1.4	*t*-Bu	OMe	70	0.71
n-Bu	95	1.5	Me	$CH=CH_2$	57/93	1.1
Ph	93	1.6	Ph	$CH=CH_2$	56/81	1.0
OAc	59	1.6	*t*-Bu	$CH=CH_2$	25/70	1.3
OEt	88	1.7	Cl	$CH=CH_2$	60/76	1.1
O-*n*-Bu	84	1.7	OMe	$CH=CH_2$	88/88	0.80
i-Pr	58	2.0	OMe	$C(OMe)=CH_2$	76/76	0.85
t-Bu	87	4.2	Disubstituted Olefins *trans*-$R^1CH=CHR^3$			
$C(Cl)=CH_2$	16/76	1.4				
$C(Ph)=CH_2$	25/81	1.5	Me	CH_2Br	25/77[d]	2.2
$C(Me)=CH_2$	36/93	1.7	Me	$CH=CH_2$	7/61	1.7
$C(t\text{-Bu})=CH_2$	45/70	2.8	Ph	$CH=CH_2$	2/90	1.7
CH=CHOMe (trans)	80/90	1.4	OMe	$CH=CH_2$	10/90	0.73
CH=CHCl (trans)	73/73	1.6	Disubstituted Olefins *cis*-$R^1CH=CHR^3$			
CH=CHCl (cis)	49/49	1.6				
CH=CHPh (trans)	88/90	1.6		$-(CH_2)_3-$	96	2.1
CH=CHPh (cis)	55/56	1.6		$-(CH_2)_4-$	90	3.8
CH=CHMe (trans)	54/61	1.6		$-(CH_2)_3O-$	91	6.5
CH=CH(*t*-Bu) (trans)	54/54	1.4	Ph	OMe	60	2.0
Trisubstituted Olefins						
2-methyl-2-butene	97	1.5	1-methylcyclohexene		80	2.7
2,5-dimethyl-2,4-hexadiene	81	1.8	1-methoxycyclohexene		78	2.5

[a] Reactions performed at 25 °C, 0.5 mol % $Rh_2(OAc)_4$. [b] Yields are presented as (% yield cyclopropane isomers)/total % yield cyclopropane products) for reactions with dienes. [c] Precision ±5% of reported value. [d] % Cyclopropane products/% cyclopropane + % ylide derived product.[31]

its associated ligands, and olefin structure on stereoselectivity. These influences distinguish the product-forming step in catalytic cyclopropanation reactions from that which governs relative reactivities for cyclopropanation at more than one olefinic center.

Results

Olefin-Dependent Stereoselectivities. Product yields and stereoisomer ratios for $Rh_2(OAc)_4$ catalyzed cyclopropanation reactions between ethyl diazoacetate and representative alkenes (eq 1) are presented in Table I.

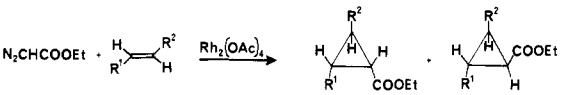


(1)

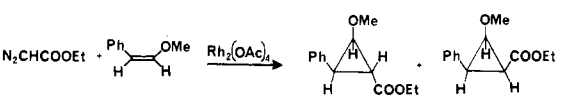
These reactions were performed at 25 °C by using a 10-fold molar excess of the reactant alkene to minimize potential secondary reactions,[27,28] with uniform addition of ethyl diazoacetate over 4–8 h to the solution containing $Rh_2(OAc)_4$ and the olefin. In all cases, $Rh_2(OAc)_4$ was employed in 0.5 mol % based on ethyl diazoacetate. For most entries in Table I, substantial uniformity in cyclopropane yields from multiple runs with the same olefin was observed. However, the presence of certain minor impurities in the olefin, particularly in reactions with dienes, did cause significant variations in product yields between runs. Thus tabulated results emphasize those reactions from multiple runs with the same olefin that resulted in the higher product yields. Stereoselectivities reported in Table I, which for individual alkenes were not observably dependent on product yields or on the amount of catalyst employed, are composite averages of at least two separate reactions.

Rhodium(II) acetate is uniformly effective for cyclopropane production with a broad range of "nucleophilic" olefins that include vinyl ethers, simple alkenes, and dienes. Cyclopropanation of "electrophilic" olefins, specifically methyl methacrylate, methyl vinyl ketone, methacrylonitrile, and acrylonitrile, does not occur under these reaction conditions and, as we have recently reported,[29] pyrazoline production by unassisted dipolar addition of ethyl diazoacetate to these α,β-unsaturated nitriles and carbonyl compounds is the dominant reaction pathway available in these cases. The presence of chloride, ether, or acetate functionalities in the reactant olefin does not measurably affect cyclopropane yields, but bromide, sulfide, and amine functional groups support ylide-derived pathways in reactions with ethyl diazoacetate.[30,31]

The stereospecificity of cyclopropane production, which has been demonstrated in copper[24] and palladium[32] catalyzed reactions, was also evident for $Rh_2(OAc)_4$ with olefins listed in Table I. Trans-disubstituted olefins yielded cyclopropanes (eq 2) with the same trans geometry of the



(2)



(3)

(27) Doyle, M. P.; van Leusen, D. *J. Org. Chem.* **1982**, *47*, 5326.
(28) Shankar, B. K. R.; Shechter, H. *Tetrahedron Lett.* **1982**, *23*, 2277.
(29) Doyle, M. P.; Dorow, R. L.; Tamblyn, W. H. *J. Org. Chem.* **1982**, *47*, 4059.
(30) Tamblyn, W. H.; Hoffmann, S. R.; Doyle, M. P. *J. Organomet. Chem.* **1981**, *216*, C64.
(31) Doyle, M. P.; Tamblyn, W. H.; Bagheri, V. *J. Org. Chem.* **1981**, *46*, 5094.
(32) Nakamura, A.; Koyama, T.; Otsuka, S. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 593.

Table II. Stereoselectivities for Cyclopropane Formation from Olefins and Ethyl Diazoacetate with Representative Catalysts[a]

		$Rh_2(OAc)_4$		$Rh_6(CO)_{16}$		$CuCl{\cdot}P(O\text{-}i\text{-}Pr)_3$		$PdCl_2{\cdot}2PhCN$	
R^1	R^2	yield,[b] %	t/c[c]	yield,[b] %	t/c[c]	yield,[b] %	t/c[c]	yield,[b] %	t/c[c]
				Monosubstituted Olefins $H_2C{=}CHR^1$					
CH_2Br		55/76[d]	1.1	30/41[d]	1.1	7/49[d]	1.8		
CH_2Cl		90/95[d]	1.2	24/26[d]	1.2	50/86[d]	1.8		
Ph		93	1.6	86	1.7	88	2.8	52	1.6
OEt		88	1.7	62	1.7	61	1.9	43	1.5
O-*n*-Bu		84	1.7	69	1.8	51	2.0	34	1.6
t-Bu		87	4.2	42	4.5	23	7.3	34	2.5
$C(Cl){=}CH_2$		22/76	1.4	24/80	1.7	5/33	2.1	*e*	
$C(Ph){=}CH_2$		25/81	1.5	20/71	1.7	7/28	2.5	5/10	1.4
$C(Me){=}CH_2$		36/93	1.8	27/70	1.7	28/81	3.4	16/24	1.0
$C(t\text{-}Bu){=}CH_2$		45/70	3.7	5/9	3.8	8/20	6.4	4/6	2.2
CH=CHOMe (trans)		80/90	1.4	58/63	1.3	48/57	1.5	16/22	1.2
CH=CHCl (trans)		73/73	1.6	21/21	2.0	17/17	2.6	*e*	
				Disubstituted Olefins $H_2C{=}CR^1R^2$					
Me	OMe	78	1.0	72	1.0	67	1.1	66	0.93
t-Bu	OMe	70	0.71	83	0.72	7	1.2	28	0.61
Me	$CH{=}CH_2$	57/93	1.1	43/70	1.1	53/81	1.3	8/24	0.90
Cl	$CH{=}CH_2$	54/76	1.1	56/80	1.1	28/33	1.3	2/4	0.93
OMe	$CH{=}CH_2$	88/88	0.80	63/63	0.82	38/38	1.0	12/12	0.71
t-Bu	$CH{=}CH_2$	25/70	1.3	4/9	1.4	12/20	1.5	2/6	0.70
				Disubstituted Olefins *cis*-$R^1CH{=}CHR^2$					
$-(CH_2)_4-$		90	3.8	88	3.9	28	6.8	31	2.2
$-(CH_2)_3O-$		91	6.5	82	6.8	18	6.3	41	3.8
				Trisubstituted Olefins					
2,5-dimethyl-2,4-hexadiene		81	1.8	87	1.9	55	2.7	20	2.3
1-methoxycyclohexene		78	2.5	59	2.6	54	4.2	39	1.5

[a] Reactions performed at 25 °C. [b] For reactions with dienes, yields are presented as (% yield of cyclopropane isomers)/(total % yield of cyclopropane products). [c] Precision ±5% of reported value. [d] % Cyclopropane products/% cyclopropane + % ylide derived products.[31] [e] Less than 8% yield of cyclopropane products.

reactant alkenes, and the cis-disubstituted olefin, β-methoxystyrene, afforded only two isomeric cyclopropane compounds, each with *cis*-Ph/OMe geometries (eq 3). However, stereoselectivities for cyclopropanation reactions of ethyl diazoacetate were low, ranging in the limit up to only 6.5 (Table I). Among monosubstituted olefins, selectivity for the more stable trans isomer was enhanced with increased steric bulk of the substituent, but a substantial change was evident only with a substituent as large as *tert*-butyl.[33] In contrast to comparable monosubstituted olefins, cyclopropanation of cis- and trans-disubstituted olefins exhibited enhanced selectivity for formation of the thermodynamically more stable isomer. Trisubstituted olefins provided surprisingly small changes in cyclopropanation stereoselectivity relative to comparable mono- and disubstituted olefins.

