The combined organic phases were extracted with 7% NaOH solution (3 × 100 mL). Acidification of the alkaline phase with concentrated HCl yielded **12** as a white powder: 864 mg (66%); mp 191-193 °C.

Acknowledgment. This work was suported by the Deutsche Forschungsgemeinschaft. Thanks are also due to J. Behrendt, E. Meier, and U. Krahmer for valuable technical assistance.

Registry No. **1a**, 83710-47-8; **1b**, 83710-48-9; **1c**, 83710-49-0; **1d**, 83710-50-3; **1e**, 77321-43-8; **1f**, 83710-51-4; **4a**, 4615-77-4; **4b**, 72007-85-3; **4c**, 1421-80-3; **4d**, 1421-81-4; **4e**, 4002-76-0; **4f**, 83710-52-5; **4g**, 63041-68-9; **5a**, 83710-53-6; **5b**, 83710-54-7; **5c**, 72378-87-1; **5d**, 83710-55-8; **5e**, 83710-56-9; **5f**, 83710-58-1; **5g**, 63077-06-5; **5h**, 83710-57-0; **6a**, 77321-41-6; **6b**, 83710-63-8; **7a**, 7702-48-9; **7b**, 41774-30-5; **7c**, 83710-64-9; **10**, 83710-59-2; 11, 73540-67-7; **12**, 77321-47-2; 1-bromo-8-methoxynaphthalene, 83710-60-5; 1-bromo-7-methoxynaphthalene, 83710-61-6; 1-bromo-6-methoxynaphthalene, 83710-62-7; 1-bromo-5-methoxynaphthalene, 74924-95-1; 1-bromo-4-methoxynaphthalene, 5467-58-3; 1-bromo-3-methoxynaphthalene, 5111-34-2; 1-bromonaphthalene, 90-11-9; 1,2-naphthalic anhydride, 5343-99-7; 1-amino-8-bromonaphthalene, 62456-34-2.

Supplementary Material Available: UV spectra of the phenols **4a-g** (7 pages). Ordering information is given on any current masthead page.

Rearrangements of Oxocyclopropanecarboxylate Esters to Vinyl Ethers. Disparate Behavior of Transition-Metal Catalysts

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Diverse transition-metal compounds catalyze the conversion of 2-alkoxycyclopropanecarboxylate esters to derivative vinyl ethers in high yield under mild conditions. With $[Rh(CO)_2Cl]_2$, $PtCl_2$·2PhCN, or $[Ru(CO)_3Cl_2]_2$, structural rearrangement occurs with concurrent epimerization of the reactant cyclopropane compound, and identical isomeric mixtures of vinyl ethers are formed from either of the two stereoisomeric cyclopropane reactants. Rhodium(II) acetate catalyzed reactions occur at higher temperatures than those required with $[Rh(CO)_2Cl]_2$, epimerization of the (*Z*)-cyclopropane isomer, but not the *E* isomer, is observed, and individual stereoisomeric cyclopropane reactants produce different isomeric mixtures of vinyl ether products. The characteristics of copper bronze and copper(I) chloride catalyzed reactions are generally similar to those of $Rh_2(OAc)_4$, except with ethyl 2-methoxy-2-vinylcyclopropanecarboxylate, which undergoes rearrangement to the isomeric ethyl 3-methoxycyclopentenecarboxylates in the presence of these copper catalysts. Participation by the carbethoxy group in rhodium(I)-, platinum(II)-, and ruthenium(II)-catalyzed reactions is indicated in results from comparative reactions with nitrile and sulfone derivatives, and the mechanistic involvement of a six-membered ring metallocycle is suggested. In rhodium(II)- and copper-catalyzed reactions, metallocyclobutane intermediates are proposed to account for their contrasting results. Catalytic rearrangement of (allyloxy)cyclopropanecarboxylate esters affords 3-allyl-4-oxoalkanoate esters in good yield by a synthetic coupling of the oxocyclopropane–vinyl ether and Claisen rearrangement transformations.

Activation by vicinal carbonyl substituents for ring-opening reactions of oxocyclopropanes has only recently become apparent in thermal[1,2] and Lewis acid promoted transformations.[3,4] β-Alkoxycyclopropanecarbonyl compounds, which are conveniently accessible from vinyl ethers and diazocarbonyl compounds,[5] have been termed "donor–acceptor cyclopropanes" in recognition of the electronic influence of their constituent substituents in ring-opening reactions. We have recently reported that β-alkoxycyclopropanecarboxylate esters undergo structural rearrangement to vinyl ethers under relatively mild conditions in the presence of a wide variety of transition-metal catalysts.[6] Rhodium(I), platinum(II), and ruthenium(II) compounds, which have known activity for structural rearrangements of small-ring hydrocarbons,[7-14] are the most effective catalysts for the conversion of oxocyclopropanes to vinyl ethers; however, copper and rhodium(II) compounds also catalyze this ring-opening transformation.

The facility with which vicinally substituted alkoxycyclopropanecarboxylates are converted to vinyl ethers contrasts with the known inhibition of cyclopropane ring opening by carboalkoxy substituents.[8] The combination of alkoxy and carboalkoxy substituents provides a synergism for cyclopropane ring opening by electrophilic reagents that intimates a specific participating role for these substituents in catalytic structural rearrangements. We now report the scope and limitations of the oxocyclopropane–vinyl ether transformation, examples of methodology for its synthetic utilization, and mechanistic details of this catalytic conversion that suggest a relationship between the oxocyclopropane–vinyl ether rearrangement and the apparent allyl CH insertion by carboalkoxycarbenoid species in catalytic cyclopropanation reactions with vinyl ethers[15] as well as with catalytic cis → trans isomerization of disubstituted cyclopropanes.[12,16a]

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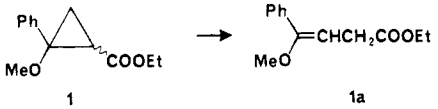
Table I. Catalyst Effectiveness for Structural Rearrangement of 1[a]

catalyst (mol %)	temp, °C	time,[b] h	1a, %	1a, E/Z
none	160	6	0	
Cu bronze (30)	160	6	90	1.1
CuCl (20)	160	2	70	1.2
CuCl·P(O-*i*-Pr)$_3$ (1.0)	160	1.5	75	1.2
PdCl$_2$·2PhCN (1.0)[c]	160	1.5	85	1.3
Rh$_2$(OAc)$_4$ (2.0)	135	1.2	93	1.8
[Rh(CO)$_2$Cl]$_2$ (2.5)	70	2	91	2.0
PtCl$_2$·2PhCN (2.5)	70	2	87	2.6
[Ru(CO)$_3$Cl$_2$]$_2$ (2.5)	70	2	92	2.4

[a] Reactant E/Z isomer ratio equal to 1.0 for each reaction. Reactions were performed without solvent. [b] Time required for complete conversion of 1 to 1a. Progress of reaction was followed by GC analysis. Reaction times were more than 10-times longer at reaction temperatures 20 °C lower than those reported. [c] Palladium(II) acetate (2.0 mol %) after 8 h at 140 °C produced 1a in 45% yield (E/Z = 1.2).

Results

Catalyst Effectiveness. Ethyl 2-methoxy-2-phenylcyclopropanecarboxylate (1) undergoes structural rearrangement to ethyl 4-methoxy-4-phenyl-3-butenoate (**1a**) in the presence of catalytic amounts of a variety of transition-metal compounds (eq 1). In the absence of these

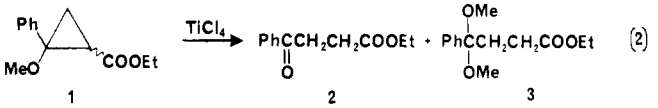


1 1a (1)

catalysts, 1 is inert to rearrangement at 160 °C over prolonged periods of time and can be distilled without decomposition at its boiling point of 210 °C. Copper and palladium catalysts are effective at relatively high temperatures, whereas [Rh(CO)$_2$Cl]$_2$, PtCl$_2$·2PhCN, and [Ru(CO)$_3$Cl$_2$]$_2$ promote structural rearrangement at temperatures as low as 70 °C. Rhodium(II) acetate falls between these two groups of catalysts in its effectiveness for vinyl ether production. Table I describes the minimum time for complete conversion of 1 (E/Z = 1.0) to **1a**, as well as isolated yields and stereoisomer ratios for the product vinyl ether.

The exceptional activities of rhodium(I) and ruthenium(II) compounds for structural rearrangements of cyclopropane compounds have been previously described,[8,10-12,14,17] but platinum(II) has not been reported to be similarly effective. However, no apparent differentiation in catalyst effectiveness between PtCl$_2$·2PhCN, [Rh(CO)$_2$Cl]$_2$, and [Ru(CO)$_3$Cl$_2$]$_2$ is evident in this investigation. In contrast, palladium(II) is often employed as an analogue of rhodium(I) for rearrangements of cyclopropane compounds,[8,16b] but in this investigation it is not as effective. At 160 °C, PdCl$_2$ is converted to metallic palladium during the course of the reaction; consequently, its relative activity cannot be established by comparison of results described in Table I. At 110 °C, both PdCl$_2$·2PhCN and (Ph$_3$P)$_2$Ir(CO)Cl catalyze the complete conversion of 1 to **1a** within 7 h, but both of these catalysts are ineffective at 70 °C.

Protonic acids promote the conversion of 1 to ethyl 3-benzoylpropionate (2) when these reactions are performed in aqueous media. In the presence of catalytic amounts of the Lewis acid TiCl$_4$ under anhydrous conditions, however, 3 is produced in addition to 2 (eq 2).



1 2 3 (2)

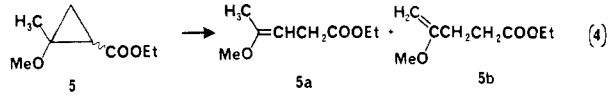
These same compounds are also evident as minor components (2, <6%; 3, <4%) of products isolated from transition metal catalyzed reactions.

The isomer ratio for **1a** is observably dependent on the reaction temperature and is moderately dependent on the catalyst that is employed (Table I). The E isomer is favored at the lower temperature, so that increasing the reaction temperature with rhodium(I), platinum(II), or ruthenium(II) catalyst from 70 °C produces a decrease in the E/Z ratio: for example, from 2.0 to 1.1 at temperatures from 70 to 140 °C for [Rh(CO)$_2$Cl]$_2$. Catalytic isomerization of vinyl ether products is not observed under reaction conditions employed for the catalytic structural rearrangement of 1.

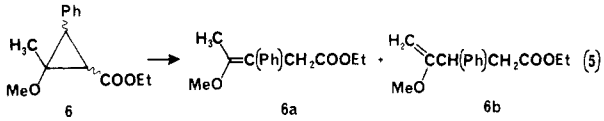
Structural Effects. Catalytic rearrangement of ethyl 2-alkoxycyclopropanecarboxylates is observed to be a general transformation that provides convenient access to vinyl ethers. In the absence of a substituent at the 2-position that possesses an α hydrogen, only one vinyl ether is produced (eq 1 and 3); when this substituent possesses

4 4a (3)

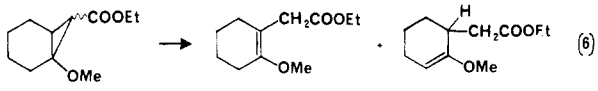
an α hydrogen, the isomeric vinyl ethers **a** and **b** are produced (eq 4–6). Isomerization of these vinyl ethers is



5 5a 5b (4)



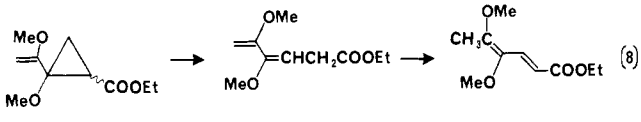
6 6a 6b (5)



7 7a 7b (6)

not generally observed nor is rearrangement to the corresponding conjugated ester. However, when a vinyl group is substituted at the 2-position of 2-alkoxycyclopropanecarboxylates, the initially formed vinyl ether undergoes slow rearrangement to the conjugated ester (eq 7 and 8)

8 8a 8b (7)



9 9a 9b (8)

with resultant production of intractable materials. Pertinent experimental results for these transformations are reported in Table II. In each reaction the (Z)-cyclopropane isomer, that in which the carbethoxy and alkoxy substituents are positioned cis, undergoes rearrangement at a faster rate than the E isomer. As indicated in the table, the product ratio **a**/**b** for catalytic rearrangements

(17) Gassman, P. G.; Mansfield, K. T.; Murphy, T. J. *J. Am. Chem. Soc.* **1969**, *91*, 1684.