Catalyst-Dependent Stereoselectivities. A growing number of transition-metal compounds are reported to be effective cyclopropanation catalysts. However, virtually all of these compounds utilize copper,[18,23,24] palladium,[32,34,35] or rhodium[10,12,19] as the active metal. To compare representative catalysts from each group, we restricted detailed investigations to those compounds whose catalytic activities were evident at 25 °C and whose ligand composition could not be inferred to markedly affect cyclopropanation stereoselectivity. Three catalysts, $Rh_6(CO)_{16}$, $CuCl{\cdot}P(O\text{-}i\text{-}Pr)_3$, and $PdCl_2{\cdot}2PhCN$, were chosen for yield and selectivity comparisons with $Rh_2(OAc)_4$, and the results of this investigation are reported in Table II. Reactions were performed under conditions identical with those employed for $Rh_2(OAc)_4$ catalyzed reactions. Results are presented for cyclopropanation of alkenes where reproducible information from at least three of the catalysts could be compared.

Rhodium(II) acetate is the obvious choice among these catalysts for the production of cyclopropane compounds. Product yields from the use of $Rh_6(CO)_{16}$ are sensitive to the olefinic system being employed, presumably as a result of the extent to which this basically insoluble carbonyl cluster forms the homogeneous active catalyst.[10,36] Neither $CuCl{\cdot}P(O\text{-}i\text{-}Pr)_3$ nor $PdCl_2{\cdot}2PhCN$, both homogeneous catalysts, offer any observable advantage to rhodium catalysts for cyclopropane production and, of these four catalysts, $PdCl_2{\cdot}2PhCN$ is the least effective. With copper catalysts, the presence of chloride and ether functional groups affect cyclopropane yields as a result of ylide-derived transformations.[31,37] The palladium catalyst produces a polymeric substance derived from ethyl diazoacetate through loss of dinitrogen in the major competing pathway to cyclopropane production.

Stereoselectivities for cyclopropane production are sensitive to the catalyst employed. In general, a higher selectivity for the formation of the more stable geometrical isomer is observed with the use of $CuCl{\cdot}P(O\text{-}i\text{-}Pr)_3$ than with $Rh_2(OAc)_4$, and a lower selectivity is characteristic of $PdCl_2{\cdot}2PhCN$ catalyzed reactions. The hexarhodium carbonyl cluster and $Rh_2(OAc)_4$ are nearly identical in their

(33) Cyclopropane compounds formed from 1-substituted 1,3-butadienes by carbenoid insertion at the 3,4 double bond did not cause isomerization at the 1,2 double bond.
(34) Armstrong, R. K. *J. Org. Chem.* **1966**, *31*, 618.
(35) Paulissen, R.; Hubert, A. J.; Teyssié, Ph. *Tetrahedron Lett.* **1972**, 1465.
(36) Kitamura, T.; Joh, T. *J. Organomet. Chem.* **1974**, *65*, 235.
(37) Ando, W.; Kondo, S.; Nakayama, K.; Ichibori, K.; Kohoda, H.; Yamato, H.; Imai, I.; Nakaido, S.; Migita, T. *J. Am. Chem. Soc.* **1972**, *94*, 3870.

Table III. Stereoselectivities for Cyclopropane Formation from Olefins and Ethyl Diazoacetate with Representative Copper Catalysts[a]

R	$CuCl\cdot P(O\text{-}i\text{-}Pr)_3$ yield,[b] %	t/c[c]	$CuCl\cdot P(OPh)_3$ yield,[b] %	t/c[c]	$Cu(OTf)_2$ yield,[b] %	t/c[c]	copper bronze yield,[b] %	t/c[c]	$Cu(acac)_2$ yield,[b] %	t/c[c]
Monosubstituted Olefins $H_2C{=}CHR$										
Ph	88	2.8	84	2.5	97	(1.9)[e]	53	(1.9)[e]	71	(2.6)[e]
OEt	61	1.9	64	2.2	55	(2.4)[d]			15	1.6
t-Bu	23	7.3			54	5.5	5	8.1	20	(10.4)[e]
$C(Ph){=}CH_2$	7/28	3.5			14/48	1.8	8/30	3.2	11/42	3.1
$C(Me){=}CH_2$	28/81	3.4	25/73	3.6	19/57	1.8	7/20	4.0	18/55	3.3
Di- and Trisubstituted Olefins										
2-phenyl-1,3-butadiene (1,2-position)	21/28	1.1			34/48	1.0	22/30	1.2	31/42	1.0
isoprene (1,2-position)	53/81	1.3	48/73	1.2	38/57	1.0	13/20	1.2	37/55	1.3
cyclohexene	28	6.8	25	7.0	80	6.8	23	7.5	18	(6.5)[e]
2,5-dimethyl-2,4-hexadiene	55	2.7	66	2.7	93	2.3	34	2.7	76	(1.8)[e]
1-methoxycyclohexene	54	4.2	35	4.5					44	4.8

[a] Unless indicated otherwise, reactions were performed at 25 °C. [b] For reactions with dienes, yields are presented as (% yield of cyclopropane isomers/(total % yield of cyclopropane products). [c] Precision ±5% of reported value. [d] Reaction performed at 0 °C. [e] Reactions performed at 60 °C.

selectivity for cyclopropane production. Significant exceptions are evident only with 3,4-dihydropyran in reactions catalyzed by $CuCl\cdot P(O\text{-}i\text{-}Pr)_3$ and with 2,5-dimethyl-2,4-hexadiene in reactions catalyzed by $PdCl_2\cdot 2PhCN$ and, in these two cases, ylide-derived competing processes[38] or vinylcyclopropane isomerization[39,40] adequately accounts for the observed results.

Palladium(II) acetate, which was employed for stereoselectivity comparison with $PdCl_2\cdot 2PhCN$, generally produced cyclopropanes in yields that were comparable to those observed with the use of $PdCl_2\cdot 2PhCN$. Styrene was the exception, in which case ethyl 2-phenylcyclopropanecarboxylate was formed in 80% yield. Stereoselectivities for cyclopropanation catalyzed by these two palladium compounds were identical within experimental error. In contrast, $[Rh(CO)_2Cl]_2$ catalysis resulted in selectivities that were even less than those observed with $PdCl_2\cdot 2PhCN$, but product yields were low, ranging from 36% with styrene to 8% with cyclohexene.

Two olefins, cyclohexene and 3,4-dihydropyran, produced results that exhibited exceptional sensitivity of product yields and stereoselectivities to reaction conditions. In the presence of air, reactions of cyclohexene with ethyl diazoacetate that were performed with any of the transition-metal compounds employed in this study as catalysts, but especially with $CuCl\cdot P(O\text{-}i\text{-}Pr)_3$, resulted in the production of 2-cyclohexen-1-one in addition to ethyl 7-bicyclo[4.1.0]heptanecarboxylate and diethyl maleate and fumarate. When these reactions were performed in air at 25 °C, the yield of cyclopropane products was variable, but always lower than when these same reactions were performed under nitrogen or argon. Results from copper-catalyzed reactions were most affected by the presence of air, and cyclopropane product yields were reduced by as much as 50% from those obtained in the absence of air. Yields from $Rh_2(OAc)_4$ catalyzed reactions were least affected.[41] Stereoselectivities for cyclopropanation of cyclohexene were also highly variable in copper-catalyzed reactions, ranging from the reported value (Table II) up to 14. With 3,4-dihydropyran, similar sensitivity of product yield and selectivity to the atmosphere employed was observed, and both 5,6-dihydro-4-pyrone and 5,6-dihydro-2-pyrone were obtained. These oxidation byproducts, and 2-cyclohexen-1-one from cyclohexene, were produced in less than 8% yield, relative to ethyl diazoacetate, but not in the absence of air or of ethyl diazoacetate.

Stereoselectivities of Copper-Catalyzed Reactions. Results obtained with $Rh_2(OAc)_4$ and $Rh_6(CO)_{16}$ suggested that the metal itself and not its attendant ligands or initial oxidation state is the principal influence on selectivity for cyclopropane isomer production. Further evaluation of this phenomenon was obtained from reactions of ethyl diazoacetate with selected olefins in the presence of five copper compounds that have been commonly employed as cyclopropanation catalysts (Table III). Surprising uniformity in selectivities were observed despite substantial differences among the copper compounds employed. In this series, copper(II) triflate (Tf = CF_3SO_2) exhibited the highest reactivity toward ethyl diazoacetate but was limited in its applicability for reactions with vinyl ethers[42] because of extensive polymer formation and acid-promoted ring opening of the oxocyclopropanecarboxylate products.[27] Copper(II) acetylacetonate and copper bronze were the least reactive of these copper catalysts; reactions that employed these catalysts often had to be performed at 60 °C to obtain product yields adequate for analysis.

Stereoselectivity values for $Cu(OTf)_2$ catalyzed reactions with styrene and conjugated dienes were closer to those obtained with $Rh_2(OAc)_4$ than with $CuCl\cdot P(O\text{-}i\text{-}Pr)_3$, and the regioselectivity value of $Cu(OTf)_2$ in catalytic cyclopropanation of 2-phenyl-1,3-butadiene (2.5) falls between those obtained with $Rh_2(OAc)_4$ (2.3) and $CuCl\cdot P(O\text{-}i\text{-}Pr)_3$ (3.2).[43] However, with simple olefins stereoselectivities

(38) Ring opening of the less stable syn isomer of cyclopropanes formed from ethyl diazoacetate and dihydropyran occurs at the faster rate.[27]

(39) Williams, J. L.; Rettig, M. F. *Tetrahedron Lett.* **1981**, *22*, 385.

(40) Ahmad, M. U.; Backvall, J.-E.; Nordberg, R. E.; Norin, T.; Stromberg, S. *J. Chem. Soc., Chem. Commun.* **1982**, 321.

(41) Allylic oxidation of olefins catalyzed by $Rh_2(OAc)_4$ has recently been reported: Uemura, S.; Patil, S. R. *Chem. Lett.* **1982**, 1743.

(42) Cyclopropanation of several vinyl ethers could be performed at 0 °C without extensive polymerization: *n*-butyl vinyl ether (47% yield, trans/cis = 2.0), 2-methoxy-3,3-dimethyl-1-butene (48% yield, E/Z = 0.77), 3,4-dihydropyran (58% yield, anti/syn = 6.3). However, even at this lower temperature 1-methoxycyclohexene underwent extensive polymerization, and substantial amounts of apparent allylic C–H insertion products were observed.

(43) One explanation of this behavior is that dienes are coordinated with the active metal so that orientation of the reacting carbon–carbon double bond is altered with respect to the carbenic center during cyclopropane formation.

from $Cu(OTf)_2$ catalyzed reactions were nearly identical with those obtained with other copper catalysts. Thus copper triflate remains an anomaly among copper catalysts, but its influence on stereoselectivity in cyclopropanation of simple olefins suggests a behavior similar to that of other copper catalysts.

Discussion

The effect of catalyst on the outcome of cyclopropanation reactions that occur with diazocarbonyl compounds has been extensively discussed.[13-17] Product yields are reported to be markedly dependent on the catalyst employed[11,17,20] and, at least with $CuCl{\cdot}P(O\text{-}i\text{-}Pr)_3$, to be dependent on the molar ratio of diazo compound to catalyst.[44,45] However, inferences regarding the characteristics of metal catalysis in cyclopropanation reactions have been drawn from limited investigations, often with just one olefin.[17] Recent investigations[11,20,30,31] and new catalytic systems[10,12,19] have removed many of the restrictions that were previously placed on catalyst utilization.

The effectiveness of a particular catalyst for the production of a desired product is dependent on the relative rates for competing reactions as well as on the existence and nature of catalyst inhibition. For example, in catalytic cyclopropanation reactions with diazo compounds the formation of carbene dimers, such as diethyl fumarate and maleate from ethyl diazoacetate, competes effectively with cyclopropanation. By reducing the rate for addition of the diazo compound to the olefin so that the concentration of "free" diazo compound in the reaction medium is negligible,[10,11] competition with carbene dimer formation can generally be minimized. Previous reports of yield dependence on catalyst concentration may be associated with this phenomenon since we generally observe that significant increases in the yields of cyclopropane products are obtained by decreasing the rate for addition of the diazo compound to the olefin, even with the Moser catalysts.[46] However, if competition with cyclopropanation is caused by alternate processes that involve catalyst inhibition, as appears to be the case with $PdCl_2{\cdot}2PhCN$,[47] this same methodology is ineffective.

Stereoselectivities have been reported to be dependent on the concentration and steric requirements of the reaction catalyst.[48] However, only results from reactions of ethyl diazoacetate with cyclohexene, which we find to undergo an unusual allylic oxidation, were reported, and product accountability with the single choice of reaction catalyst, $CuI{\cdot}[P(OMe)_3]_n$ (n = 1–3), was low when 25 mol % of this catalytic system was employed. Our results confirm that the anti/syn ratios for cyclopropane products derived from cyclohexene and ethyl diazoacetate are variable, but this variability is restricted mainly to results obtained with copper catalysts and is most noticeable when these reactions are performed without exclusion of air. The numerical changes in the anti/syn ratio, extending from 6.8 to as high as 14 in copper-catalyzed reactions, only represent a ±3% change in the relative yields of the isomeric cyclopropane compounds and, consequently, can be relegated to influences of reaction byproducts on the active catalyst. For the vast majority of individual systems that we have examined, stereoselectivities are invariant to changes in catalyst concentration (0.5–4.0 mol %), to the rate of addition of the diazo compound, and to the molar ratio of olefin to diazo compound. Isomeric ratios reported in Tables I–III are generally reproducible to within 5% of their reported values.

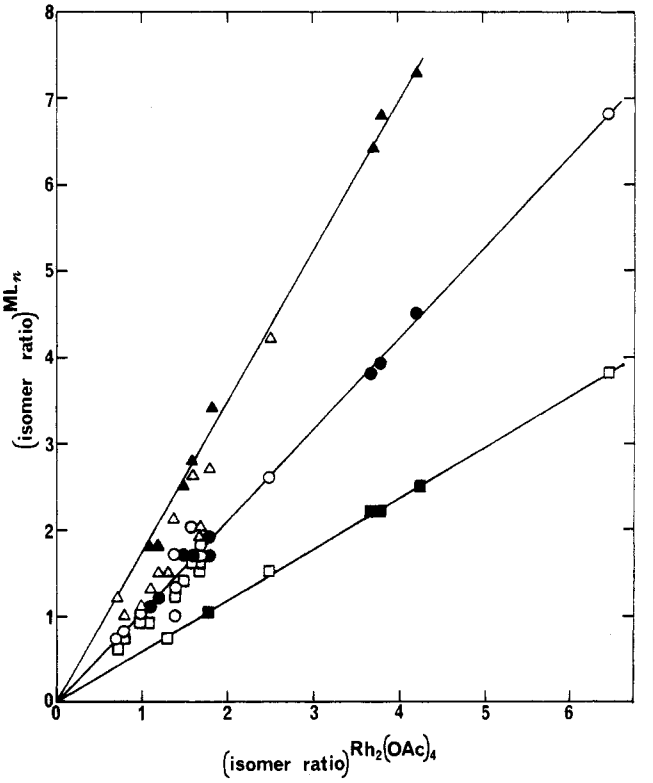


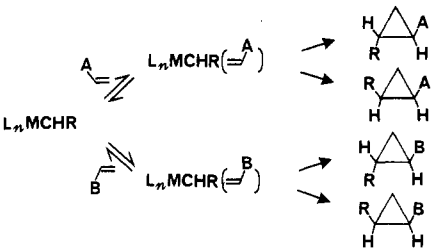
Figure 1. Plot of Observed Stereoselectivities from $Rh_2(OAc)_4$ catalyzed reactions of ethyl diazoacetate with simple olefins (▲, ●, ■) or vinyl ethers and dienes (△, ○, □) vs. those from $CuCl{\cdot}P(O\text{-}i\text{-}Pr)_3$ (▲, △), $Rh_6(CO)_{16}$ (●, ○), and $PdCl_2{\cdot}2PhCN$ (■, □) catalyzed cyclopropanation reactions.

In contrast to the inherent problems associated with the use of composite product yields for comparisons of catlaysts, selectivity monitors the product-determining step in cyclopropanation reactions and offers an intimate view of the nature of the steric and electronic constraints that are placed on these transformation. We have previously observed that regioselectivities in reactions of ethyl diazoacetate with monosubstituted 1,3-butadienes are dependent on the catalyst employed. We now find that stereoselectivities for olefin cyclopropanation by ethyl diazoacetate are observably dependent on the transition metal but, within the constraints of the series of catalysts examined, not on its initial oxidation state or its attendant ligands. In our examination of regioselectivities, we found that regioisomer ratios from reactions with a series of dienes correlated linearly with the reaction catalyst.[25] A similar plot of stereoselectivities for cyclopropanation reactions catalyzed by $CuCl{\cdot}P(O\text{-}i\text{-}Pr)_3$, $Rh_6(CO)_{16}$, and $PdCl_2{\cdot}2PhCN$ also describes a linear correlation with stereoselectivities from $Rh_2(OAc)_4$ catalyzed reactions (Figure 1).

Among the 22 olefins whose selectivities are recorded in Figure 1, deviations from the linear relationship occur with vinyl ethers in $CuCl{\cdot}P(O\text{-}i\text{-}Pr)_3$ catalyzed reactions and with both vinyl ethers and dienes, except for isoprene, with $PdCl_2{\cdot}2PhCN$. In all other cases the selectivity correlations are remarkable. Vinyl ethers are the most

(44) Peace, B. W.; Wulfman, D. S. *Tetrahedron Lett.* **1971**, 3799.
(45) Peace, B. W.; Wulfman, D. S. *Synthesis* **1973**, 137.
(46) For example, cyclopropanation of styrene using 0.5 mol % $CuCl{\cdot}P(O\text{-}i\text{-}Pr)_3$ occurred in 12% yield when ethyl diazoacetate was added at 2.4 mmol/h whereas an 88% yield was realized when the addition rate was decreased to 0.3 mmol/h.
(47) The rate of addition of ethyl diazoacetate had no apparent influence on the yield of cyclopropane products from vinyl ethers, simple olefins, or dienes.
(48) Wulfman, D. S.; McGibboney, B. G.; Steffen, E. K.; Thinh, N. V.; McDaniel, R. S., Jr.; Peace, B. W. *Tetrahedron* **1976**, *32*, 1257.

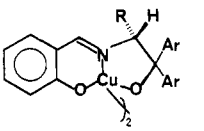
Scheme I



reactive of the olefins employed, and they are also the most sensitive to ylide transformations[37] or to isomerization.[27] Similarly, vinylcyclopropanes are subject to selective chloropalladation[40] or isomerization[39] so that these deviations are not surprising. Values for the slopes of the lines in Figure 1, which provide indices of relative stereoselectivity, are 1.74 for $CuCl{\cdot}P(O\text{-}i\text{-}Pr)_3$, 1.04 for $Rh_6(CO)_{16}$, and 0.59 for $PdCl_2{\cdot}2PhCN$.