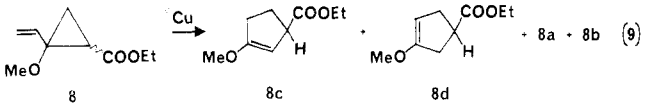
Table II. Transition Metal Catalyzed Rearrangements of 2-Alkoxycyclopropanecarboxylate Esters[a]

reactant (Z/E)[b]	catalyst (mol %)	temp, °C	time, min	yield a + b, %	a/b	a, E/Z
1 (1.0)	$PtCl_2 \cdot 2PhCN$ (1.0)	110	10	98		1.2
	$[Rh(CO)_2Cl]_2$ (0.5)	110	60	98		1.8
	Cu bronze (10)	210	5	97		1.0
4 (0.15)[c]	$PtCl_2 \cdot 2PhCN$ (1.0)	100	60	86		
	Cu bronze (20)	180	240	80		
5 (0.5)	$PtCl_2 \cdot 2PhCN$ (0.5)	110	30	70[d,e]	1.0	4.7
	$[Rh(CO)_2Cl]_2$ (0.5)	110	60	92	1.3	2.7
	Cu bronze (20)	160	150	83[d]	1.0	2.3
6[f]	$[Rh(CO)_2Cl]_2$ (0.5)	120	60	69	3.6	2.8
7 (2.2)	$PtCl_2 \cdot 2PhCN$ (1.0)	100	20	98	0.5	
	$[Rh(CO)_2Cl]_2$ (0.5)	110	60	98	0.6	
	$Rh_2(OAc)_4$ (0.5)	140	480	88	0.6	
	Cu bronze (20)	180	10	94	0.6	
8 (1.1)	$PtCl_2 \cdot 2PhCN$ (1.0)	100	45[g]	30	>10	1.6
	$[Rh(CO)_2Cl]_2$ (5.0)[e]	110	60	56	5	1.6
	$Rh_2(OAc)_4$ (2.0)[h]	135	240	60	0.5	1.2
9 (1.2)	$Rh_2(OAc)_4$ (2.0)	170	240	56	2.6	2.0
	$Rh_2(OAc)_4$ (2.0)[i]	150	24 h[j]	70	3.6	2.2

[a] Unless specified otherwise, reactions were performed on the neat reactant without solvent. Yields were determined for products isolated by distillation. [b] Isomer ratio for reactant cyclopropane. [c] With $Rh_2(OAc)_4$ at 140 °C for 3 h, only the Z(syn) isomer had reacted to form 4a. [d] Ethyl 4-oxopentanoate was obtained in 20% yield from $PtCl_2 \cdot 2PhCN$-catalyzed reactions and in 10% yield from reactions catalyzed by copper bronze. [e] Reaction performed in toluene. [f] All four stereoisomers are present. [g] Rearrangement was 80% complete; 20% starting material obtained. [h] Reaction performed in nitrobenzene. [i] Time course of reaction: 16 h (45% 9, 50% 9a, 5% 9b), 42 h (10% 9, 44% 9a, 18% 9b), 63 h (6% 9, 18% 9a, 13% 9b). [j] 16% 9 recovered.

of 5 and 7 is not observed to be a sensitive function of temperature.

With copper catalysts, vinylcyclopropane 8 undergoes rearrangement by a different course from that observed with rhodium(II), rhodium(I), and platinum(II) catalysts to produce cyclopentenecarboxylates 8c and 8d, along with variable amounts of 8a and 8b (eq 9). Higher yields of



8 8c 8d

8c and 8d are achieved with copper bronze (10 mol %, 2 h/160 °C; 41% yield, **c/d** = 1.1) than with copper(I) chloride (10 mol %, 4 h/135 °C; 22% yield, **c/d** = 1.6), and more of the acyclic products 8a and 8b are formed with CuCl [estimated 40% yield, (*Z*)-8a/(*E*)-8a > 5] than with copper bronze [estimated 30% yield, (*Z*)-8a/(*E*)-8a > 5]. Since 8a is converted to 8b and the resultant combination is relatively unstable at temperatures near 150 °C, presumably due to [4 + 2] cycloaddition of 8b to 8a,[18] 8c and 8d can be conveniently distilled from these reaction mixtures free of contamination by 8a or 8b. These cyclopentenecarboxylate esters are unique to reactions performed with copper catalysts and are not observed in rhodium- or platinum-catalyzed transformations of 8. Both 8c and 8d were stable under the reaction conditions employed for this study, and catalytic interconversion between 8c and 8d did not occur. Under similar conditions to those employed for catalytic rearrangements of 8, 9 did not produce cyclic products analogous to 8c and 8d in copper-catalyzed reactions.

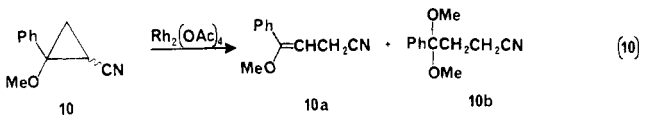
Catalytic rearrangements of 2-alkoxycyclopropanecarboxylates are usually performed without solvent, but selected solvents, such as toluene, do not generally affect the outcome of these reactions. However, in the presence of polar organic compounds, cyclopropane rearrangement occurs with the loss of the methyl group from the methyl ether. For example, in the presence of *n*-butyl vinyl ether, 1 is converted exclusively to 2 by $[Rh(CO)_2Cl]_2$. Increased production of 2 is also observed when the rearrangement of 1 is performed in diethyl fumarate or diethyl methylenemalonate, but in neither case are adducts of the reactant with the solvent produced. Acetone does not affect the rearrangement of 1 to 1a, but methyl vinyl ketone directs the conversion of 1 to 2 exclusively in the presence of $PtCl_2 \cdot 2PhCN$. The vinyl ether products derived from cyclopropane rearrangements are themselves inert to these solvents under identical reaction conditions.

As previously communicated,[6] cyclopropane compounds analogous to those reported here, but without either the vicinal alkoxy or carbethoxy substituent, do not undergo structural rearrangement under reaction conditions analogous to those reported in Table II. The compounds examined included 1-methoxy-1-phenylcyclopropane, which was inert to ring opening by $PtCl_2 \cdot 2PhCN$ even at 160 °C;[19] diethyl *trans*-1,2-cyclopropanedicarboxylate, which was recovered unchanged after treatment with either copper or rhodium catalysts at 200 °C; diethyl 1,1-cyclopropanedicarboxylate, which was inert to ring opening by either copper catalysts or by $PtCl_2 \cdot 2PhCN$ at 160 °C; and ethyl 2-(*trans*-β-methoxyvinyl)cyclopropanecarboxylate, which was recovered unchanged after treatment with copper or rhodium catalysts at 145 °C. In addition, replacement of the carbethoxy group of 1 by either the cyano (**10**) or *p*-toluenesulfonyl (**11**) group provided substantial inhibition of catalytic structural rearrangement. Whereas with the carbethoxy derivative 1 rearrangement occurred at 70 °C in the presence of $[Rh(CO)_2Cl]_2$ or $PtCl_2 \cdot 2PhCN$, no reaction was observed with the cyano derivative 9 in the presence of either of these catalysts at temperatures up to 120 °C. After 7 h at 160 °C in the presence of 1.0 mol % $Rh_2(OAc)_4$, however, **10** (E/Z = 1.0) was converted to vinyl ethers **10a** (E/Z = 1.2) and ketal **10b** (eq 10) in 75 and 8% yield, respectively (67% **10a** and 6% **10b** after distillation). Copper catalysts were ineffective at 160 °C, and **10** was thermally stable at this temperature. Similarly,

(18) Sauer, J. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 16.

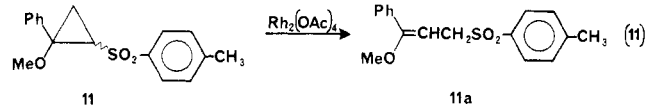
(19) In the presence of 1.0 molar equiv of water and 5 mol % of $PtCl_2 \cdot 2PhCN$, 1-methoxy-1-phenylcyclopropane was converted at 100 °C to propiophenone as the sole monomeric product (62% isolated yield).

(20) The toluenesulfonyl analogue of 5 did not produce vinyl ethers but instead formed 1-(*p*-toluenesulfonyl)-3-butanone as the sole reaction product in $PtCl_2 \cdot 2PhCN$ and copper-catalyzed reactions performed at temperatures between 160 and 210 °C. This cyclopropane compound was also inert to catalytic rearrangement at temperature at or below 120 °C.



10 10a 10b

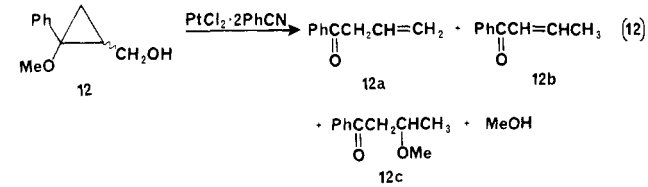
the tosyl derivative **11** (E/Z = 0.91), which was inert to $PtCl_2$·2PhCN-catalyzed rearrangement at 110 °C, was converted to the corresponding vinyl ether **11a** (E/Z = 0.82) in 82% yield at 160 °C in the presence of 2.0 mol % $Rh_2(OAc)_4$ after 4 h (eq 11). Both $[Rh(CO)_2Cl]_2$ and



11 11a

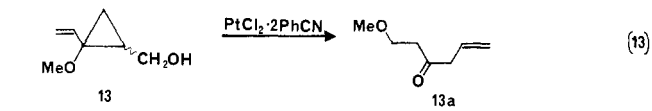
$PtCl_2$·2PhCN were also active at 160 °C, but monomeric product yields were considerably lower than those obtained with $Rh_2(OAc)_4$ (e.g., with $[Rh(CO)_2Cl]_2$, **10a** and **10b** were produced in 23 and 33% yield, respectively), and reaction times for complete conversion with these catalysts were comparable to those from reactions with $Rh_2(OAc)_4$. However, the structural integrity of rhodium(I) and platinum(II) catalysts could not be maintained with these systems at 160 °C, and rigorous comparisons between these catalytic systems could not be determined.

Reduction of **1** with lithium aluminum hydride produced alcohol **12**, which was stable toward thermal decomposition and toward $Rh_2(OAc)_4$-catalyzed decomposition at temperatures as high as 190 °C but underwent conversion to **12a–c** and methanol at 110 °C in the presence of $PtCl_2$·2PhCN (eq 12). Isomerization of **12a** to **12b** occurred



12 12a 12b 12c

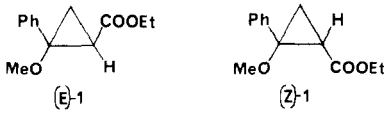
during the course of this reaction. In the absence of solvent, these compounds were isolated in only 48% yield, and no significant yield improvement was obtained when this reaction was performed in toluene (53% yield). Similarly **13**, which was also thermally stable and inert to decomposition by copper catalysts, produced **13a** when heated at 110 °C in the presence of $PtCl_2$·2PhCN (eq 13),



13 13a

but product yields were less than 30%.

Catalytic Isomerization of 2-Alkoxycyclopropanecarboxylates. As previously mentioned, (*Z*)-2-alkoxycyclopropanecarboxylates are more reactive toward structural rearrangement than their corresponding *E* isomers. In order to identify the specific outcome of these catalytic reactions, the individual geometrical isomers of **1** were separated by distillation, treated with selected



catalysts at appropriate temperatures, and their conversion to products was monitored at regular intervals. Figures 1 and 2 describe the time courses for rearrangement of the *Z* and *E* isomers of ethyl 2-methoxy-2-phenylcyclopropanecarboxylate (**1**) catalyzed by $[Rh(CO)_2Cl]_2$ at 70 °C. Surprisingly, both the (*E*)- and (*Z*)-cyclopropane

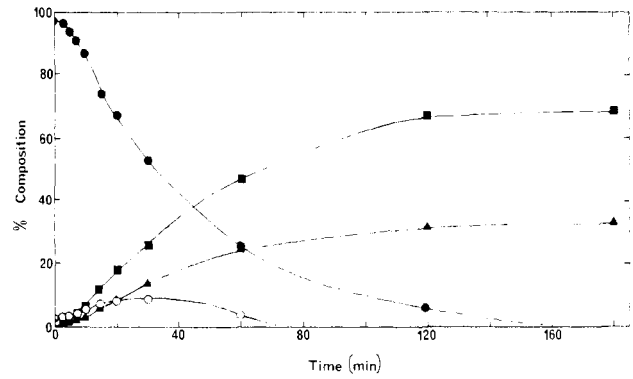


Figure 1. Rearrangement of ethyl (*E*)-2-methoxy-2-phenylcyclopropanecarboxylate (97% *E*, 3% *Z*) at 70 °C in the presence of 2.5 mol % bis(chlorodicarbonylrhodium): (●) (*E*)-**1**; (○) (*Z*)-**1**; (■) (*E*)-**1a**; (▲) (*Z*)-**1a**. Actual product yields are reported.

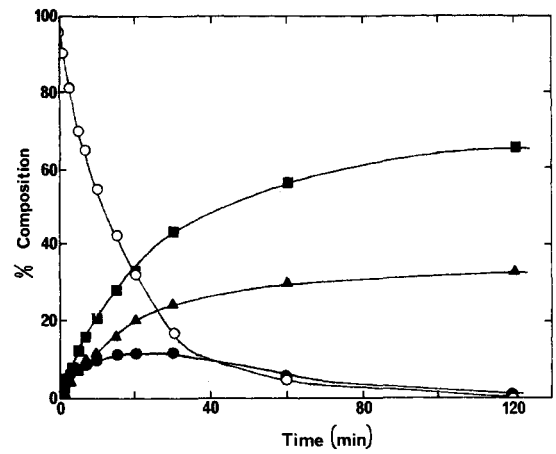
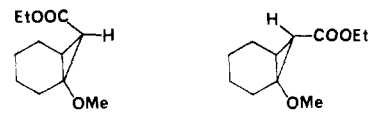


Figure 2. Rearrangement of ethyl (*Z*)-2-methoxy-2-phenylcyclopropanecarboxylate (94% *Z*, 6% *E*) at 70 °C in the presence of 2.5 mol % bis(chlorodicarbonylrhodium): (●) (*Z*)-**1**; (○) (*E*)-**1**; (■) (*E*)-**1a**; (▲) (*Z*)-**1a**. Actual product yields are reported.

isomers are interconvertible, and the E/Z vinyl ether isomer ratio obtained from either reactant cyclopropane is 2.0. As anticipated, (*Z*)-**1** is more reactive than (*E*)-**1**, but the times for 50% conversion of **1** to **1a** differ by only a factor of two at 70 °C. Similar results were observed in comparable investigations performed at 100 °C, at which temperature cyclopropane rearrangement to vinyl ether **1a** occurred 30-times faster than at 70 °C when the same amount of catalyst was employed. Use of $[Rh(CO)_2Cl]_2$ in amounts ranging from 1.0 to 10 mol % resulted in rates for cyclopropane rearrangement that were linearly dependent on the amount of catalyst employed. Isomerization of the reactant cyclopropane was also observed in $PtCl_2$·2PhCN-catalyzed reactions of **1**.