In their classic publication, Salomon and Kochi report that regioselectivity in copper-catalyzed cyclopropanation of an isolated diene or in competitive cyclopropanation of simple olefins exhibits a striking dependence on the nature of ligands on the catalyst, and they suggest that this dependence results from the ability of various copper(I) catalysts to coordinate olefins.[24] We anticipated that a similar dependence on olefin coordination[49,50] should be evident in product stereoselectivities and in regioselectivities with conjugated dienes. However, the data reported in Table III do not indicate significant differences. Product stereoselectivities are strikingly similar, and regioselectivities for the cyclopropanation of two butadienes are identical for the five copper catalysts employed. In addition, relative reactivities for cyclopropanation reactions with ethyl diazoacetate that are catalyzed by palladium(II) acetate, copper(II) triflate, and rhodium(II) acetate commonly exhibit the order Rh(II) < Cu(II) < Pd(II) or Rh(II) > Cu(II) > Pd(II),[20] which is specifically different from the order of these same catalysts in their influence on stereoselectivity (Figure 1) or on regioselectivities in reactions with conjugated dienes.[25] Thus, electronic and/or steric influences that govern relative reactivities appear to be different from those that affect cyclopropane stereoselectivities or regioselectivities in reactions with conjugated dienes. Scheme I, which describes olefin coordination with an electrophilic metal carbene as preceeding cyclopropane formation, is in accord with these observations.[51] Relative reactivities of olefins are influenced in the initial association of olefins with the carbene carbon of the electrophilic metal carbene, which is expected to be reversible. The stereoisomer distribution is influenced by electronic and steric effects that are integral to orientation of the coordinated olefin for carbenoid insertion. Relative reactivities and reaction selectivities, which are often used in combination to define kinetic and mechanistic inluences in these transformations, do not appear to be directly related, and factors that affect these measurable quantities should be considered separately.

Four variables, the transition metal, its associated ligands, the diazo compound, and the olefin, are potential sources for stereochemical control in catalytic cyclopropanation reactions. Figure 1 depicts the effect of the transition metal on stereoselectivity, and the data in Tables II and III show that, among those catalysts examined, ligands associated with the metal have minimal influence on regioselectivity with conjugated dienes and on stereoselectivity. Similarly, structural modification at R and Ar in the chiral copper catalyst 1[22] (R = Me, $PhCH_2$, *i*-Pr,



1

i-Bu, Ph; Ar = 2-R^1O-5-$R^2C_6H_3$ where R^1 = Me, *i*-Pr, *n*-Bu, *n*-octyl and R^2 = H, Me, *t*-Bu) does not greatly affect stereoselectivities for cyclopropanation of 2,5-dimethyl-2,4-butadiene with ethyl diazoacetate (trans/cis = 1.4–2.0), although significant changes in asymmetric induction are observed with these structural changes in the copper ligand. In contrast, increasing the steric bulk of the alkyl group of the diazoacetate from ethyl through *tert*-butyl to 2,3,4-trimethyl-3-pentyl changes the trans/cis ratios for the chrysanthemic esters from 1.0 to 11.5 when 1 (R = Me; R^1 = *n*-octyl; R^2 = *t*-Bu) is employed.[23]

The influence of olefin structure on stereoselectivity is surprisingly weak. However, distinct trends are observable. Increasing the steric bulk of the olefinic substituent results in an enhancement of the relative percentage of the sterically less encumbered cyclopropane product. Substituents of vicinally disubstituted olefins ordinarily exert a stronger influence on stereoselectivity than do individual substituents of monosubstituted olefins. Geminal disubstitution weakens the influence of the individual substituents.

Experimental Section

General Methods. Proton magnetic resonance spectra were obtained with the Varian FT-80A spectrometer; chemical shifts are reported in δ units with tetramethylsilane as the internal standard. Mass spectra were obtained with the Hewlett-Packard 5993-Option 95 GC–mass spectrometer operated in the electron ionization mode at 70 eV. Analytical gas chromatographic analyses were obtained with a Varian Aerograph Model 2720 gas chromatograph with thermal conductivity detectors and with a Varian Vista 44 gas chromatography system with flame ionization detectors. Elemental analyses were performed by Galbraith Laboratories, Inc. With the exception of (triisopropyl phosphite)-copper(I) chloride and the analogous triphenyl phosphite complex,[18] copper bronze,[52] and copper(II) trifluoromethanesulfonate,[53] which were prepared by standard procedures, the transition-metal compounds employed in this investigation were commercially available. Vinyl ethers that were not commercially available were prepared from their corresponding acetal or ketal derivatives by standard methods[54-56] or, in the case of phenyl vinyl ether, from β-bromophenetole.[57] With the exception of (*Z*)-1-phenyl-1,3-butadiene, which was synthesized by the coupling of (*Z*)-β-bromostyrene[58] with vinylmagnesium bromide in the presence of tetrakis(triphenylphosphine)palladium,[59] the dienes employed for this investigation that were not commercially available were prepared by literature methods.

(49) Salomon, R. G.; Kochi, J. K. *J. Am. Chem. Soc.* **1973**, *95*, 1889.
(50) Hartley, F. R. *Chem. Rev.* **1973**, *73*, 163.
(51) The involvement of transition-metal carbenes in these catalytic transformations is discussed in the following paper: Doyle, M. P.; Griffin, J. H.; Bagheri, V.; Dorow, R. L. *Organometallics*, following paper in this issue.
(52) Fuson, R. C.; Cleveland, E. A. "Organic Synthesis"; Wiley: New York, 1955; Collect. Vol. III, p 339.
(53) Salomon, R. G.; Salomon, M. F.; Heyne, T. R. *J. Org. Chem.* **1975**, *40*, 756.
(54) Newman, M. S.; Vander Zwan, M. C. *J. Org. Chem.* **1973**, *38*, 2910.
(55) Taskinen, E. *Acta Chem. Scand., Ser. B* **1974**, *B28*, 357.
(56) Norris, R. O.; Verbanc, J. J.; Hennion, G. F. *J. Am. Chem. Soc.* **1928**, *60*, 1160.
(57) McElvain, S. M.; Fajardo-Puizou, B. *J. Am. Chem. Soc.* **1945**, *67*, 652.
(58) Grovenstein, E., Jr., Lee, D. E. *J. Am. Chem. Soc.* **1953**, *75*, 2639.
(59) Yamamura, M.; Mortitani, I.; Murahashi, S. J. *J. Organomet. Chem.* **1975**, *91*, C39.

Table IV. Gas Chromatographic Analyses of Ethyl Vinylcyclopropanecarboxylates

1,3-butadiene	column[a]	initial temp,[b] °C	cyclopropane, retention time, min			
			trans-3,4	*cis*-3,4	*trans*-1,2	*cis*-1,2
2-methyl	15% Carbowax 20M	60	27.0	27.5	24.7 (*E*)	25.5 (*Z*)
	Carbowax 20M[c]	50	15.6	15.8	14.1 (*E*)	14.6 (*Z*)
trans-1-methyl	10% EGA	80	13.0	12.4	9.7	9.9
2-chloro	10% EGA	90	11.1	13.4	12.8 (*Z*)	9.3 (*E*)
	Carbowax 20M[c]	50	13.3	14.9	14.5 (*Z*)	12.0 (*E*)
trans-1-chloro	15% Carbowax 20M	100	23.0	23.6		
cis-1-chloro	15% Carbowax 20M	100	22.2	20.7		
2-phenyl	20% OV-17	100	36.2	36.8	31.6 (*Z*)	32.4 (*E*)
	Carbowax 20M[c]	50	19.3	19.8	16.0 (*Z*)	16.3 (*E*)
trans-1-phenyl	15% Carbowax 20M	120	33.3	29.8	18.4	19.8
cis-1-phenyl	20% OV-17	140	27.0	28.6		
2-methoxy	15% Carbowax 20M	120			10.9 (*Z*)	12.5 (*E*)
trans-1-methoxy	15% Carbowax 20M	120	14.8	13.9	10.9	8.5
2-*tert*-butyl	15% QF-1	100	24.6	25.6	23.5 (*Z*)	24.5 (*E*)
	Carbowax 20M[c]	50	11.7	13.7	12.2 (*Z*)	13.5 (*E*)
trans-1-*tert*-butyl	20% SE-30	120	11.8	10.6		

[a] 2-m columns; flow rate at 80 mL/min. [b] Program temperature at 4 °C/min to 180 °C (EGA), 230 °C (Carbowax 20M, QF-1), and 250 °C (OV-17, SE-30). [c] 25-m glass capillary column, program to 120 °C at 10 °C/min, then 4 °C/min to 220 °C.

Catalytic Cyclopropanation Reactions. Ethyl diazoacetate (2.0 mmol) was added at a controlled rate over a 6–8-h period to a stirred mixture of the alkene (20.0 mmol) or diene (10.0 mmol) and the transition-metal compound (0.01–0.02 mol) under nitrogen and ordinarily at 25 °C. For copper triflate catalyzed reactions of ethyl diazoacetate with vinyl ethers, the diazo ester dissolved in the vinyl ether was added to $Cu(OTf)_2$ in ethyl ether in order to minimize vinyl ether polymerization. Olefins were generally purified by distillation prior to their use. The initial solubility of the transition-metal compound was dependent on the olefin employed, and, with the exception of $Rh_6(CO)_{16}$, $Cu(acac)_2$, and copper bronze, homogeneous solutions were obtained prior to or immediately after the initial addition of ethyl diazoacetate. At 1 h after addition was complete, dibenzyl ether (0.30 mmol) was added to the reaction mixture as the internal standard. Ether was then added, and the resulting solution was washed twice with saturated aqueous sodium bicarbonate and dried over anhydrous magnesium sulfate. Ether and excess olefin were distilled under reduced pressure. The product mixture was then subjected to NMR and GC analyses. Product yields were determined by GC through the use of experimentally measured response ratios. Duplicate experiments were minimally performed for each reported reaction, and for those reactions that resulted in low product yields additional comparative experiments were performed with more reactive olefins for a consistency in results which demanded that the cause of low product yields was not the quality of the transition-metal compound employed as the reaction catalyst. GC results were consistent with those obtained from integration of characteristic NMR absorptions for the cyclopropane products relative to those of the internal standard.