The time courses for catalytic rearrangement of the *E* and *Z* isomers of **1** with $Rh_2(OAc)_4$ at 135 °C are depicted in Figures 3 and 4. With this catalyst, only the conversion of (*Z*)-**1** to (*E*)-**1** is detectable, and the isomer ratio of vinyl ethers is dependent on the geometry of the cyclopropane reactant: E/Z (**1a**) = 3.3 from (*Z*)-**1** and 2.0 from (*E*)-**1**. The relative rate for rearrangement of (*Z*)-**1** to **1a** is twice that for the conversion of (*E*)-**1** to **1a**.

The contrasting behavior of $[Rh(CO)_2Cl]_2$ and $Rh_2(OAc)_4$ is also evident in the rearrangement of the syn and anti isomers of **7**. With $[Rh(CO)_2Cl]_2$, reaction of either



syn-7 anti-7

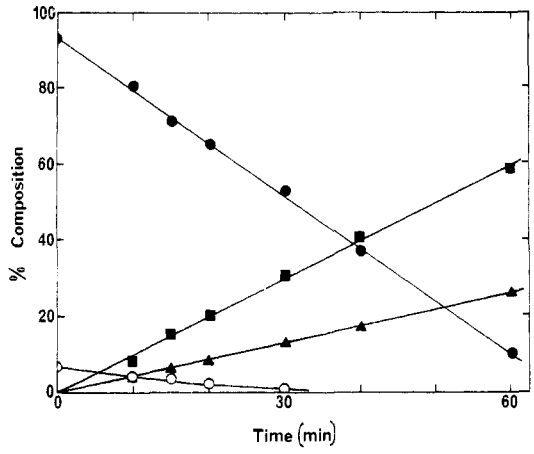


Figure 3. Rearrangement of ethyl (*E*)-2-methoxy-2-phenylcyclopropanecarboxylate (93% *E*, 7% *Z*) at 135 °C in the presence of 2.5 mol % rhodium(II) acetate: (●) (*E*)-**1**; (○) (*Z*)-**1**; (■) (*E*)-**1a**; (▲) (*Z*)-**1a**. Actual product yields are reported.

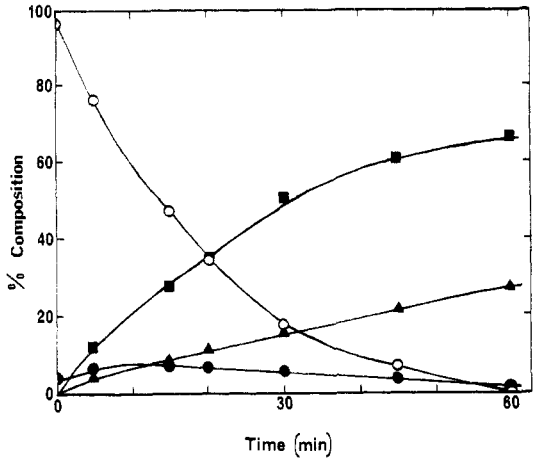
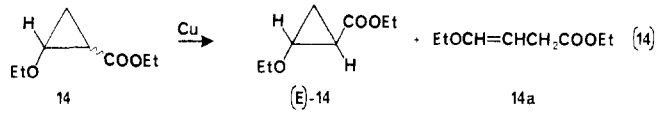


Figure 4. Rearrangement of ethyl (*Z*)-2-methoxy-2-phenylcyclopropanecarboxylate (96% *Z*, 4% *E*) at 135 °C in the presence of 2.5 mol % rhodium(II) acetate: (●) (*Z*)-**1**; (○) (*E*)-**1**; (■) (*E*)-**1a**; (▲) (*Z*)-**1a**. Actual product yields are reported.

cyclopropane isomer at 140 °C yields **7a** and **7b** with approximately identical ratios (**7b**/**7a** = 2.0 ± 0.1), and the same product ratio is observed from catalytic rearrangement of a 37:63 mixture of the syn and anti isomers of **7**. With $Rh_2(OAc)_4$ at 140 °C, however, *anti*-**7** produces a **7b**/**7a** product ratio of 2.9, *syn*-**7** produces a **7b**/**7a** product ratio of 0.55, and a 37:63 mixture of the syn and anti isomers of **7** produce a **7b**/**7a** product ratio of 1.7, precisely that which would be predicted from stereochemical results with the individual cyclopropane isomers.

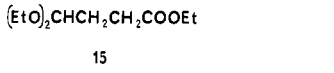
Treatment of (*Z*)-2-methoxy-2-phenylcyclopropanenitrile (**10**) with 1.0 mol % $Rh_2(OAc)_4$ at 175 °C resulted in the production of vinyl ethers **10a** and in partial epimerization of the reactant cyclopropane. At 50% conversion of (*Z*)-**10** to productds, (*E*)-**10** was present in its maximum overall yield (12%), and the *E*/*Z* ratio for **10a** was 0.6. (*E*)-2-Methoxy-2-phenylcyclopropanenitrile did not exhibit observable epimerization under the same conditions but produced vinyl ethers **10a** with an *E*/*Z* ratio of 1.6. The *E*/*Z* ratios for **10a** from $[Rh(CO)_2Cl]_2$- and $PtCl_2$·2PhCN-catalyzed reactions were also dependent on the geometry of the reactant cyclopropane: 1.0 from (*Z*)-**10** and 1.8 from (*E*)-**10** in $[Rh(CO)_2Cl]_2$-catalyzed reactions and 1.2 from (*Z*)-**10** and 2.0 from (*E*)-**10** in $PtCl_2$·2PhCN-catalyzed reactions, both at 160 °C.

Selective Catalytic Rearrangement of (*Z*)-2-Alkoxycyclopropanecarboxylates. 2-Alkoxycyclopropanecarboxylates without aryl or alkyl substituents at the 2-position undergo catalytic structural rearrangement only at very high temperatures relative to those reported in Table II, but only the *Z* isomer is reactive. In the presence of 15 mol % copper bronze at 190 °C, ethyl 2-ethoxycyclopropanecarboxylate (**14**, *E*/*Z* = 1.6) is converted after 2.5 h to a mixture of (*E*)-**14** and ethyl 4-ethoxy-3-butenoate (**14a**, *E*/*Z* = 1.4) in 90% isolated yield (eq 14). The



(14)

amount of (*E*)-**14** recovered from this reaction was greater than that initially employed by 13%, which suggests that (*Z*)-**14** undergoes competitive decomposition to (*E*)-**14** and **14a**. Heating for an additional 5 h at 190 °C produced no further change in the ratio of **14a** to (*E*)-**14**. Neither $PtCl_2$·2PhCN at 100 °C (3 h) nor $[Rh(CO)_2Cl]_2$ at 155 °C (1 h) were effective in converting **14** to **14a**; however, with either catalyst, (*Z*)-**14** was the only isomer to under decomposition. Acetal **15** was the only monomeric product



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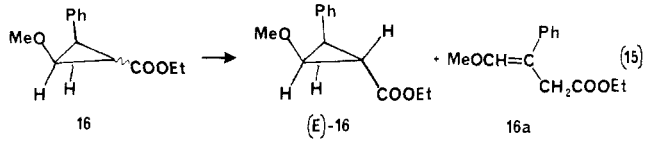
formed, albeit in relatively low yield (<20%), and a considerable amount of nonvolatile products resulted from these transformations.

Catalytic rearrangement of the cyclopropane isomers (**16**), derived from the reaction between *cis*-β-methoxystyrene and ethyl diazoacetate, were performed with copper catalysts and $Rh_2(OAc)_4$ at elevated temperatures. With anhydrous copper(I) chloride (10 mol %) at 250 °C for 15 min, the isomeric cyclopropane mixture (**16**, *E*/*Z* = 2.0) was transformed (eq 15) to (*E*)-**16** and the vinyl



(15)

ether **16a** (*E*/*Z* = 1.5) in 96% isolated yield. Since only (*Z*)-**16** was reactive under these conditions, the resultant products and their respective yields [83% (*E*)-**16**; 13% **16a**) define the net transformation as a partitioning of (*Z*)-**16** between (*E*)-**16** and **16a** in 55 and 45% yield, respectively. Similar results were obtained with copper bronze at 200 °C (2 h) and $Rh_2(OAc)_4$ at 160 °C (2 h). Isomerization of (*Z*)-**16** to (*E*)-**16** occurred without formation of any observable quantities of cyclopropane isomers possessing the *trans*-phenyl/methoxy geometry.

Catalytic Rearrangement of 2-(Allyloxy)cyclopropanecarboxylates. Allyl vinyl ethers undergo selective cyclopropanation of the vinyl group in $Rh_2(OAc)_4$-catalyzed reactions with ethyl diazoacetate. This selectivity provides a molecular construction designed for catalytic conversion of the reactant cyclopropane to its derivative allyl vinyl ethers (Scheme I) with subsequent Claisen rearrangement[21-23] of these intermediates. Four (allyloxy)cyclopropanecarboxylate systems (**17**–**20**) were constructed to evaluate this catalytic transformation (eq

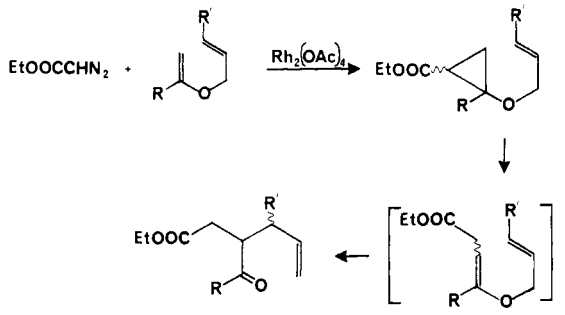
(21) Rhoads, S. J. *Org. React.* **1975**, *22*, 1.
(22) Ziegler, F. E. *Acc. Chem. Res.* **1977**, *10*, 227.
(23) Bennett, G. *Synthesis* **1977**, 590.

Table III. Product Yields from Rhodium-Catalyzed Rearrangements of Ethyl 2-(Allyloxy)cyclopropanecarboxylates[a]

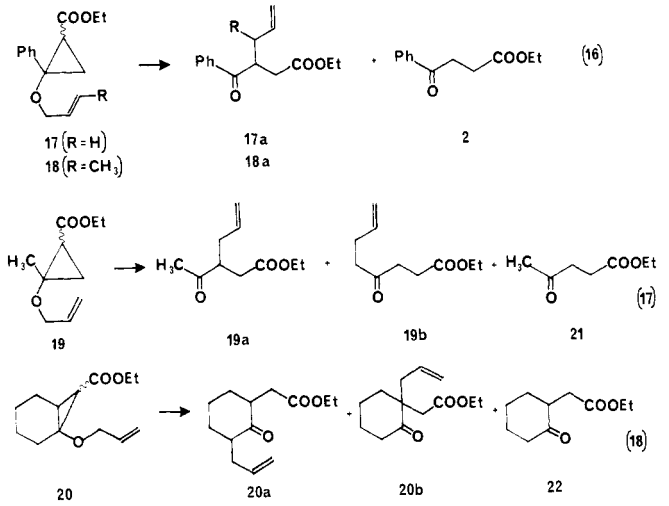
reactant (Z/E)	catalyst (mol %)	temp, °C	time,[b] min	product (yield, %)
17 (1.1)	$[Rh(CO)_2Cl]_2$ (1.0)	110	60	17a (72), 2 (26)
18 (1.2)	$[Rh(CO)_2Cl]_2$ (1.0)	110	120	18a (78), 2 (20)
19 (0.8)	$[Rh(CO)_2Cl]_2$ (1.0)	120	60	19a (49), 19b (8), 21 (38)
20 (2.3)	$[Rh(CO)_2Cl]_2$ (1.0)	140	45	20a (62), 20b (19), 22 (5)
20 (2.3)	$Rh_2(OAc)_4$ (2.5)	140	480	20a (58), 20b (19), 22 (9)

[a] Reactions were performed on the neat reactant. Yields were determined for products after separation from the catalyst. [b] Reaction times are those for ≥95% conversion of reactants to products. At shorter reaction times, reactant cyclopropane was observed.

Scheme I



16–18), and the composite results are reported in Table III.



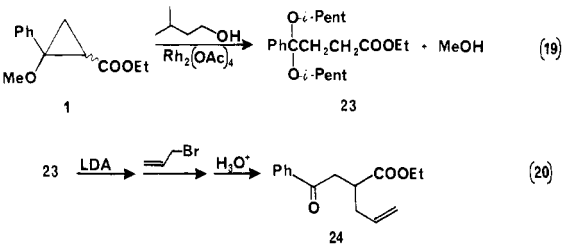
Catalytic rearrangement of (allyloxy)cyclopropanecarboxylates affords 3-allyl-4-oxoalkanoates in good yield and is accountable by the sequence of transformations reported in Scheme I. The specificity of the Claisen rearrangement is demonstrated by the conversion of **18** to **18a**; the isomeric 2-buten-1-yl derivative was not observed. In all catalytic transformations, however, a significant amount of product without the substituent allyl group (**2**, **21**, and **22**) was formed. Since these reactions were performed with the rigorous exclusion of water and the results obtained were reproducible, it is unlikely that hydrolysis of the intermediate vinyl ether could account for the formation of these unsubstituted 4-oxoalkanoate esters. Rearrangement of **19** shows a definite preference for **19a** (**a**/**b** = 6.1), which is surprising in view of the formation of nearly equal amounts of **5a** and **5b** from the analogous methyl ether under comparable conditions (Table II). In contrast, rearrangement of **20** forms **20a** with a selectivity [**a**/**b** = 3.2 with $[Rh(CO)_2Cl]_2$ and 3.0 with $Rh_2(OAc)_4$] that is compatible with the 2:1 preference for **7b** relative to **7a** in catalytic rearrangements of methyl ether **7**.

Table IV. Product Yields from Catalytic Rearrangement of 25[a]

catalyst (mol %)	temp, °C	time, min	yield, % 25a (E/Z)	25b	26
$PtCl_2 \cdot 2PhCN$ (5.0)	120	10	53 (1.3)	30	11
$[Ru(CO)_3Cl_2]_2$ (2.5)	120	10	69 (0.6)	17	1
$Rh_2(OAc)_4$ (2.5)	140	180	79 (1.8)	15	0
$[Rh(CO)_2Cl]_2$ (2.5)	140	10	90 (2.0)	8	0

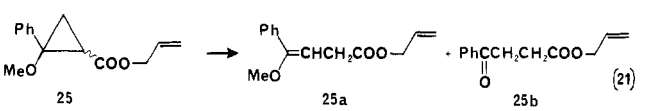
[a] Reactions were performed on the neat reactant (E/Z = 2.0). Yields were determined for products after separation from catalyst.

In the presence of isopentyl alcohol, $Rh_2(OAc)_4$ catalyzes the conversion of **1** to ketal **23** (eq 19), which was employed

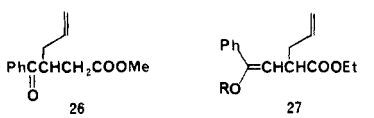


for the preparation of **24** (eq 20) in order to distinguish this compound, the product of a homo-Claisen rearrangement of **1**, from **17a**. Formation of vinyl ether **1a** precedes ketal formation, and the mixed ketal from isopentyl alcohol addition to **1a** is observed, but only limited conversion to **2** occurs in $Rh_2(OAc)_4$-catalyzed reactions. However, when the analogous transformation between allyl alcohol and **1** was attempted with either $[Rh(CO)_2Cl]_2$ or $PtCl_2 \cdot 2PhCN$, only keto ester **2** was formed (isolated in 98% yield).

Catalytic Rearrangement of Allyl 2-Methoxy-2-phenylcyclopropanecarboxylate. Allyl 2-methoxy-2-phenylcyclopropanecarboxylate (**25**) was prepared from **1** by transesterification and then subjected to reaction conditions for ring opening in the presence of a selection of transition metal catalysts (eq 21). As anticipated, the



principal products formed in these reactions were the vinyl ether isomers **25a** and derivative keto ester **25b**, whose yield was dependent on the catalyst employed (Table IV). However, with $PtCl_2 \cdot 2PhCN$, rearrangement product **26**,



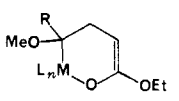
which results from allyl group rearrangement and methyl ether/ester interchange, was also observed; this same compound was present in trace amounts in mixtures pro-

duced from reactions catalyzed by $[Ru(CO)_3Cl_2]_2$ but not from reactions catalyzed by $[Rh(CO)_2Cl_2]_2$ or $Rh_2(OAc)_4$. Compound **26** was not formed from **25a**, nor did reaction of **27** (R = isopentyl) with $PtCl_2$·2PhCN lead to a product analogous to **26**.[24] Attempts to define the specificity of the conversion of **25** to **26** through the use of the *trans*-2-buten-1-yl ester analogue of **25** were unsuccessful because of the occurrence of $PtCl_2$·2PhCN-catalyzed [3,3]sigmatropic rearrangement of this allyl carboxylate, which is analogous to the previously reported $PdCl_2$·2PhCN-catalyzed rearrangement.[25,26]

Discussion

Results obtained for catalytic structural rearrangement of 2-alkoxycyclopropanecarboxylates suggest a general capability among diverse transition-metal compounds to promote the formation of vinyl ethers. The synthetic advantages of this transformation relative to thermolysis[2,3] are addressed in the examples provided in Tables II–IV, which indicate the versatility of the oxocyclopropane–vinyl ether rearrangement for entry to 1,4-dicarbonyl compounds and, through coupling of this process with the Claisen rearrangement of allyl vinyl ethers, to allyl substituted 1,4-dicarbonyl compounds. Although ring cleavage of alkoxycyclopropanecarboxylates is facilitated by Lewis acids, such as $TiCl_4$, conversion to 4-oxocarboxylates rather than to vinyl ethers is preferred, thus suggesting that hydrogen transfer to the α position of the carboxylate group is a principal function of the participating metal in the catalytic process.

The transition-metal compounds that have been employed for the oxocyclopropane–vinyl ether rearrangement can be divided into three groups based on their comparative effectiveness for structural rearrangement, on specific differences in comparative reaction dynamics between catalysts, and on the existence of divergent pathways for rearrangement of ethyl 2-methoxy-2-vinyl-cyclopropanecarboxylate (**8**). As demonstrated by the results presented in Table I, $[Rh(CO)_2Cl]_2$, $PtCl_2$·2PhCN, and $[Ru(CO)_3Cl_2]_2$ are the most reactive catalysts for the oxocyclopropane–vinyl ether rearrangement. With this group of catalysts, transformation of 2-alkoxycyclopropanecarboxylates into vinyl ethers is accompanied by interconversion of the isomeric cyclopropanes (Figures 1 and 2). In addition, each cyclopropane isomer produces the same ratio of vinyl ether products, whether from a comparison of geometrical isomers, as is observed in the catalytic rearrangement of ethyl (*E*)- and (*Z*)-2-methoxy-2-phenylcyclopropanecarboxylates (**1**) or from a comparison of positional isomers, as is observed in the catalytic rearrangement of ethyl (*E*)- and (*Z*)-1-methoxybicyclo[4.1.0]heptane-7-carboxylate (**7**). These observations suggest the existence of a single reaction intermediate that can be entered from either the (*E*)- and (*Z*)-cyclopropane isomer and from which both cyclopropane and vinyl ether isomers can be formed. Metallocycle **28** is consistent with these observations and



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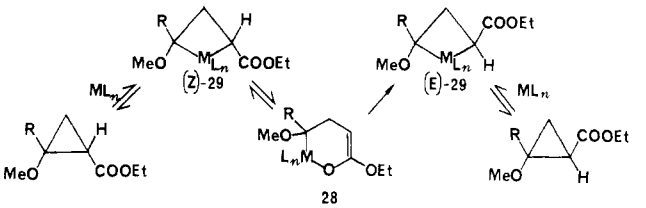
efficiently accounts for the distinctive features of the $[Rh(CO)_2Cl]_2$, $PtCl_2$·2PhCN, and $[Ru(CO)_3Cl_2]_2$-catalyzed

Scheme II



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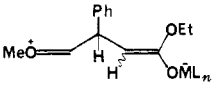
reactions. An analogous metallocyclohexane has been proposed to account for epimerization of *syn*-7-vinylbicyclo[4.1.0]heptane, although in this case only the syn → anti isomerization was observed, and isomeric diene products formed by structural rearrangement were dependent on the geometry of the reactant cyclopropane.[12] The present results provide the first examples that suggest the commonality of a six-membered ring metallocycle in structural rearrangements of isomeric cyclopropane derivatives. Alternate explanations that invoke metallocyclobutanes or their acyclic counterparts are not consistent with interconversion of epimeric cyclopropanes (Figures 1 and 2), the insensitivity of the isomeric vinyl ether product ratio to reactant cyclopropane geometry, or the relative unreactivity of cyano and sulfone derivatives (**10** and **11**) with this group of catalysts.

Results obtained for structural rearrangement of 2-alkoxycyclopropanecarboxylates by $Rh_2(OAc)_4$ define a more complex mechanistic relationship that is characteristic of a second group of catalysts. Epimerization of (*Z*)-**1**, but not of (*E*)-**1**, is observed (Figures 3 and 4), and vinyl ether isomer ratios obtained from structural rearrangement of ethyl (*E*)- and (*Z*)-2-methoxy-2-phenylcyclopropanecarboxylates (**1**) and of ethyl (*E*)- and (*Z*)-1-methoxybicyclo[4.1.0]heptane-7-carboxylate (**7**) are dependent on the geometry of the cyclopropane reactant. These observations are consistent with a mechanistic scheme in which metallocyclobutane intermediates (*Z*)-**29** and (*E*)-**29**, analogous to those employed to explain ring-opening transformations of simpler cyclopropane compounds[7,8,9,12] are entered directly from the individual cyclopropane isomers (Scheme II). Epimerization of the (*Z*)-cyclopropane isomer is explained by isomerization of metallocyclobutane (*E*)-**29** to the six-membered ring metallocycle **28**. An alternate explanation, that catalytic ring opening involves metal-induced formation of alkoxy-stabilized acyclic carbenium ion intermediates, such as **30** (from **16**,



30

eq 15), is inconsistent with the absence of any observable quantity of cyclopropane isomers possessing the *trans*-phenyl/methoxy geometry.[27] A similar scheme involving acyclic carbenium ion intermediates, invoked to account for rhodium(I)-catalyzed ring-cleavage rearrangements of

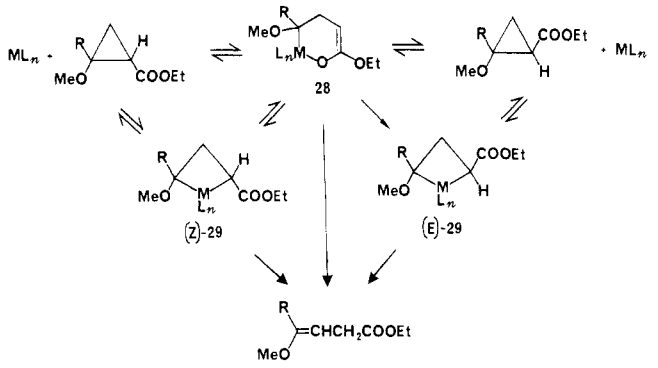
(24) Only 1,2-bond migration of the allyl substituent was observed in reactions performed at 120 °C for 15 min.

(25) Grieco, P. A.; Takigawa, T.; Bongers, S. L.; Tanaka, H. *J. Am. Chem. Soc.* **1980**, *102*, 7587.

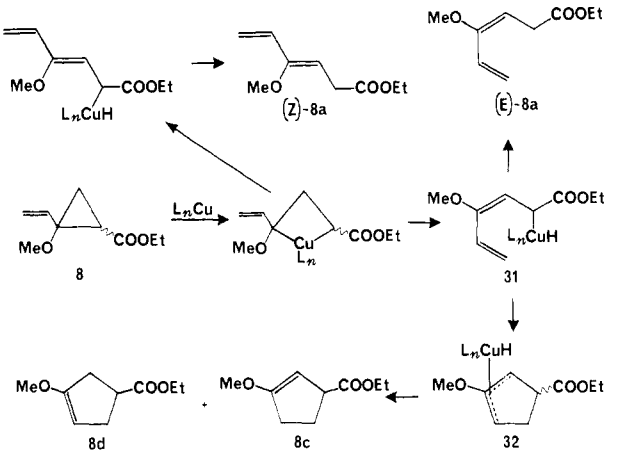
(26) Overman, L. E.; Knoll, F. M. *Tetrahedron Lett.* **1979**, 321.

(27) However, acyclic carbenium ion intermediates similar to **30** may contribute to the overall characteristics of oxocyclopropane decomposition. Relatively weak nucleophiles, such as esters, ketones, and vinyl ethers, present as reaction solvents, increase the production of 4-keto esters. These normally minor byproducts, which are major products from Lewis acid promoted reactions of 2-alkoxycyclopropanecarboxylate esters (e.g., eq 2), conceivably arise from alkoxy-stabilized carbenium ions by intermolecular alkyl transfer, and their formation may be indicative of the involvement of acyclic carbenium ions in transition-metal catalyzed reactions. The extent of their involvement in the formation of vinyl ethers and in cyclopropane epimerization, based on the absence of such processes in Lewis acid promoted reactions, can reasonably assumed to be minimal.

Scheme III



Scheme IV



vinylcyclopropanes,[28,29] has been discounted by results from a recent detailed examination of this rearrangement process.[12]

Comparison of the reaction temperatures required for catalytic ring opening of ethyl 2-methoxy-2-phenylcyclopropanecarboxylate (1) and its analogous nitrile (10) and tosyl (11) derivatives demonstrates the unique activity of $[Rh(CO)_2Cl]$, $PtCl_2 \cdot 2PhCN$, and $[Ru(CO)_3Cl_2]_2$ for ring opening of the carbethoxy derivative. Rearrangement of 1 is complete within 2 h at 70 °C, whereas with either 10 or 11 no reaction is observed at temperatures up to 120 °C. In contrast, the $Rh_2(OAc)_4$-catalyzed rearrangement of 1 is complete within 1 h at 140 °C, and with either 10 or 11 at 160 °C, ring opening appears to occur with the same facility as in reactions with $[Rh(CO)_2Cl]_2$ and $PtCl_2 \cdot 2PhCN$ under identical reaction conditions. These results suggest that in $[Rh(CO)_2Cl]_2$, $PtCl_2 \cdot 2PhCN$, and $[Ru(CO)_3Cl_2]_2$-catalyzed reactions of 2-alkoxycyclopropanecarboxylates, the six-membered ring metallocycle 28 is entered directly from the cyclopropane reactant without initial involvement of metallocyclobutanes 29 (Scheme III), whereas in $Rh_2(OAc)_4$-catalyzed reactions, metal insertion results in the formation of metallocyclobutanes. Substitution of the cyano or tosyl functional group for the carbethoxy group, as anticipated, severely inhibits coordination that could result in the direct production of 28 but, as is evident in comparative results from $Rh_2(OAc)_4$-catalyzed reactions of 1, 10, and 11, does not substantially inhibit entry into the reaction manifold through metallocyclobutane intermediates. Participation of metallocyclobutane intermediates in vinyl ether production for $[Rh(CO)_2Cl]_2$-, $PtCl_2 \cdot 2PhCN$-, and $[Ru(CO)_3Cl_2]_2$-catalyzed reactions of 2-alkoxycyclopropanecarboxylates subsequent to the formation of 28 cannot be determined with data available from these investigations; however, such strained systems are anticipated to be relatively unimportant from prior investigations of the effect of ring size on β-hydrogen elimination with platinum(II) metallocycles.[30]

Vinyl ether isomer ratios in the transition metal catalyzed oxocyclopropane–vinyl ether rearrangement are consistent with a mechanism involving β-hydrogen elimination from metallocyclobutane intermediates or from metallocycle 28 (Scheme III). However, the absence of stereospecificity in these transformations, particularly for the conversion of 16 to 16a, precludes convincing definition of the exact mechanism for vinyl ether production. Although the mechanistic features of this transformation may be written to include η^3-enolate complexes, as well as 28 or 29, the relative degree of coordination unsaturation for η^1-enolate complexes provides a reasonable and efficient structural basis for discussion of selectivity in β-hydrogen elimination. Metallocycles undergo concerted β-hydrogen elimination from the syn periplanar molecular geometry,[31-33] which is sufficiently constrained in the proposed metallocyclobutanes to account for the observed dependence of the vinyl ether isomer ratio on the geometry of the reactant cyclopropane and on the reaction temperature.[34] Hydrogen transfer in metallocycle 28 can be viewed similarly but, in this case, the vinyl ether isomer ratio should be, and is experimentally, independent of the geometry of the reactant cyclopropane.