Stereoselectivities in Reactions with Alkenes. Cyclopropane geometrical isomers were generally separable with base line resolution on Carbowax 20M columns; in reactions with vinyl ethers, the *E* isomer eluted first. Individual isomers were collected and analyzed spectroscopically. GC response ratios were determined from the collected sample relative to the internal standard. As a separate check on reaction stereoselectivities in several cases, cyclopropane products were collected together and their isomer ratios were determined by integration of characteristic NMR absorptions for each isomer. Spectral information for cyclopropane products formed from allyl halides,[31] vinyl ethers,[11,27] and cycloalkenes[11,12,20] have been previously reported.

Ethyl 2-Phenoxycyclopropanecarboxylate. ^{1}H NMR ($CDCl_3$): for *E* (trans) isomer, δ 7.45–7.15 (m, 3 H), 7.10–6.85 (m, 2 H), 4.20 (q, *J* = 7.1 Hz, CH_2O), 4.06 (d of d of d, *J* = 6.2, 4.3, 2.2 Hz, *CH*OPh), 1.95 (d of d of d, *J* = 8.1, 6.1, 2.2 Hz, *CH*COOEt), 1.60–1.25 (m, 2 H), 1.29 (t, *J* = 7.1 Hz, CH_3CH_2O); for *Z* (cis) isomer, δ 7.45–7.15 (m, 3 H), 7.10–6.85 (m, 2 H), 4.1–3.8 (m, *CH*OPh), 3.98 (q, *J* = 7.1 Hz, CH_2O), 2.15–1.50 (m, 2 H), 1.30 (d of d of d, *J* = 8.6, 6.4, 6.0 Hz, 1 H), 1.03 (t, *J* = 7.1 Hz, CH_3CH_2O).

Ethyl 2-*tert*-Butyl-2-methoxycyclopropanecarboxylate. ^{1}H NMR ($CDCl_3$): for *E* isomer, δ 4.14 (d of q, *J* = 7.1 and 1.5 Hz, CH_2O), 3.35 (s, CH_3O), 1.87 (d of d, *J* = 8.1 and 6.3 Hz, *CH*COOEt), 1.69 (d of d, *J* = 6.3, 5.6 Hz, 1 H), 1.25 (t, *J* = 7.1 Hz, CH_3CH_2O), 1.12 (d of d, *J* = 8.1, 5.6 Hz, 1 H), 0.95 (s, $C(CH_3)_3$); for *Z* isomer, δ 4.14 (q, *J* = 7.1 Hz, CH_2O), 3.33 (s, CH_3O), 1.6–1.0 (m, 3 H), 1.27 (t, *J* = 7.1 Hz, CH_3CH_2O), 1.02 (s, $C(CH_3)_3$).

Ethyl 2-Isopropylcyclopropanecarboxylate. ^{1}H NMR ($CDCl_3$): for trans isomer, δ 4.10 (q, *J* = 7.1 Hz, CH_2O), 1.50–0.90 (m, 3 H), 1.25 (t, *J* = 7.1 Hz, CH_3CH_2O), 0.98 (d, *J* = 1.2 Hz, $CH(CH_3)_2$), 0.85–0.60 (m, 2 H); for cis isomer, δ 4.14 (q, *J* = 7.1 Hz, CH_2O), 1.68 (d of d of d, *J* = 8.9, 7.7, 6.1 Hz, *CH*COOEt), 1.26 (t, *J* = 7.1 Hz, CH_3CH_2O), 1.3–0.7 (m, 4 H), 1.02 and 0.88 (two d, *J* = 6.5 and 6.3 Hz, $CH(CH_3)_2$).

Ethyl 2-*tert*-Butylcyclopropanecarboxylate. ^{1}H NMR ($CDCl_3$): for trans isomer, δ 4.12 (q, *J* = 7.1 Hz, CH_2O), 1.43 (d of d of d, *J* = 8.1, 4.8, 3.3 Hz, *CH*COOEt), 1.25 (t, *J* = 7.1 Hz, CH_3CH_2O), 1.35–0.65 (m, 3 H), 0.86 (s, *t*-Bu); for cis isomer, δ 4.14 and 4.13 (two q, *J* = 7.2 and 7.0 Hz, CH_2O), 1.61 (d of d of d, *J* = 9.2, 7.8, 7.0 Hz, *CH*COOEt), 1.27 (t, *J* = 7.1 Hz, CH_3CH_2O), 1.30–0.80 (m, 3 H), 0.95 (s, *t*-Bu).

Ethyl 2,2,3-Trimethylcyclopropanecarboxylate. ^{1}H NMR: ($CDCl_3$) for trans isomer, δ 4.08 (q, *J* = 7.1 Hz, CH_2O), 1.4–0.8 (m, 2 H), 1.25 (t, *J* = 7.1 Hz, CH_3CH_2O), 1.20 (s, CH_3), 1.16 (d, *J* = 5.9 Hz, $CHCH_3$), 1.13 (s, CH_3); for cis isomer, δ 4.10 (q, *J* = 7.1 Hz, CH_2O), 1.25 (t, *J* = 7.1 Hz, CH_3CH_2O), 1.20 (s, CH_3), 1.3–1.0 (m, 2 H), 1.13 (s, CH_3), 1.12 (d, *J* = 6.4 Hz, $CHCH_3$); (C_6D_6) for trans isomer, δ 4.00 (q, *J* = 7.1 Hz), 1.4–0.8 (m, 2 H), 1.28 (d, *J* = 5.9 Hz, $CHCH_3$) 1.28 (s, CH_3), 1.00 (t, *J* = 7.1 Hz, CH_3CH_2O), 0.88 (s, CH_3); for cis isomer, 4.01 (q, *J* = 7.1 Hz, CH_2O), 1.28 (s, CH_3), 1.01 (t, *J* = 7.1 Hz, CH_3CH_2O), 0.88 (s, CH_3), 0.84 (d, *J* = 6.4 Hz, $CHCH_3$).

Stereoselectivities in Reactions with Dienes. Reaction mixtures were subjected to GC analyses under conditions that provided separation of each of as many as four isomeric products (Table IV). Individual isomers were collected and analyzed spectroscopically. The mass spectra of reaction mixture components were employed to confirm the presence or absence of individual cyclopropane components and to provide structural identity to regioisomers. When individual components were not separable on the GC column employed for analytical determinations, they were collected together and their isomeric ratio was determined on a second GC column and confirmed by NMR analysis. Full spectral information for cyclopropane products formed from reactions of ethyl diazoacetate with 2-methoxy- and *trans*-1-methoxy-1,3-butadiene has been reported.[27] Partial spectral information is available for regioisomeric products derived from 1,3-pentadiene[60] and isoprene.[20]

Ethyl 2-Methyl-2-vinylcyclopropanecarboxylate. ^{1}H NMR ($CDCl_3$): for *E* isomer, δ 5.65–5.22 (m, $CH{=}CH_2$), 5.15–4.89 (m,

(60) Lishanskii, I. S.; Guliev, A. M.; Pomerantsvev, V. I.; Turkova, L. D.; Klachaturov, A. S. *J. Org. Chem. USSR (Engl. Transl.)* **1970**, *6*, 924.

CH=CH_2), 4.14 (q, J = 7.1 Hz, CH_2O), 1.72 (d of d, J = 8.3, 6.0 Hz, CHCOOEt), 1.31 (s, CH_3), 1.31 (d of d, J = 6.0, 4.4 Hz, 1 H), 1.26 (t, J = 7.1 Hz, CH_3CH_2O), 1.08 (d of d, J = 8.3, 4.4 Hz, 1 H); for Z isomer, δ 5.95 (d of d, J = 17.5, 10.4 Hz, CH=CH_2), 5.12 (d of d, J = 17.5, 1.7 Hz, 1 H), 5.07 (d of d, J = 10.4, 1.7 Hz, 1 H), 4.11 (q, J = 7.1 Hz, CH_2O), 1.78 (d of d, J = 7.9, 5.9 Hz, CHCOOEt), 1.42 (d of d, J = 5.9, 4.5 Hz, 1 H), 1.28 (s, CH_3), 1.25 (t, J = 7.1 Hz, CH_3CH_2O), 1.09 (d of d, J = 7.9, 4.5 Hz, 1 H).

Ethyl 2-(2-Isopropenyl)cyclopropanecarboxylate. ^{1}H NMR ($CDCl_3$): for trans isomer, δ 4.80–4.75 (m, C=CH_2), 4.14 (q, J = 7.1 Hz, CH_2O), 2.02 (d of d of d, J = 8.8, 6.8, 4.5 Hz, CHCOOEt), 1.8–1.6 (m, 1 H), 1.65 (t, J = 1.1 Hz, =CCH_3), 1.4–1.2 (m, 1 H), 1.26 (t, J = 7.1 Hz, CH_3CH_2O), 1.06 (d of d of d, J = 8.5, 6.8, 4.2 Hz, 1 H); for cis isomer, δ 4.96–4.92 (m, 1 H), 4.85–4.82 (m, 1 H), 4.10 (q, J = 7.1 Hz, CH_2O), 1.95–1.5 (m, 2 H), 1.73 (m, =CCH_3), 1.50–0.95 (m, 2 H), 1.22 (t, J = 7.1 Hz, CH_3CH_2O).