Copper bronze and copper(I) chloride are representatives of the third group of catalysts whose differential characteristics are seen in the vinylcyclopropane–cyclopentene rearrangement of 8 that is described in eq 9. The formation of both 8c and 8d under conditions where these two isomers are not interconvertible demonstrates that their production is not derived from previously examined vinylcyclopropane–cyclopentene rearrangement processes.[35-37] Consideration of the analogous behavior of copper and rhodium(II) acetate with other cyclopropane systems suggests that the copper-promoted conversion of vinylcyclopropane 8 to cyclopentenes 8c and 8d is a direct consequence of the η^1-pentadienyl to η^3-cyclopentenyl (31 → 32) rearrangement described in Scheme IV.[38] The relative absence of (*E*)-8a in reaction mixtures from copper-catalyzed reactions and the observed yield optimization of 8c/8d at less than 50% are supportive of the stereospecific rearrangement of 33 to 34. The effect of methoxy substitution on the vinyl group (9) in preventing cyclopentene formation is indicative of the delicate balance that exists between the acyclic and cyclic pathways for product formation.[39]

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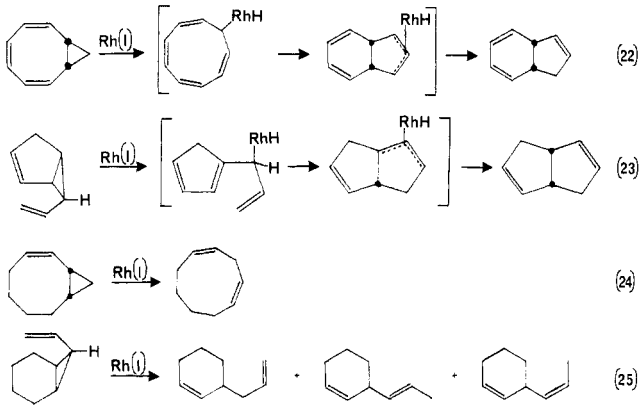
The pentadienyl to cyclopentenyl rearrangement of vinyl cyclopropanes also accounts for the previously unexplained contrasting results from catalytic structural rearrangements of divinylcyclopropanes (e.g., eq 22[40] and 23[41]) and



monovinylcyclopropanes (e.g., eq 24[12,40] and 25[12]). Divinylcyclopropanes are converted to cyclopentenes in rhodium-(I) promoted transformations, whereas monovinylcyclopropanes are converted to diene products. These transformations and those reported in this study are strikingly analogous and suggest a previously undefined generality for the outcome of transition metal catalyzed rearrangements of mono- and divinylcyclopropanes and their carboxylate analogues.

Catalytic structural rearrangement of (allyloxy)cyclopropanecarboxylates (Table III) provides direct entry to products derived from the Claisen rearrangement of allyl vinyl ethers formed by the oxocyclopropane–vinyl ether rearrangement process (eq 16–18). Isomeric α-allylcarboxylates, anticipated from the presumptive homo-Claisen rearrangement, were not observed. In contrast to reactions performed with methoxycyclopropanes, however, rhodium(I)-catalyzed rearrangements of the corresponding (allyloxy)cyclopropanes produced significant amounts of 4-oxoalkanoates, and allyl transfer to rhodium in **28** or **29** that is competitive with hydrogen transfer represents an attractive explanation of these results.[42] Isomerization of these allyl cyclopropyl ethers to their corresponding vinyl ethers[43] was not observed.

Allyl 2-methoxy-2-phenylcyclopropanecarboxylate (**25**) was constructed with the intention of trapping **28** through a sequential Claisen rearrangement process but, as is evident from the results presented in Table IV, without success. Instead, in $PtCl_2$·2PhCN-catalyzed reactions and, to a limited extent, in $[Ru(CO)_3Cl_2]_2$-catalyzed reactions, methyl 3-allyl-3-benzoylpropanoate (**26**), a product resulting from ester/ether alkyl exchange, is observed. The exact nature of this complex process is undefined in this investigation but, as is evident here and with the catalytic rearrangement of cyclopropylcarbinol **12**, the behavior of $PtCl_2$·2PhCN toward cyclopropane compounds is more complex than is that of either $[Rh(CO)_2Cl_2]$ or $[Ru(CO)_3Cl_2]_2$.

(39) We attribute the absence of cyclopentene products to dipolar repulsion of methoxy groups in the syn conformation of the acyclic diene that is required for the pentadienyl to cyclopentenyl rearrangement.
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(42) Subsequent steps in this explanation are not obvious. However, allyl α-styryl ether undergoes rapid decomposition at 60 °C in the presence of either $[Rh(CO)_2Cl]_2$ or $PtCl_2$·2PhCN to produce a mixture of products of which acetophenone, but not the Claisen rearrangement product, is a major constituent.
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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. Infrared spectra were recorded on a Perkin-Elmer Model 621 grating spectrophotometer, and 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. Elemental analyses were performed by Galbraith Laboratories, Inc. With the exception of (triisopropylphosphite)copper(I) chloride[44] and copper bronze,[45] which were prepared by standard procedures, the transition metal compounds employed in this investigation were commercially available. Vinyl ethers used for the synthesis of cyclopropane reactants that were not commercially available were prepared from their corresponding acetal or ketal derivatives by standard methods.[46–48] Allyl vinyl ethers were prepared from their corresponding methyl acetals or ketals by *p*-toluenesulfonic acid catalyzed exchange/elimination with allyl alcohol and were distilled at temperatures below 110 °C to avoid the Claisen rearrangement.[49,50]

Synthesis of Ethyl 2-Alkoxycyclopropanecarboxylates. Reactant cyclopropane compounds were prepared by addition of ethyl diazoacetate at a controlled rate to an equivalent amount of the requisite vinyl ether in the presence of catalytic amounts of $Rh_2(OAc)_4$ at 25 °C in ethyl ether.[5] Cyclopropane geometrical isomers were generally separable with base-line resolution on Carbowax 20M or SE-30 columns; in all cases, the *E* isomer eluted first. With the exception of **1**, whose isomers were separable by distillation,[5] individual isomers were collected and analyzed following GC separation. Catalyst ratios, yields for distilled products, and analytical data for previously unreported cyclopropane compounds are listed in Table V; isomer ratios of reactant cyclopropanes are reported in Tables I–IV. Physical and spectral data for the cyclopropanecarboxylates employed in this investigation, with the exception of those for **1**, **5**, **7**, and **14** which were previously described,[5] are reported below.

Ethyl 2-oxabicyclo[4.1.0]heptane-7-carboxylate (4): bp 90–111 °C (13 torr). *E*(anti) isomer: ^{1}H NMR δ 4.06 (q, J = 7.1 Hz, CH_2O), 3.9–3.2 (m, 3 H), 2.1–1.2 (m, 6 H), 1.18 (t, J = 7.1 Hz, CH_3CH_2O). *Z*(syn) isomer: ^{1}H NMR ($CDCl_3$) δ 4.13 (q, J = 7.1 Hz, CH_2O), 3.95–3.3 (m, 3 H), 2.46 (d of d, J = 6.6 and 7.8 Hz, CHCOOEt), 1.8–1.0 (m, 5 H), 1.26 (t, J = 7.1 Hz, CH_3CH_2O).

Ethyl 2-methoxy-2-methyl-3-phenylcyclopropanecarboxylate (6): bp 110–120 °C (0.5 torr). Four isomers in 36:10:48:6 ratio from elution of peaks from a 10-m 5% Carbowax 20M column programmed 10 °C/min from 100 to 200 °C. Major isomers: ^{1}H NMR ($CDCl_3$) δ 7.45–7.05 (m, phenyl) 4.21 and 4.07 (q, CH_2O), 3.34 and 3.35 (s, OCH_3), 1.55 and 1.20 (s, CH_3), 1.29 and 1.19 (t, CH_3CH_2O); minor isomers exhibited absorptions for the methoxy substituent at δ 3.30 and 3.27. Mass spectra of components in order of elution from a Carbowax 20M column, m/e (relative abundance): first component, 235 (0.5, M + 1), 234 (2.9, M), 162 (13), 161 (100), 145 (6), 131 (20), 130 (7), 129 (48), 128 (14), 127 (6), 115 (10), 103 (21), 91 (33); second component, 235 (6.8 M + 1), 234 (39, M), 189 (7, M – C_2H_5O), 174 (11), 173 (27), 162 (6), 161 (49), 160 (15), 159 (73), 157 (15), 146 (8), 145 (26), 144 (27), 143 (12), 131 (14), 130 (15), 129 (100), 128 (38), 127 (19), 118 (8), 117 (38), 116 (12), 115 (39), 105 (13), 104 (14), 103 (11), 102 (7), 92 (8), 91 (92); third component, 235 (0.4, M + 1), 234 (2.0, M), 162 (12), 161 (100), 145 (6), 131 (19), 130 (7), 129 (47), 128 (13), 127 (6), 115 (9), 103 (20), 91 (33); fourth component,

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Table V. Cyclopropanecarboxylates from Catalytic Cyclopropanation of Vinyl Ethers with Ethyl Diazoacetate[a]

alkene	[EDA]/[$Rh_2(OAc)_4$]	cyclopropane[b]	yield,[c] %
1-methoxystyrene	100	1	94
2-methoxy propene	200	5	65
1-methoxycyclohexene	2000	7	80
2-methoxy-1,3-butadiene	1000	8	60
1-methoxy-1,3-butadiene	1000	*d*	51
2,3-dimethoxy-1,3-butadiene	1000	9	76
ethyl vinyl ether	300	14	75
1-(2-propen-1-yloxy)cyclohexene	400	20	30

[a] Equivalent amounts of vinyl ether and ethyl diazoacetate were employed. Rate of addition of ethyl diazoacetate corresponded to values reported in ref 5. [b] Satisfactory combustion analyses were reported for these compounds. [c] Yield of isolated product based on ethyl diazoacetate. [d] Ethyl 2-(*trans*-β-methoxyvinyl)cyclopropanecarboxylate.

235 (5.9, M + 1), 234 (36, M), 189 (8, M − C_2H_5O), 174 (12), 173 (26), 162 (6), 161 (49), 160 (14), 159 (68), 158 (7), 157 (18), 145 (25), 144 (24), 143 (10), 131 (11), 130 (15), 129 (100), 128 (39), 127 (18), 118 (8), 117 (40), 116 (10), 115 (36), 105 (9), 103 (8), 92 (7), 91 (89).

Ethyl 2-methoxy-2-vinylcyclopropanecarboxylate (8): bp 85–92 °C (16 torr); IR (neat) $\bar{\nu}_{C=O}$ 1729 cm^{-1}, $\bar{\nu}_{C=C}$ 1638 cm^{-1}; ^1H NMR ($CDCl_3$), for *E* isomer, δ 5.85 (d of d, *J* = 10.1 and 17.3 Hz, C*H*=CH_2), 5.50–5.18 (m, CH=C*H*$_2$), 4.12 (q, *J* = 7.1 Hz, CH_2O), 3.33 (s, CH_3O), 2.14 (d of d, *J* = 8.7 and 8.0 Hz, C*H*COOEt), 1.49 (d, *J* = 8.0 Hz, 1 H), 1.48 (d, *J* = 8.7 Hz, 1 H), 1.25 (t, *J* = 7.1 Hz, C*H*$_3$$CH_2O$); for *Z* isomer, δ 5.64 (d of d, *J* = 10.0 and 16.6 Hz, C*H*=CH_2), 5.38–5.10 (m, CH=C*H*$_2$), 4.18 (q, *J* = 7.1 Hz, CH_2O), 3.30 (s, CH_3O), 2.05–1.75 (m, 2 H), 1.27 (t, *J* = 7.1 Hz, C*H*$_3$$CH_2O$), 1.12 (d of d, *J* = 9.0 and 5.9 Hz, 1 H).

Ethyl 2-(*trans*-β-methoxyvinyl)cyclopropanecarboxylate from *trans*-1-methoxy-1,3-butadiene: bp 104–109 °C (13 Torr); ^1H NMR ($CDCl_3$), for *E* isomer, δ 6.48 (d, *J* = 12.7 Hz, =C*H*OMe), 4.89–4.62 (m, 1 H), 4.14 (q, *J* = 7.1 Hz, CH_2O), 3.49 (s, CH_3O), 1.95–1.53 (m, 2 H), 1.25 (t, *J* = 7.1 Hz, C*H*$_3$$CH_2O$), 1.34–1.04 (m, 2 H); for *Z* isomer, δ 6.44 (d of d, *J* = 12.6 and 0.5 Hz, =C*H*OMe), 4.48 (d of d, *J* = 12.6 and 7.4 Hz, CHC*H*=), 4.12 (q, *J* = 7.1 Hz, CH_2O), 3.48 (s, CH_3O), 2.05–1.75 (m, 1 H), 1.62–1.30 (m, 2 H), 1.25 (t, *J* = 7.1 Hz, C*H*$_3$$CH_2O$), 0.88 (m, *J* = 8.1, 6.4, and 4.0 Hz, 1 H). **Ethyl 2-methoxy-3-vinylcyclopropanecarboxylate** possessing the same *trans*-2-methoxy-3-vinyl geometry as the reactant *trans*-1-methoxy-1,3-butadiene and with the carbethoxy and methoxy groups related cis was a minor component of this product mixture (12% of total): ^1H NMR ($CDCl_3$) δ 5.57 (m, *J* = 16.8, 9.8, and 7.0 Hz, C*H*=CH_2), 5.13 (d of d, *J* = 9.8 and 2.0 Hz, 1 H), 5.10 (d of d, *J* = 16.8 and 2.0 Hz, 1 H), 4.24 (q, *J* = 7.1 Hz, CH_2O), 3.45 (d of d, *J* = 6.9 and 4.0 Hz, C*H*OMe), 3.34 (s, CH_3O), 2.49 (m, *J* = 7.0, 6.3, 4.0, and 0.7 Hz, C*H*CH=), 1.83 (d of d, *J* = 6.9 and 6.3 Hz, C*H*COOEt), 1.30 (t, *J* = 7.1 Hz, C*H*$_3$$CH_2O$).

Ethyl 2-methoxy-2-(α-methoxyvinyl)cyclopropanecarboxylate (9): bp 75–85 °C (0.3 torr); ^1H NMR ($CDCl_3$), for *E* isomer, δ 4.34 (d, *J* = 2.5 Hz, 1 H), 4.28 (d, *J* = 2.5 Hz, 1 H), 4.10 (q, *J* = 7.1 Hz, CH_2O), 3.55 (s, CH_3O), 3.30 (s, CH_3O), 2.09 (d of d, *J* = 9.4 and 6.8 Hz, C*H*COOEt), 1.57 (d of d, *J* = 6.8 and 5.4 Hz, 1 H), 1.32 (d of d, *J* = 9.4 and 5.4 Hz, 1 H), 1.22 (t, *J* 7.1 Hz, C*H*$_3$$CH_2O$); for *Z* isomer, δ 4.42 (d, *J* = 2.5 Hz, 1 H), 4.18 (d, *J* = 2.5 Hz, 1 H), 4.31–4.03 (m, CH_2O), 3.54 (s, CH_3O), 3.33 (s, CH_3O), 2.18 (d of d, *J* = 9.0 and 6.9 Hz, C*H*COOEt), 1.70 (d of d, *J* = 6.9 and 5.4 Hz, 1 H), 1.39 (d of d, *J* = 9.0 and 5.4 Hz, 1 H), 1.27 (t, *J* = 7.1 Hz, C*H*$_3$$CH_2O$).

2-Methoxy-2-phenylcyclopropanemethanol (12) was prepared in 96% yield by lithium aluminum hydride reduction of 1: bp 118–124 °C (0.4 torr); ^1H NMR ($CDCl_3$) δ 7.6–7.2 (m, 5 H), 4.2–3.6 (m, CH_2O), 3.25 and 3.10 (s, CH_3O), 2.3 (br s, OH), 2.1–0.8 (m, 3 H).

2-Methoxy-2-vinylcyclopropanemethanol (13) was prepared in 94% yield by lithium aluminum hydride reduction of **5**: bp 116–120 °C (13 torr); IR (neat) $\bar{\nu}_{O-H}$ 3400 cm^{-1}, $\nu_{C=C}$ 1639 cm^{-1}; ^1H NMR ($CDCl_3$), for *E* isomer, δ 5.66 (d of d, *J* = 17.1 and 10.2 Hz, C*H*=CH_2), 5.14 (d of d, *J* = 17.1 and 2.0 Hz, 1 H), 5.07 (d of d, *J* = 10.2 and 2.0 Hz, 1 H), 4.15–3.45 (m, 3 H), 3.33 (s, CH_3O), 1.79 (d of d, *J* = 7.4 and 5.1 Hz, 1 H), 1.42–1.15 (m, C*H*CH_2OH), 0.96–0.80 (m, 1 H); for *Z* isomer, δ 5.80 (d of d, *J* = 17.8 and 9.5 Hz, C*H*=CH_2), 5.30 (d of d, *J* = 17.8 and 2.4 Hz, 1 H), 5.28 (d of d, *J* = 9.5 and 2.4 Hz, 1 H), 3.85–3.21 (m,3 H), 3.28 (s, CH_3O), 1.85–1.25 (m, C*H*CH_2OH), 1.13 (d of d, *J* = 10.0 and 5.4 Hz, 1 H), 0.69 (d of d, *J* = 6.4 and 5.4 Hz, 1 H).

Ethyl 2-methoxy-3-phenylcyclopropanecarboxylate (16): bp 130–140 °C (15 torr); ^1H NMR ($CDCl_3$), for (*E*)-**16**, δ 7.26 (s, 5 H), 4.16 (q, *J* = 7.1 Hz, CH_2O), 3.82 (d of d, *J* = 6.9 and 2.8 Hz, C*H*OMe), 3.29 (s, CH_3O), 2.68 (d of d, *J* = 6.9 and 6.3 Hz, C*H*Ph), 2.20 (d of d, *J* = 6.3 and 2.8 Hz, C*H*COOEt), 1.27 (t, *J* = 7.1 Hz, C*H*$_3$$CH_2O$); for (*Z*)-**16**, δ 7.5–7.2 (m, 5 H), 4.08 (q, *J* = 7.1 Hz, CH_2O), 3.67 (d of d, *J* = 7.2 and 6.0 Hz, C*H*OMe), 3.41 (s, CH_3O), 2.55 (d of d, *J* = 10.3 and 7.2 Hz, C*H*Ph), 2.03 (d or d, *J* = 10.3 and 6.0 Hz, C*H*COOEt), 1.10 (t, *J* = 7.1 Hz, C*H*$_3$$CH_2O$); mass spectra, *m/e* (relative abundance), for (*E*)-**16**, 220 (0.4, M), 188 (13), 159 (5), 148 (11), 147 (100), 132 (4), 131 (17), 129 (4), 117 (16), 116 (12), 115 (80), 105 (5), 104 (8), 103 (26), 102 (5), 91 (26); for (*Z*)-**16**, 221 (0.3, M + 1), 220 (2.6, M), 188 (12), 159 (6), 148 (11), 147 (100), 132 (4), 131 (16), 129 (4), 117 (18), 116 (13), 115 (79), 105 (6), 104 (9), 103 (28), 102 (6), 91 (28).

Ethyl 2-(2-propen-1-yloxy)-2-phenylcyclopropanecarboxylate (17): bp 120–125 °C (0.5 torr); ^1H NMR ($CDCl_3$), for *E* isomer, δ 7.55–7.15 (m, 5 H), 6.05–5.55 (m, C*H*=CH_2), 5.30–5.00 (m, CH=C*H*$_2$), 3.86 (q, *J* = 7.1 Hz, CH_2O), 3.83 (m, *J* = 5.3, 2.5, and 1.3 Hz, C*H*$_2$CH=), 2.38 (d of d, *J* = 9.4 and 6.7 Hz, C*H*COOEt), 1.84 (d of d, *J* = 5.6 and 6.7 Hz, 1 H), 1.53 (d of d, *J* = 9.4 and 5.6 Hz, 1 H), 0.97 (t, *J* = 7.1 Hz, C*H*$_3$$CH_2O$); for *Z* isomer, δ 7.35 (s, 5 H), 6.10–5.60 (m, C*H*=CH_2), 5.32–5.00 (m, CH=C*H*$_2$), 4.20 (q, *J* = 7.1 Hz, CH_2O), 3.88 (m, *J* = 5.3, 2.5, and 1.3 Hz, C*H*$_2$CH=), 2.07 (d of d, *J* = 11.4 and 6.8 Hz, C*H*COOEt), 1.52 (d of d, *J* = 11.4 and 5.4 Hz, 1 H), 1.40 (d of d, *J* = 6.8 and 5.4 Hz, 1 H), 1.28 (t, *J* = 7.1 Hz, C*H*$_3$$CH_2O$). The ^1H NMR spectra of ethyl 2-(*trans*-2-buten-1-yloxy)-2-phenylcyclopropanecarboxylate (**18**) were identical with those of **17**, except in the vinyl region [δ 5.65–5.40 (2 H, m)], for the OC*H*$_2$-CH= absorption [δ 3.85–3.70 (2 H, m)] and for the =CHC*H*$_3$ absorption [δ 1.64 (d, *J* = 4.8 Hz)]: bp 115–125 °C (0.4 torr).

Ethyl 2-(2-propen-1-yloxy)-2-methylcyclopropanecarboxylate (19): bp 35–45 °C (0.5 torr); ^1H NMR ($CDCl_3$) δ 6.2–5.7 (m, C*H*=CH_2), 5.45–5.00 (m, CH=C*H*$_2$), 4.20 and 4.19 (q, *J* = 7.1 Hz, CH_2O of individual geometrical isomers), 4.2–3.9 (m, C*H*$_2$CH=), 1.92 (d of d, *J* = 9.2 and 7.0 Hz, C*H*COOEt of *E* isomer), 1.52 (d, *J* = 0.4 Hz, CH_3 of *E* isomer), 1.46 (d, *J* = 0.5 Hz, CH_3 of *Z* isomer), 1.26 (t, *J* = 7.1 Hz, C*H*$_3$$CH_2O$ of both geometrical isomers), 0.96 (d of d, *J* = 11.8 and 8.8 Hz, 1 H of *Z* isomer).

Ethyl 1-(2-propen-1-yloxy)bicyclo[4.1.0]heptane-7-carboxylate (20): bp 92–104 °C (0.5 torr); ^1H NMR ($CDCl_3$), for *E*(syn) isomer, δ 6.15–5.65 (m, C*H*=CH_2), 5.40–5.05 (m, CH=C*H*$_2$), 4.12 (q, *J* = 7.1 Hz, CH_2O), 4.10–3.95 (m, C*H*$_2$CH=), 2.25–1.10 [m with 3 sets of absorptions, maximum absorptions at δ 2.1, 1.8, and 1.45, (10 H)], 1.27 (t, *J* = 7.1 Hz, C*H*$_3$$CH_2O$); for *Z*(anti) isomer, δ 6.15–5.65 (m, C*H*=CH_2), 5.40–5.05 (m, CH=C*H*$_2$), 4.12 (q, *J* = 7.1 Hz, CH_2O), 4.10–3.70 (m, C*H*$_2$CH=), 2.25–1.00 [m with 2 sets of absorptions, maximum absorptions at δ 2.1 and 1.3 (10 H)], 1.25 (t, *J* = 7.1 Hz, C*H*$_3$$CH_2O$).

Allyl 2-methoxy-2-phenylcyclopropanecarboxylate (23) was prepared from 1 and allyl alcohol in 75% yield by transesterification in the presence of sodium hydroxide: bp 140 °C (0.4 torr); ^1H NMR ($CDCl_3$), for *E* isomer, δ 6.00–5.45 (m, C*H*=CH_2), 5.30–4.95 (m, CH=C*H*$_2$), 4.40–4.25 (m, C*H*$_2$CH=), 3.13 (s, CH_3O); for *Z* isomer, 6.25–5.65 (m, C*H*=CH_2), 5.40–5.15 (m, CH=C*H*$_2$), 4.75–4.60 (m, C*H*$_2$CH=), 3.23 (s, CH_3O); phenyl and

cyclopropane proton absorptions are analogous to those previously reported for 1.[5]

Synthesis of 2-Methoxy-2-phenylcyclopropanenitrile (10). Diazoacetonitrile was prepared in methylene chloride from the hydrochloride salt of aminoacetonitrile by treatment with sodium nitrite and aqueous sulfuric acid.[51] After extracting with methylene chloride and drying over anhydrous calcium chloride, with suitable caution to avoid concentration of this explosive diazo compound,[52] we added the diazoacetonitrile solution over a 30-min period to a 5-fold molar excess of α-methoxystyrene (9.75 g, 0.073 mol) in anhydrous methylene chloride containing 2 mol % of $Rh_2(OAc)_4$, based on diazoacetonitrile. After gas evolution was complete, the reaction solution was filtered through neutral alumina, and the solvent was evaporated. Distillation of the resulting colorless oil at 0.6 torr yielded 2.26 g of **10** (89% yield): bp 95–108 °C (0.6 torr); ^{1}H NMR ($CDCl_3$), for *E* isomer, δ 7.60–7.30 (m, 5 H), 3.18 (s, CH_3O), 2.05 (d of d, *J* = 9.8 and 6.9 Hz, C*H*CN), 1.70 (d, *J* = 6.9 Hz, 1 H), 1.68 (d, *J* = 9.8 Hz, 1 H); for *Z* isomer, δ 7.37 (s, 5 H), 3.33 (s, CH_3O), 1.90–1.60 (m, 3 H). Anal. Calcd for $C_{11}H_{11}NO$: C, 76.28; H, 6.40; N, 8.09. Found: C, 76.34; H, 6.51; N, 8.06.