Ethyl 2((*E*)-1-Propenyl)cyclopropanecarboxylate. ^{1}H NMR ($CDCl_3$): for trans isomer, δ 5.66 (d of q, J = 15.2, 6.4 Hz, =CHCH$_3$), 5.08 (d of d of q, J = 15.2, 7.8, 1.4 Hz, CHCH=CHCH$_3$), 4.16 (q, J = 7.1 Hz, CH_2O), 2.2–1.7 (m, 2 H), 1.70 (d of d, J = 6.4, 1.4 Hz, CH_3), 1.5–1.2 (m, 1 H), 1.30 (t, J = 7.1 Hz, CH_3CH_2O), 0.94 (d of d of d, J = 8.3, 6.4, 4.1 Hz, 1 H); for cis isomer, δ 5.66 (d of q, J = 15.4, 6.1 Hz, =CHCH$_3$), 5.6–5.3 (m, 1 H), 4.10 (q, J = 7.1 Hz, CH_2O), 2.05–1.50 (m, 2 H), 1.64 (d, J = 5.0 Hz, CH_3), 1.22 (t, J = 7.1 Hz, CH_3CH_2O), 1.3–1.0 (m, 2 H).

Ethyl 2-Methyl-3-vinylcyclopropanecarboxylate. ^{1}H NMR ($CDCl_3$): δ 5.44–4.83 (m, CH=CH_2), 4.14 and 4.11 (q, J = 7.1 Hz, CH_2O of cis and trans isomers, respectively), 2.0–1.1 (m, 3 H), 1.26 and 1.25 (t, J = 7.1 Hz, CH_3CH_2O of trans and cis isomers, respectively), 1.26 and 1.11 (d; J = 4.1 Hz, CH_3 of cis and trans isomers, respectively).

Ethyl 2-Chloro-2-vinylcyclopropanecarboxylate. ^{1}H NMR ($CDCl_3$): for E isomer, δ 5.98 (d of d, J = 16.5, 9.9 Hz, CH=CH_2), 5.54 (d of d, J = 16.5, 1.8 Hz, 1 H), 5.28 (d of d, J = 9.9, 1.8 Hz, 1 H), 4.16 (q, J = 7.1 Hz, CH_2O), 2.46 (d of d, J = 9.2, 7.2 Hz, CHCOOEt), 1.8–1.5 (m, 2 H), 1.27 (t, J = 7.1 Hz, CH_3CH_2O); for Z isomer, δ 5.70 (d of d, J = 16.2, 9.1 Hz, CH=CH_2), 5.36 (d of d, J = 9.1, 2.2 Hz, 1 H), 5.18 (d of d, J = 16.2, 2.2 Hz, 1 H), 4.22 (q, J = 7.1 Hz, CH_2O), 2.11 (d of d, J = 8.1, 7.1 Hz, CHCOOEt), 1.92 (d of d, J = 7.1, 5.3 Hz, 1 H), 1.47 (d of d, J = 8.1, 5.3 Hz, 1 H), 1.29 (t, J = 7.1 Hz, CH_3CH_2O). Mass spectrum, m/e (relative abundance): for E isomer, 177 (0.1, M + 3), 176 (0.7, M + 2), 175 (0.3, M + 1), 174 (2.2, M), 139 (17, M – Cl), 129 (8), 111 (54), 103 (12), 102 (6), 101 (39), 100 (11), 83 (10), 67 (10), 66 (16), 65 (100), 55 (27), 53 (11); for Z isomer, 176 (0.3, M + 2), 175 (0.1, M + 1), 174 (0.8, M), 139 (16, M – Cl), 129 (9), 111 (48), 103 (12), 102 (6), 101 (37), 100 (10), 83 (9), 67 (9), 66 (16), 65 (100), 55 (24), 53 (10).

Ethyl 2-(1-Chlorovinyl)cyclopropanecarboxylate. ^{1}H NMR ($CDCl_3$): for trans isomer, δ 5.31 (d, J = 1.4 Hz, 1 H), 5.24 (d, J = 1.4 Hz, 1 H), 4.16 (q, J = 7.1 Hz, CH_2O), 2.31 (d of d of d, J = 8.2, 6.8, 4.3 Hz, 1 H), 1.97 (d of d of d, J = 8.2, 6.1, 4.3 Hz, 1 H), 1.5–1.2 (m, 2 H), 1.27 (t, J = 7.1 Hz, CH_3CH_2O); for cis isomer, δ 5.37 (d, J = 1.4 Hz, 1 H), 5.29 (d, J = 1.4 Hz, 1 H), 4.14 (q, J = 7.1 Hz, CH_2O), 2.4–1.8 (m, 2 H), 1.6–1.4 (m, 1 H), 1.4–1.2 (m, 1 H), 1.31 (t, J = 7.1 Hz, CH_3CH_2O). Mass spectrum, m/e (relative abundance): for trans isomer, 177 (0.2, M + 3), 176 (1.6, M + 2), 175 (0.6, M + 1), 174 (4.6, M), 139 (12, M – Cl), 129 (20), 111 (64), 103 (20), 102 (13), 101 (62), 100 (26), 83 (11), 67 (14), 66 (24), 65 (100), 55 (30), 53 (11); for cis isomer, 177 (0.3, M + 3), 176 (2.8, M + 2), 175 (1.1, M + 1), 174 (8.1, M), 139 (14, M – Cl), 129 (20), 111 (72), 103 (11), 102 (8), 101 (34), 100 (14), 83 (12), 67 (9), 66 (14), 65 (100), 55 (24), 53 (24). Anal. Calcd for $C_8H_{11}ClO_2$: C, 55.02; H, 6.36. Found (isomer composite): C, 55.10; H, 6.28.

Ethyl 2-((*E*)-2-Chlorovinyl)cyclopropanecarboxylate. ^{1}H NMR ($CDCl_3$): for trans isomer, δ 6.10 (d of d, J = 13.1, 0.4 Hz, =CHCl), 5.49 (d of d, J = 13.2, 8.5 Hz, CHCH=), 4.14 (q, J = 7.1 Hz, CH_2O), 2.04 (d of d of d of d of d of d, J = 8.6, 8.5, 6.2, 4.0, 0.4 Hz, CHCH=), 1.67 (d of d of d, J = 8.6, 5.2, 4.2 Hz, CHCOOEt), 1.5–1.2 (m, 1 H), 1.26 (t, J = 7.1 Hz, CH_3CH_2O), 0.94 (d of d of d, J = 8.5, 6.2, 4.2 Hz, 1 H); for cis isomer δ 6.13 (d of d, J = 13.4, 0.8 Hz, =CHCl), 5.96 (d of d, J = 13.4, 9.6 Hz, CHCH=), 4.14 (q, J = 7.1 Hz, CH_2O), 2.05–1.60 (m, 2 H), 1.4–1.1 (m, 2 H), 1.26 (t, J = 7.1 Hz, CH_3CH_2O). Anal. Calcd for $C_8H_{11}ClO_2$: C, 55.02; H, 6.36. Found (isomer composite): C, 55.04; H, 6.25.

Ethyl 2-((*Z*)-2-Chlorovinyl)cyclopropanecarboxylate. ^{1}H NMR ($CDCl_3$): for trans isomer, δ 6.06 (d of d, J = 7.2, 0.8 Hz, =CHCl), 5.20 (d of d, J = 9.2, 7.2 Hz, CHCH=), 4.15 (q, J = 7.1 Hz, CH_2O), 2.42 (d of d of d of d of d of d, J = 9.2, 8.6, 6.2, 4.1, 0.8 Hz, CHCH=), 1.70 (d of d of d, J = 8.2, 5.2, 4.1 Hz, CHCOOEt), 1.48 (d of d of d, J = 8.6, 5.2, 4.1 Hz, 1 H), 1.27 (t, J = 7.1 Hz, CH_3CH_2O), 0.98 (d of d of d, J = 8.2, 6.2, 4.1 Hz, 1 H); for cis isomer, δ 6.08 (d of d, J = 7.2, 0.5 Hz, =CHCl), 5.82 (d of d, J = 8.7, 7.2 Hz, CHCH=), 4.14, J = 7.1 Hz, CH_2O), 2.6–2.1 (m, CHCH=), 2.02 (d of d of d, J = 8.7, 8.4, 7.2 Hz, CHCOOEt), 1.5–1.2 (m, 2 H), 1.26 (t, J = 7.1 Hz, CH_3CH_2O). Anal. Calcd for $C_8H_{11}ClO_2$: C, 55.02; H, 6.36; Cl, 20.30. Found (isomer composite): C, 55.00; H, 6.43; Cl, 20.04.

Ethyl 2-Phenyl-2-vinylcyclopropanecarboxylate. ^{1}H NMR ($CDCl_3$): for Z isomer, δ 7.25 (s, 5 H), 5.67 (d of d, J = 16.7, 10.4 Hz, CH=CH_2), 4.98 (d of d, J = 10.4, 1.2 Hz, 1 H), 4.65 (d of d, J = 16.7, 1.2 Hz, 1 H), 3.86 and 3.85 (two q, J = 7.2 and 7.0 Hz, CH_2O), 2.15 (d of d, J = 7.5, 6.0 Hz, CHCOOEt), 1.97 (d of d, J = 5.9, 4.3 Hz, 1 H), 1.37 (d of d, J = 7.5, 4.3 Hz, 1 H), 0.96 (t, J = 7.1 Hz, CH_3CH_2O); for E isomer, δ 7.31 (s, 5 H), 6.10 (d of d, J = 17.1, 10.5 Hz, CH=CH_2), 5.07 (d of d, J = 10.5, 1.6 Hz, 1 H), 4.20 (d of d, J = 17.1, 1.6 Hz, 1 H), 4.20 (q, J = 7.1 Hz, CH_2O), 2.26 (d of d, J = 8.4, 6.1 Hz, CHCOOEt), 1.76 (d of d, J = 6.1, 4.6 Hz, 1 H), 1.55 (d of d, J = 8.4, 4.6 Hz, 1 H), 1.29 (t, J = 7.1 Hz, CH_3CH_2O). Mass spectrum; m/e (relative abundance): for Z isomer, 217 (0.3, M + 1), 216 (1.7, M), 187 (8, M – Et), 171 (6, M – OEt), 144 (13), 143 (100), 142 (52), 141 (47), 129 (16), 128 (71), 127 (13), 115 (55), 91 (18), 89 (12), 77 (10), 65 (14), 63 (12), 55 (10), 51 (13); for E isomer, 216 (1.5, M), 187 (8, M – Et), 171 (5, M – OEt), 144 (13), 143 (100), 142 (52), 141 (48), 129 (17), 128 (72), 127 (13), 115 (57), 91 (19), 89 (12), 77 (11), 65 (14), 63 (13), 55 (10), 51 (14). Anal. Calcd for $C_{14}H_{16}O_2$: C, 77.74; H, 7.47. Found (isomer composite): C, 77.47; H, 7.59.

Ethyl 2-(α-Styryl)cyclopropanecarboxylate. ^{1}H NMR ($CDCl_3$): for trans isomer, δ 7.6–7.2 (m, 5 H), 5.01 (d, J = 0.8 Hz, 1 H), 4.18 (q, J = 7.1 Hz, CH_2O), 2.4–2.2 (m, CHC(Ph)=), 1.74 (d of d of d, J = 9.6, 8.4, 5.0 Hz, CHCOOEt), 1.51 (d of d of d, J = 8.6, 5.0, 4.0 Hz, 1 H), 1.28 (t, J = 7.1 Hz, CH_3CH_2O), 1.15 (d of d of d, J = 8.4, 6.7, 4.0 Hz, 1 H); for cis isomer, δ 7.6–7.2 (m, 5 H), 5.63 (s, 1 H), 5.21 (d, J = 1.1 Hz, 1 H), 3.88 (q, J = 7.1 Hz, CH_2O), 2.35–2.05 (m, CHC(Ph)=), 1.7–1.1 (m, 3 H), 0.99 (t, J = 7.1 Hz, CH_3CH_2O). Mass spectrum, m/e (relative abundance): for trans isomer, 217 (1.4, M + 1), 216 (8.5, M), 187 (3, M – Et), 171 (8, M – OEt), 144 (13), 143 (100), 142 (63), 141 (34), 129 (18), 128 (68), 127 (11), 115 (35), 103 (18), 91 (18), 77 (23), 65 (13), 63 (9), 55 (8), 51 (16); for cis isomer, 217 (2.4, M + 1), 216 (15, M), 187 (3, M – Et), 171 (7, M – OEt), 144 (13), 143 (100), 142 (66), 141 (34), 129 (19), 128 (66), 127 (12), 115 (35), 103 (19), 91 (19), 77 (26), 65 (13), 63 (10), 55 (12), 51 (19).

Ethyl 2-((*E*)-β-Styryl)cyclopropanecarboxylate. ^{1}H NMR ($CDCl_3$): for trans isomer, δ 7.35–7.15 (m, 5 H), 6.54 (d, J = 15.8 Hz, =CHPh), 5.74 (d of d, J = 15.8, 8.4 Hz, CHCH=), 4.15 (q, J = 7.1 Hz, CH_2O), 2.17 (d of d of d of d of d, J = 8.4, 8.2, 6.1, 4.1 Hz, CHCH=), 1.74 (d of d of d, J = 8.2, 5.1, 4.1 Hz, CHCOOEt), 1.46 (d of d of d, J = 8.2, 5.1, 4.1 Hz, 1 H), 1.27 (t, J = 7.1 Hz, CH_3CH_2O), 1.07 (d of d of d, J = 8.2, 6.1, 4.1 Hz, 1 H); for cis isomer, δ 7.4–7.1 (m, 5 H), 6.60 (d, J = 15.8 Hz, =CHPh), 6.20 (d of d of d, J = 15.8, 7.0, 1.4 Hz, CHCH=), 4.15 (q, J = 7.1 Hz, CH_2O), 2.2–1.9 (m, 2 H), 1.5–1.2 (m, 2 H), 1.25 (t, J = 7.1 Hz, CH_3CH_2O).

Ethyl 2-Phenyl-3-vinylcyclopropanecarboxylate. ^{1}H NMR ($CDCl_3$): δ 7.5–7.0 (m, 5 H), 6.0–5.0 (m, CH=CH_2), 4.08 and 3.84 (q, J = 7.1 Hz, CH_2O of cis and trans isomers, respectively), 2.8–2.5 (m, CHPh), 2.3–2.0 (m, 2 H), 1.5–0.9 (m, 2 H), 1.20 and 0.93 (t, J = 7.1 Hz, CH_3CH_2O of cis and trans isomers, respectively).

Ethyl 2-((*Z*)-β-Styryl)cyclopropanecarboxylate. ^{1}H NMR ($CDCl_3$): for trans isomer, δ 7.35–7.15 (m, 5 H), 6.36 (d, J = 11.5 Hz, =CHPh), 5.02 (d of d, J = 11.5, 9.6 Hz, CHCH=), 4.06 (q, J = 7.1 Hz, CH_2O), 2.38 (d of d of d of d of d, J = 9.6, 8.6, 6.5, 4.2 Hz, CHCH=), 1.65 (d of d of d, J = 8.3, 5.0, 4.2 Hz, CHCOOEt), 1.45 (d of d of d, J = 8.6, 5.0, 4.1 Hz, 1 H), 1.18 (t, J = 7.1 Hz, CH_3CH_2O), 0.90 (d of d of d, J = 8.3, 6.5, 4.1 Hz, 1 H); for cis isomer, δ 7.35–7.15 (m, 5 H), 6.44 (d of d, J = 11.5, 0.5 Hz, =CHPh), 5.58 (d of d, J = 11.5, 9.2 Hz, CHCH=), 4.08 (q, J = 7.1 Hz, CH_2O), 2.5–2.2 (m, CHCH=), 1.93 (d of d of d, J = 9.0, 8.8, 6.0 Hz, CHCOOEt), 1.5–1.1 (m, 2 H), 1.17 (t, J = 7.1 Hz,

CH_3CH_2O). Anal. Calcd for $C_{14}H_{16}O_2$: C, 77.74; H, 7.47. Found (isomer composite): C, 77.93; H, 7.57.

Ethyl 2-*tert*-Butyl-2-vinylcyclopropanecarboxylate. ^{1}H NMR ($CDCl_3$): for *E* isomer, δ 6.25 (d of d, *J* = 17.4, 11.0 Hz, CH=CH_2), 4.97 (d of d, *J* = 11.0, 1.5 Hz, 1 H), 4.94 (d of d, *J* = 17.4, 1.5 Hz, 1 H), 4.13 and 4.14 (two q, *J* = 7.3 and 7.0 Hz, CH_2O), 1.75–1.00 (m, 3 H), 1.26 (t, *J* = 7.1 Hz, CH_3CH_2O), 0.95 (s, $C(CH_3)_3$); for *Z* isomer, δ 6.10–5.70 (m, CH=CH_2), 5.30–5.00 (m, CH=CH_2), 4.08 (q, *J* = 7.1 Hz, CH_2O), 1.85 (d of d, *J* = 7.8, 5.4 Hz, CHCOOEt), 1.45–1.00 (m, 2 H), 1.12 (t, *J* = 7.1 Hz, CH_3CH_2O), 0.90 (s, $C(CH_3)_3$). Mass spectrum, *m/e* (relative abundance): for *Z* isomer, 197 (0.2, M + 1), 196 (1.0, M), 151 (9, M − OEt), 123 (35), 122 (12), 107 (27), 105 (18), 96 (58), 95 (10), 93 (9), 91 (10), 81 (100), 79 (16), 77 (14), 67 (22), 57 (50), 55 (55), 53 (18); for *E* isomer, 197 (0.2, M + 1), 196 (0.8, M), 151 (9, M − OEt), 123 (37), 122 (13), 107 (29), 105 (16), 96 (57), 95 (10), 93 (10), 91 (9), 81 (100), 79 (16), 77 (27), 67 (22), 57 (32), 55 (44), 53 (14).

Ethyl 2-(3,3-Dimethyl-1-buten-2-yl)cyclopropanecarboxylate. ^{1}H NMR ($CDCl_3$): for trans isomer, δ 4.76 (d, *J* = 0.5 Hz, 1 H), 4.53 (d, *J* = 0.3 Hz, 1 H), 4.15 (q, *J* = 7.1 Hz, CH_2O), 2.15–1.50 (m, 2 H), 1.5–0.9 (m, 2 H), 1.26 (t, *J* = 7.1 Hz, CH_3CH_2O), 1.12 (s, $C(CH_3)_3$); for cis isomer, δ 5.02 (d, *J* = 0.8 Hz, 1 H), 4.79 (d, *J* = 0.3 Hz, 1 H), 4.04 (q, *J* = 7.1 Hz, CH_2O), 2.0–0.9 (m, 4 H), 1.19 (t, *J* = 7.1 Hz, CH_3CH_2O), 1.08 (s, $C(CH_3)_3$). Mass spectrum, *m/e* (relative abundance): for trans isomer, 197 (1.1, M + 1), 196 (7.7, M), 181 (11), 151 (10), 140 (12), 139 (34), 135 (13), 124 (10), 123 (96), 122 (30), 121 (13), 112 (12), 111 (69), 109 (26), 108 (22), 107 (100), 96 (10), 95 (21), 93 (34), 91 (32), 83 (44), 81 (65), 79 (34), 77 (24), 69 (12), 68 (10), 67 (51), 66 (16), 65 (21), 57 (87), 55 (88), 53 (26); for cis isomer, 198 (0.3, M + 2), 197 (2.3, M + 1), 196 (17, M), 181 (12), 151 (1.3), 140 (10), 139 (41), 135 (13), 124 (9), 123 (81), 122 (23), 121 (13), 112 (10), 111 (65), 109 (36), 108 (22), 107 (100), 96 (10), 95 (22), 93 (34), 91 (30), 83 (38), 81 (58), 79 (32), 77 (22), 69 (11), 67 (48), 66 (14), 65 (19), 57 (75), 55 (83), 55 (22).