Synthesis of (Tolylsulfonyl)cyclopropanes. (*p*-Tolylsulfonyl)diazomethane was prepared in the dark from ethyl *N*-nitro-*N*-[(*p*-tolylsulfonyl)methyl]carbamate by decarboxylation in anhydrous ether with the use of alumina.[53] Nitrosium tetrafluoroforate was used in place of nitrosyl chloride to prepare the reactant *N*-nitrosocarbamate in 99% isolated yield. To 0.804 g (6.0 mmol) of α-methoxystyrene in 5 mL of anhydrous ethyl ether containing 52 mg of $Rh_2(OAc)_4$ (2.0 mol %) was added 1.18 g of (*p*-tolylsulfonyl)diazomethane (6.0 mmol) in 5 mL of ether at a rate of 1.0 mL/h. After addition was complete, the reaction mixture was filtered through neutral alumina with 400 mL of ether. Evaporation of the ether left 1.63 g of a colorless oil, which by NMR spectroscopy was greater than 95% **11** (5.1 mmol, 86% yield) with an *E*/*Z* isomer ratio of 0.91: ^{1}H NMR ($CDCl_3$), for *E* isomer, δ 7.92 (d, 2 H), 7.5–7.1 (m, 7 H), 3.05 (s, CH_3O), 2.39 (s, CH_3), 2.3–1.6 (m, 3 H); for *Z* isomer, δ 7.92 (d, 2 H), 7.5–7.1 (m, 7 H), 3.30 (s, CH_3O), 2.69 (d of d, *J* = 9.6 and 6.6 Hz, C*H*SO_2Tol), 2.43 (s, CH_3), 2.23 (t, *J* = 6.6 Hz, 1 H), 1.82 (d of d, *J* = 9.6 and 6.6 Hz, 1 H). Attempts to purify this compound by chromatography and crystallization were unsuccessful. However, **2-methoxy-2-methyl-1-(*p*-tolylsulfonyl)cyclopropane**, prepared from 2-methoxypropene in 77% yield by an analogous procedure, was amenable to crystallization. An *E*/*Z* isomer ratio of 0.82 for the cyclopropane product was initially obtained from which the *Z* isomer was selectively isolated by repeated recrystallizations from ether/pentane: mp 78–80 °C; ^{1}H NMR ($CDCl_3$), for *Z* isomer, δ 7.74 (d, *J* = 8.4 Hz, 2 H), 7.31 (d, *J* = 8.4 Hz, 2 H), 3.42 (s, CH_3O), 2.43 (s, CH_3), 2.36 (d of d, *J* = 9.1 and 6.3 Hz, C*H*SO_2), 1.94 (d of d, *J* = 6.3 and 6.2 Hz, 1 H), 1.18 (d of d, *J* = 9.1 and 6.2 Hz, 1 H). Anal. Calcd for $C_{12}H_{16}O_3S$: C, 59.97; H, 6.71; S, 13.34. Found: C, 60.20; H, 6.76; S, 13.58. The ^{1}H NMR spectrum of the *E* isomer exhibited absorptions at δ 7.78 (d, *J* = 8.3 Hz, 2 H), 7.33 (d, *J* = 8.3 Hz, 2 H), 3.18 (s, CH_3O), 2.52 (d of d, *J* = 9.1 and 8.0 Hz, 1 H), 2.44 (s, CH_3), 1.7–1.3 (m, 2 H).

Acid-Promoted Reactions of Oxocyclopropanes. Oxycyclopropanes undergo proton-induced ring opening to their corresponding carbonyl derivative under remarkably mild conditions. For example, ethyl 4-oxopentanoate (**21**) was isolated in 93% yield following treatment of ethyl 2-methoxy-2-methylcyclopropanecarboxylate (**5**) with concentrated sulfuric acid (0.5 mmol/mmol of cyclopropane) in 98% aqueous acetone (10 mL/mmol of cyclopropane) for 2 h at room temperature. Similarly, acetal or ketal derivatives of 4-oxoalkanoates were obtained from the reactant cyclopropane compound through reaction with sulfuric acid in the presence of the requisite alcohol. For example, ethyl 4,4-diethoxybutanoate (**15**) was isolated in 84% yield following treatment of ethyl 2-ethoxycyclopropanecarboxylate (**14**) with concentrated sulfuric acid (0.5 mmol/mmol cyclopropane) in ethanol (10 mL/mmol cyclopropane) for 12 h at room temperature. In the absence of hydroxylic solvents, proton-induced ring opening resulted in the formation of high molecular weight compounds; 4-oxoalkanoates were isolated in low yield.

In the presence of titanium tetrachloride in nonhydroxylic solvents, ring-opening reactions of oxocyclopropanes generally resulted in the production of significant amounts of polymeric materials. For example, addition of 0.44 g of ethyl 2-methoxy-2-phenylcyclopropanecarboxylate (**1**, 2.0 mmol) in 2 mL of anhydrous ethyl ether to 0.035 g of titanium tetrachloride (0.2 mmol) in 2 mL of ether produced a dark-colored solution. After 30 min the reaction solution was diluted with ether and filtered through neutral alumina, and the filtrate was distilled under reduced pressure to yield 0.19 g of a mixture composed of 85% ethyl 3-benzoylpropanoate (**2**) and 15% ethyl 4,4-dimethoxy-4-phenylbutanoate (**3**): ^{1}H NMR ($CDCl_3$), for **3**, δ 7.6–7.0 (m, 5 H), 4.00 (q, 2 H), 3.20 (s, 6 H), 2.4–1.8 (m, 4 H), 1.15 (t, 3 H). Boron trifluoride etherate was relatively ineffective in promoting ring opening of **1**; less than 10% conversion of **1** to **2** occurred during 6 h at room temperature when catalytic amounts of this Lewis acid were employed.

General Procedure for Catalytic Rearrangements of Oxocyclopropanes to Vinyl Ethers. The methods generally employed for these transformations are exemplified by the following procedures. Reaction temperatures, reaction times, and catalyst quantities are described in Tables I and II. The use of a solvent, such as toluene in $PtCl_2$·2PhCN or $[Rh(CO)_2Cl]_2$ catalyzed reactions, did not generally offer advantage and usually resulted in longer reaction times.

Ethyl 4-Methoxy-4-phenyl-3-butenoate (1a). A mixture of 220 mg of ethyl 2-methoxy-2-phenyl-1-cyclopropanecarboxylate (**1**; 1.00 mmol) and 5.0 mg of $PtCl_2$·2PhCN (0.011 mmol) in a 1-mL sample vial was heated in an oil bath at 110 °C for 10 min and then directly distilled in a Buchi Kugelrohr apparatus under reduced pressure to yield 216 mg of **1a** (0.982 mmol, 98% isolated yield): bp 103.5–104.5 °C (4.0 torr); IR (neat) $\tilde{\nu}_{C=O}$ 1738 cm^{-1}; ^{1}H NMR ($CDCl_3$), for *E* isomer, δ 7.55–7.20 (m, 5 H), 4.89 (t, *J* = 7.5 Hz, C*H*CH_2), 4.14 (g, *J* = 7.1 Hz, CH_2O), 3.69 (s, CH_3O), 3.06 (d, *J* = 7.5 Hz, CHC*H*$_2$), 1.24 (t, *J* = 7.1 Hz, C*H*$_3$$CH_2O$); for *Z* isomer, δ 7.55–7.20 (m, 5 H), 5.42 (t, *J* = 7.1 Hz, C*H*CH_2), 4.16 (q, *J* = 7.1 Hz, CH_2O), 3.51 (s, CH_3O), 3.32 (d, *J* = 7.1 Hz, CHC*H*$_2$), 1.27 (t, *J* = 7.1 Hz, C*H*$_3$$CH_2O$). Anal. Calcd for $C_{13}H_{16}O_3$: C, 70.89; H, 7.32. Found: C, 70.97; H, 7.44. **4-Methoxy-4-phenyl-3-buten-1-ol** was prepared from **1a** in 94% yield by lithium aluminum hydride reduction: ^{1}H NMR ($CDCl_3$) δ 7.55–7.20 (m, 5 H), 5.30 and 4.70 (t, *J* = 7.4 and 7.7 Hz, respectively, *Z* and *E* isomers, respectively, C*H*CH_2), 3.68 (t, *J* = 6.7 Hz, CH_2O), 3.64 and 3.51 (s, CH_3O, *E* and *Z* isomers, respectively), 2.65–2.20 (m, CHC*H*$_2$$CH_2$), 2.3–2.0 (br s, OH).

Ethyl (3,4-Dihydro-2*H*-pyran-5-yl)acetate (4a). A mixture of 441 mg of **4** (2.59 mmol) and 30 mg of copper bronze (0.48 mmol) was heated under reflux (150 °C) with stirring for 4 h and then directly distilled in a Buchi Kugelrohr apparatus under reduced pressure to yield 352 mg of **4a** (2.07 mmol, 80% isolated yield): bp 82 °C (16 torr); ^{1}H NMR ($CDCl_3$) δ 6.38 (t, *J* = 0.6 Hz, =CH), 4.16 (q, *J* = 7.1 Hz, CH_2O), 3.94 (t, *J* = 7.4 Hz, OC*H*$_2$$CH_2$), 2.85 (d, *J* = 0.6 Hz, C*H*$_2$COOEt), 2.20–1.70 (m, 4 H), 1.25 (t, *J* = 7.1 Hz, C*H*$_3$$CH_2O$). Anal. Calcd for $C_9H_{14}O_3$: C, 63.51; H, 8.30. Found: C, 63.35; H, 8.15. The half-life for structural rearrangement of **4** under these conditions was 1.2 h. Only *Z*-(*endo*)-**4** underwent rearrangement to **4a** when **4** was heated with 2 mol % of $Rh_2(OAc)_4$ at 140 °C for 3 h.

Ethyl 4-Methoxypentenoate (5a,b). A mixture of 7.91 g of ethyl 2-methoxy-2-methyl-1-cyclopropanecarboxylate (**5**; 50.0 mmol) and 630 mg of copper bronze (9.91 mmol) was heated under reflux for 2.5 h and then directly distilled under reduced pressure to yield 6.60 g of a composite of **2a** and **2b** (41.7 mmol, 83% isolated yield): bp 82–88 °C (16 torr); IR (neat) $\tilde{\nu}_{C=O}$ 1739 cm^{-1}; ^{1}H NMR ($CDCl_3$) for **5a**, *Z* isomer, δ 4.60 (t of q, *J* = 7.2 and 0.9 Hz, =CH), 4.11 (q, *J* = 7.1 Hz, CH_2O), 3.55 (s, CH_3O), 3.08 (d of q, *J* = 7.2 and 1.3 Hz, CHC*H*$_2$), 1.86 (d of t, *J* = 1.3 and 0.9 Hz, CH_3), 1.26 (t, *J* = 7.1 Hz, C*H*$_3$$CH_2O$); for **5a**, *E* isomer, δ 4.53 (d of t, *J* = 7.2 and 0.7 Hz, =CH), 4.12 (q, *J* = 7.1 Hz, CH_2O), 3.52 (s, CH_3O), 3.00 (d, *J* = 7.2 Hz, CHC*H*$_2$), 1.78 (d, *J* = 0.7 Hz, CH_3), 1.26 (t, *J* = 7.1 Hz, C*H*$_3$$CH_2O$); for **5b**, 4.12 (q, *J* = 7.1 Hz, CH_2O), 3.88 (s, =CH_2), 3.52 (s, CH_3O), 2.45 (s, CH_2CH_2), 1.25 (t, *J* = 7.1 Hz, C*H*$_3$$CH_2O$). Anal. Calcd for $C_8H_{14}O_3$: C, 60.74; H, 8.92. Found: C, 60.57; H, 9.03. Rearrangement of **5** catalyzed

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by $PtCl_2$·2PhCN in toluene yielded **5a,b** in greater yield (Table II) than when performed at 100 °C (30 min) in the absence of toluene (50% **5a,b** and 30% ethyl 4-oxopentanoate).

Ethyl 4-Methoxy-3-phenylpentenoate (6a,b). A stirred mixture of 230 mg of ethyl 2-methoxy-2-methyl-3-phenylcyclopropanecarboxylate (**6**; 1.0 mmol) and 1.9 mg of $[Rh(CO)_2Cl]_2$ (0.05 mmol) was heated at 120 °C for 1 h. The progress of the reaction was monitored by GC, and reaction products were collected: ^1H NMR ($CDCl_3$) for **6a**, *Z* isomer,[54] δ 7.25 (s, 5 H), 4.08 (q, *J* = 7.1 Hz, CH_2O), 3.50 (s, CH_3O), 3.30 (q, *J* = 0.5 Hz, CH_2COOEt), 1.99 (t, *J* = 0.5 Hz, CH_3), 1.20 (t, *J* = 7.1 Hz, CH_3CH_2O); for **6a**, *E* isomer, δ 7.25 (s, 5 H), 4.06 (q, *J* = 7.1 Hz, CH_2O), 3.62 (s, CH_3O), 3.42 (q, *J* = 0.8 Hz, CH_2COOEt), 1.84 (t, *J* = 0.8 Hz, CH_3), 1.16 (t, *J* = 7.1 Hz, CH_3CH_2O); for **6b** δ 7.21 (s, 5 H), 4.07 (q, *J* = 7.1 Hz, CH_2O), 3.99 (d, *J* = 1.5 Hz, $=CH_2$), 3.50 (s, CH_3O), 3.45–3.30 (m, CHPh), 2.81 (d of d, *J* = 7.8 and 6.5 Hz, CH_2COOEt), 1.16 (t, *J* = 7.1 Hz, CH_3CH_2O).

Ethyl Methoxycyclohexeneacetate (7a,b). A mixture of 4.95 g of **7** (25 mmol) and 0.315 g of copper bronze (5.0 mmol) was heated under reflux for 10 min and then directly distilled under reduced pressure to yield 4.65 g of **7a,b** (23.5 mmol, 94% yield): bp 73–76 °C (0.5 torr); IR (neat) $\bar{\nu}_{C=O}$ 1735 cm^{-1}; ^1H NMR ($CDCl_3$) for **7a**, δ 4.62 (d of t, *J* = 3.9 and 0.4 Hz, =CH), 4.14 (q, *J* = 7.1 Hz, CH_2O), 3.46 (s, CH_3O), 2.80–1.40 (m, 9 H), 1.25 (t, *J* = 7.1 Hz, CH_3CH_2O); for **7b**, δ 4.12 (q, *J* = 7.1 Hz, CH_2O), 3.49 (s, CH_3O), 3.09 (s, CH_2), 2.30–1.35 (m, 8 H), 1.25 (t, *J* = 7.1 Hz, CH_3CH_2O). Anal. Calcd for $C_{11}H_{18}O_3$: C, 66.64; H, 9.15. Found: C, 66.87; H, 8.97.