Ethyl 2-((*E*)-3,3-Dimethyl-1-buten-1-yl)cyclopropanecarboxylate. ^{1}H NMR ($CDCl_3$): for trans isomer, δ 5.63 (d of d, *J* = 15.6, 0.5 Hz, =CH(*t*-Bu)), 4.88 (d of d, *J* = 15.6, 8.0 Hz, $CHCH$=), 4.12 (q, *J* = 7.1 Hz, CH_2O), 1.96 (d of d of d of d of d, *J* = 8.2, 8.0, 6.5, 4.2, 0.5 Hz, CHCH=), 1.56 (d of d of d, *J* = 8.4, 5.1, 4.2 Hz, CHCOOEt), 1.35 (d of d of d, *J* = 8.2, 5.1, 4.0 Hz, 1 H), 1.26 (t, *J* = 7.1 Hz, CH_3CH_2O), 0.97 (s, $C(CH_3)_3$), 0.90 (d of d of d, *J* = 8.4, 6.5, 4.0 Hz, 1 H); for cis isomer, δ 5.70 (d, *J* = 15.7 Hz, =CH(*t*-Bu)), 5.30 and 5.24 (two d of d, *J* = 15.7, 8.2 Hz and *J* = 15.7, 4.4 Hz, $CHCH$=), 4.12 (q, *J* = 7.1 Hz, CH_2O), 2.00–1.65 (m, 2 H), 1.3–0.9 (m, 2 H), 1.25 (t, *J* = 7.1 Hz, CH_3CH_2O), 0.98 (s, $C(CH_3)_3$). Anal. Calcd for $C_{12}H_{20}O_2$: C, 73.41; H, 10.29. Found (isomer composite): C, 73.16; H, 10.22.

Acknowledgment. We gratefully acknowledge the financial support of the National Science Foundation for this work and for funding provided for the purchase of the GC/mass spectrometer and capillary GC employed for product determinations.

Registry No. H_2C=$CHCH_2Br$, 106-95-6; H_2C=$CHCH_2Cl$, 107-05-1; H_2C=CHOPh, 766-94-9; H_2C=CH-*n*-Bu, 592-41-6; H_2C=CHPh, 100-42-5; H_2C=CHOAc, 108-05-4; H_2C=CHOEt, 109-92-2; H_2C=CHO-*n*-Bu, 111-34-2; H_2C=CH-*i*-Pr, 563-45-1; H_2C=CH-*t*-Bu, 558-37-2; H_2C=CHC(Cl)=CH_2, 126-99-8; H_2C=CHC(Ph)=CH_2, 2288-18-8; H_2C=CHC(Me)=CH_2, 78-79-5; H_2C=CHC(*t*-Bu)=CH_2, 2495-32-1; H_2C=CHCH=CHOMe, 10034-09-0; *trans*-H_2C=CHCH=CHCl, 16503-25-6; *cis*-H_2C=CHCH=CHCl, 10033-99-5; *trans*-H_2C=CHCH=CHPh, 16939-57-4; *cis*-H_2C=CHCH=CHPh, 31915-94-3; *trans*-H_2C=CHCH=CHMe, 2004-70-8; *trans*-H_2C=CHCH=CH(*t*-Bu), 36320-14-6; H_2C=CMeOMe, 116-11-0; H_2C=CPhOMe, 4747-13-1; H_2C=C-*t*-BuOMe, 60693-17-6; H_2C=COMeCH=CH_2, 3588-30-5; H_2C=COMeC(OMe)=CH_2, 3588-31-6; *trans*-MeCH=$CHCH_2Br$, 29576-14-5; *cis*-$(CH_2)_3CH$=CH, 142-29-0; *cis*-$(CH_2)_4CH$=CH, 110-83-8; *cis*-$(CH_2)_3OCH$=CH, 110-87-2; *cis*-PhCH=CHOMe, 14371-19-8; $Rh_2(OAc)_4$, 15956-28-2; $Rh_6(CO)_{16}$, 28407-51-4; CuCl·P(O-*i*-Pr)$_3$, 39721-89-6; $PdCl_2$·2PhCN, 14220-64-5; CuCl·P(OPh)$_3$, 24484-07-9; $Cu(OTf)_2$, 34946-82-2; $Cu(acac)_2$, 13395-16-9; copper bronze, 12597-70-5; 2-methyl-2-butene, 513-35-9; 1-methylcyclohexene, 591-49-1; 2,5-dimethyl-2,4-hexadiene, 764-13-6; 1-methoxycyclohexene, 931-57-7; ethyl diazoacetate, 623-73-4; ethyl *trans*-2-phenoxycyclopropanecarboxylate, 2120-92-5; ethyl *cis*-2-phenoxycyclopropanecarboxylate, 2120-91-4; ethyl *trans*-2-(*tert*-butyl)-2-methoxycyclopropanecarboxylate, 84989-74-2; ethyl *cis*-2-(*tert*-butyl)-2-methoxycyclopropanecarboxylate, 84989-73-1; ethyl *trans*-2-isopropylcyclopropanecarboxylate, 87901-35-7; ethyl *cis*-2-isopropylcyclopropanecarboxylate, 87901-36-8; ethyl *trans*-2-*tert*-butylcyclopropanecarboxylate, 87901-37-9; ethyl *cis*-2-*tert*-butylcyclopropanecarboxylate, 87901-38-0; ethyl *trans*-2,2,3-trimethylcyclopropanecarboxylate, 82470-89-1; ethyl *cis*-2,2,3-trimethylcyclopropanecarboxylate, 82470-84-6; ethyl *trans*-2-methyl-2-vinylcyclopropanecarboxylate, 52345-60-5; ethyl *cis*-2-methyl-2-vinylcyclopropanecarboxylate, 52345-63-8; ethyl *trans*-2-(2-isopropenyl)cyclopropanecarboxylate, 52345-59-2; ethyl *cis*-2-(2-isopropenyl)cyclopropanecarboxylate, 52390-22-4; ethyl *trans*-2-((*E*)-1-propenyl)cyclopropanecarboxylate, 28363-87-3; ethyl *cis*-2-((*E*)-1-propenyl)cyclopropanecarboxylate, 28363-86-2; ethyl 2-methyl-3-vinylcyclopropanecarboxylate, 51607-42-2; ethyl *trans*-2-chloro-2-vinylcyclopropanecarboxylate, 37066-08-3; ethyl *cis*-2-chloro-2-vinylcyclopropanecarboxylate, 87901-39-1; ethyl *trans*-2-(1-chlorovinyl)cyclopropanecarboxylate, 87901-40-4; ethyl *cis*-2-(1-chlorovinyl)cyclopropanecarboxylate, 87901-41-5; ethyl *trans*-2-((*E*)-2-chlorovinyl)cyclopropanecarboxylate, 87936-35-4; ethyl *cis*-2-((*E*)-2-chlorovinyl)cyclopropanecarboxylate, 87936-36-5; ethyl *trans*-2-((*Z*)-2-chlorovinyl)cyclopropanecarboxylate, 87936-37-6; ethyl *cis*-2-((*Z*)-2-chlorovinyl)cyclopropanecarboxylate, 87936-38-7; ethyl *cis*-2-phenyl-2-vinylcyclopropanecarboxylate, 87901-42-6; ethyl *trans*-2-phenyl-2-vinylcyclopropanecarboxylate, 87901-43-7; ethyl *trans*-2-(α-styryl)cyclopropanecarboxylate, 87901-44-8; ethyl *cis*-2-(α-styryl)cyclopropanecarboxylate, 87901-45-9; ethyl *trans*-2-((*E*)-β-styryl)cyclopropanecarboxylate, 67463-07-4; ethyl *cis*-2-((*E*)-β-styryl)cyclopropanecarboxylate, 67428-06-2; ethyl 2-phenyl-3-vinylcyclopropanecarboxylate, 82896-54-6; ethyl *trans*-2-((*Z*)-β-styryl)cyclopropanecarboxylate, 87936-39-8; ethyl *cis*-2-((*Z*)-β-styryl)cyclopropanecarboxylate, 87936-40-1; ethyl *trans*-2-*tert*-butyl-2-vinylcyclopropanecarboxylate, 87901-46-0; ethyl *cis*-2-*tert*-butyl-2-vinylcyclopropanecarboxylate, 87901-47-1; ethyl *trans*-2-(3,3-dimethyl-1-buten-2-yl)cyclopropanecarboxylate, 87901-48-2; ethyl *cis*-2-(3,3-dimethyl-1-buten-2-yl)cyclopropanecarboxylate, 87901-49-3; ethyl *trans*-2-((*E*)-3,3-dimethyl-1-buten-1-yl)cyclopropanecarboxylate, 87901-50-6; ethyl *cis*-2-((*E*)-3,3-dimethyl-1-buten-1-yl)cyclopropanecarboxylate, 87936-41-2.