Ethyl 4-Methoxy-3,5-hexadienoate (8a). A mixture of 85 mg of ethyl 2-methoxy-2-vinylcyclopropanecarboxylate (**8**; 0.50 mmol) and 8.5 mg of $[Rh(CO)_2Cl]_2$ (0.022 mmol) in 1.0 mL of toluene was heated at reflux with stirring for 1 h. The resulting solution was analyzed by GC on a 20% SE-30 column with reference to an internal standard; individual products were collected and subjected to spectra analysis: ^1H NMR ($CDCl_3$) for **8a**, *E* isomer, δ 6.18 (d of d of d, *J* = 17.2, 10.8, and 0.4 Hz, 5-H), 5.36 (d of d, *J* = 17.2, 0.9 Hz, 6-H), 5.17 (d of d, *J* = 10.8, 0.9 Hz, 6-H), 5.18 (d of t, *J* = 7.1 and 0.4 Hz, 3-H), 4.14 (q, *J* = 7.1 Hz, CH_2O), 3.61 (s, CH_3O), 3.22 (d, *J* = 7.1 Hz, $CHCH_2$), 1.26 (t, *J* = 7.1 Hz, CH_3CH_2O); **8a**, for *Z* isomer, δ 6.46 (d of d of d, *J* = 17.0, 10.8, and 0.4 Hz, 5-H), 5.68 (d of d, *J* = 17.0, 2.0 Hz, 6-H), 5.20 (d of d of d, *J* = 10.8, 2.0, and 1.8 Hz, 6-H), 4.80 (d of d of t, *J* = 7.6, 1.8, and 0.4 Hz, 3-H), 4.14 (q, *J* = 7.1 Hz, CH_2O), 3.62 (s, CH_3O), 3.15 (d, *J* = 7.6 Hz, $CHCH_2$), 1.26 (t, *J* = 7.1 Hz, CH_3CH_2O); for **8b**, *E,E* isomer, δ 7.49 (d, *J* = 15.4 Hz, 2-H), 6.20 (d of d, *J* = 15.4 and 0.4 Hz, 3-H), 5.03 (d of q, *J* = 7.4 and 0.4 Hz, 5-H), 4.22 (q, *J* = 7.1 Hz, CH_2O), 3.58 (s, CH_3O), 1.83 (d, *J* = 7.4 Hz, CH_3), 1.29 (t, *J* = 7.1 Hz, CH_3CH_2O); for **8b** *E,Z* isomer, δ 7.05 (d, *J* = 15.2 Hz, 2-H), 6.00 (d, *J* = 15.2 Hz, 3-H), 5.45 (q, *J* = 7.5 Hz, 5-H), 4.21 (q, *J* = 7.1 Hz, CH_2O), 3.62 (s, CH_3O), 1.78 (d, *J* = 7.5 Hz, CH_3), 1.29 (t, *J* = 7.1 Hz, CH_3CH_2O). Order of elution on a 20% SE-30 column: (*E*)-**8a**, (*Z*)-**8a**, (*E,Z*)-**8b**, (*E,E*)-**8b**; ratio of (*E,Z*)-**8b** to (*E,E*)-**8b** was 0.6.

Ethyl 3-Methoxycyclopentenecarboxylate (8c,d). A stirred mixture of 1.00 g of ethyl 2-methoxy-2-vinylcyclopropanecarboxylate (**8**; 5.88 mmol) and 0.100 g of copper bronze (1.59 mmol, 27 mol %) was heated under reflux for 2 h and then directly distilled in a Buchi Kugelrohr apparatus under reduced pressure to yield 0.41 g of **8c,d** (2.4 mmol, 41% isolated yield): bp 148–153 °C (16 torr); ^1H NMR ($CDCl_3$), for **8c**, δ 4.33 (d, *J* = 7.2 Hz, =CH), 4.16 (q, *J* = 7.1 Hz, CH_2O), 3.59 (s, CH_3O), 3.1–2.4 (m, 5 H), 1.26 (t, *J* = 7.1 Hz, CH_3CH_2O); for **8d**, δ 4.56–4.46 (m, =CH), 4.14 (q, *J* = 7.1 Hz, CH_2O), 3.62 (s, CH_3O), 2.6–2.0 (m, 5 H), 1.26 (t, *J* = 7.1 Hz, CH_3CH_2O). Treatment of **8c,d** in acetone with 1.2 M aqueous hydrochloric acid produced 3-carbethoxycyclopentanone as the only cyclopentanone product. The corresponding 2-carbethoxycyclopentanone was not detected by GC analysis.

Ethyl 4,5-Dimethoxy-3,5-hexadienoate (9a). A stirred mixture of 0.250 g of ethyl 2-methoxy-2-(α-methoxyvinyl)cyclopropanecarboxylate (**9**; 1.25 mmol) and 0.011 g of $Rh_2(OAc)_4$ (0.025 mmol) was heated at 150 °C. The progress of the reaction was monitored by GC analysis on a 20% SE-30 column; individual products were collected and subjected to spectral analysis: ^1H NMR ($CDCl_3$), for **9a**, *E* isomer, δ 4.86 (t, *J* = 7.5 Hz, $CHCH_2$), 4.43 (d, *J* = 1.2 Hz, 1 H), 4.31 (d, *J* = 1.2 Hz, 1 H), 4.14 (q, *J* = 7.1 Hz, CH_2O), 3.60 (s, 6 H), 3.24 (d, *J* = 7.5 Hz, $CHCH_2$), 1.26 (t, *J* = 7.1 Hz, CH_3CH_2O); for **9a**, *Z* isomer, δ 5.63 (t, *J* = 7.3 Hz, $CHCH_2$), 4.50 (d, *J* = 1.4 Hz, 1 H), 4.40 (d, *J* = 1.4 Hz, 1 H), 4.15 (q, *J* = 7.1 Hz, CH_2O), 3.60 (s, 6 H), 3.20 (d, *J* = 7.3 Hz, $CHCH_2$), 1.26 (t, *J* = 7.1 Hz, CH_3CH_2O); for **9b**, *E,E* or *E,Z* isomer) δ 7.4 (d, *J* = 15 Hz, 2-H), 6.0 (d, *J* = 15 Hz, 3-H), 4.2 (t, *J* = 7.1 Hz, CH_2O), 3.78 (s, CH_3O), 3.58 (s, CH_3O), 2.10 (s, CH_3), 1.30 (t, *J* = 7.1 Hz, CH_3CH_2O).

4-Methoxy-4-phenyl-3-butenenitrile (10a). A stirred mixture of 186 mg of 2-methoxy-2-phenylcyclopropanenitrile (**10**; 1.08 mmol) and 4.4 mg of $Rh_2(OAc)_4$ (0.01 mmol) was heated in an oil bath at 160 °C for 7 h and then directly distilled in a Buchi Kugelrohr apparatus under reduced pressure to yield 135 mg of a mixture composed of 92% **10a** and 8% 4,4-dimethoxy-4-phenylbutanenitrile (**10b**): ^1H NMR ($CDCl_3$),[55] for **10a**, *E* isomer, δ 7.38 (s, 5 H), 4.70 (t, *J* = 7.8 Hz, $CHCH_2$), 3.71 (s, CH_3O), 3.06 (d, *J* = 7.8 Hz, $CHCH_2$); for **10a**, *Z* isomer, δ 7.38 (s, 5 H), 5.10 (t, *J* = 7.0 Hz, $CHCH_2$), 3.55 (s, CH_3O), 3.30 (d, *J* = 7.0 Hz, $CHCH_2$); for **10b**, δ 7.36 (s, 5 H), 3.16 (s, 6 H), 2.40–1.85 (m, 4 H); IR (neat) **10b** $\bar{\nu}_{CN}$ 2230 cm^{-1}. Hydrolysis of **10b** with 10% aqueous hydrochloric acid in acetone produced 3-benzoylpropanenitrile as the sole product. Anal. Calcd for $C_{11}H_{11}NO$ (**10a**): C, 76.28; H, 6.40; N, 8.09. Found: C, 76.08; H, 6.36; H, 7.95.

1-Methoxy-1-phenyl-3-(*p*-tolylsulfonyl)prop-1-ene (11a). Treatment of **11** with 2.0 mol % of $Rh_2(OAc)_4$ at 160 °C for 4 h in the manner previously described for **10** resulted in the production of **11a** in 82% yield: ^1H NMR ($CDCl_3$),[55] for **11a**, *E* isomer, δ 7.68 (d, *J* = 8 Hz, 2 H), 7.5–7.1 (m, 7 H), 4.75 (t, *J* = 7.8 Hz, $CHCH_2$), 3.78 (d, *J* = 7.8 Hz, $CHCH_2$), 3.64 (s, CH_3O), 2.40 (s, CH_3); for **11a**, *Z*-isomer, δ 7.84 (d, *J* = 8 Hz, 2 H), 7.5–7.1 (m, 7 H), 5.11 (t, *J* = 7.4 Hz, $CHCH_2$), 4.05 (d, *J* = 7.4 Hz, $CHCH_2$), 3.10 (s, CH_3O), 2.36 (s, CH_3). Treatment of 2-methoxy-2-phenyl-1-(*p*-tolylsulfonyl)cyclopropane with copper catalysts at 160 and 210 °C and with $PtCl_2$·2PhCN at 180 °C for short periods of time (>30 min) resulted in extensive polymerization; no evidence of vinyl ether formation was obtained and 4-(*p*-tolylsulfonyl)butan-2-one was the only product distilled from the reaction mixture: ^1H NMR ($CDCl_3$) δ 7.80 (d, 2 H), 7.42 (d, 2 H), 3.37 (complex t, 2 H), 2.90 (complex t, 2 H), 2.44 (s, CH_3), 2.16 (s, $COCH_3$).

Catalytic Rearrangement of 2-Methoxy-2-phenylcyclopropanemethanol (12). A stirred mixture of 150 mg of **12** (0.84 mmol) and 30 mg of $PtCl_2$·2PhCN (0.078 mmol) in 3.0 mL of toluene was heated at reflux for 70 min. Toluene was evaporated, and the resulting solution was distilled in a Buchi Kugelrohr apparatus under reduced pressure to yield 65 mg of a mixture composed of **12a** (5%), *trans*-**12b** (63%), *cis*-**12b** (21%), and **12c** (11%). By following the course of this reaction at various times through GC analysis on a 20% SE-30 column, we observed formation of **12a** to precede production of **12b**, and **12c** was formed at the expense of **12b**. Similar results were obtained from the $PtCl_2$·2PhCN-catalyzed rearrangement of 2-methoxy-2-methylcyclopropanemethanol (**13**). Reaction of 4-methoxy-4-phenyl-3-buten-1-ol (158 mg, 0.89 mmol) with 30 mg of $PtCl_2$·2PhCN (0.078 mmol) in 3 mL of refluxing toluene for 20 min resulted in the production of a mixture composed of 3-benzoyl-1-propanol, 2-phenyltetrahydrofuran, and 2-phenylfuran [98 mg, bp 115–125 °C (13 torr)].

Catalytic Isomerization of 2-Alkoxycyclopropanecarboxylates. (*E*)- and (*Z*)-cyclopropane isomers were obtained by fractional distillation (1) or by collection of GC-separated fractions. The following example illustrates the procedure employed. A homogeneous mixture of 70 mg of (*E*)-1 (0.32 mmol) and 3.0 mg of $[Rh(CO)_2Cl]_2$ (2.5 mol %) contained in a round-bottom flask was heated in an oil bath at 70 ± 1 °C. Aliquots of the reaction mixture were removed at regular intervals, quenched by addition to an ether solution containing tri-

(54) Assignment of *E* and *Z* geometry based on homoallylic transoid and cisoid coupling constants: Jackman, L. M., Sternhell, S. "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", 2nd ed.; Pergamon Press: New York, 1969; Chapter 4-4C.

(55) Geometric isomer assignments based on chemical-shift comparisons between **1a**, **10a**, and **11a**.

phenylphosphine, and analyzed by GC with 20% SE-30 columns. Control experiments were performed to ensure that the cyclopropane compound did not decompose during analysis and that the vinyl ether products did not isomerize under the reaction conditions. Product yields and isomer ratios were confirmed by ^{1}H NMR analyses following complete conversion of **1** to products.

Catalytic Rearrangement of Ethyl (*Z*)-2-Ethoxycyclopropanecarboxylate (14). A mixture of 1.94 g of **14** (12.3 mmol, *E*/*Z* = 1.6) and 100 mg of copper bronze (1.59 mmol, 13 mol %) was heated at reflux (190 °C) for 2.5 h. The resulting mixture was then directly distilled at 100 °C in a Buchi Kugelrohr apparatus at 16 torr to yield 1.75 g of a mixture composed of (*E*)-**14** (8.55 mmol) and ethyl 4-ethoxy-3-butenoate (**14a**: 2.55 mmol, *E*/*Z* = 1.4). Further heating of this distillate at 190 °C for an additional 5 h over copper bronze produced no subsequent change in product composition.

Catalytic Rearrangement of Ethyl (*Z*)-2-Methoxy-3-phenylcyclopropanecarboxylate (16). A mixture of 1.00 g of **16** (4.55 mmol, *E*/*Z* = 2.0) and 0.100 g of copper(I) chloride (1.02 mmol, 22 mol %) was heated at 250 °C for 15 min. The resulting mixture was then directly distilled at 140 °C in a Buchi Kugelrohr apparatus at 16 torr to yield 0.96 g of a mixture composed of (*E*)-**16** (3.78 mmol) and ethyl 4-methoxy-3-phenyl-3-butenoate (**16a**; 0.59 mmol, *E*/*Z* = 1.5): ^{1}H NMR ($CDCl_3$), for **16a**, *E* isomer,[54] δ 7.45–7.20 (m, 5 H), 6.21 (t, *J* = 1.0 Hz, C*H*OMe), 4.08 (q, *J* = 7.1 Hz, CH_2O), 3.41 (s, CH_3O), 3.24 (d, *J* = 1.0 Hz, CH_2COOEt), 1.10 (t, *J* = 7.1 Hz, CH_3CH_2O); **16a**, *Z* isomer, δ 7.55–7.20 (m, 5 H), 6.50 (t, *J* = 0.6 Hz, C*H*OMe), 4.02 (q, *J* = 7.1 Hz, CH_2O), 3.70 (s, CH_3O); 3.50 (d, *J* = 0.6 Hz, CH_2COOEt), 1.15 (t, *J* = 7.1 Hz, CH_3CH_2O).

Catalytic Rearrangement of 2-(Allyloxy)cyclopropanecarboxylates. The following example illustrates the procedure employed. A mixture of 150 mg of **17** (0.60 mmol) and 2.4 mg of $[Rh(CO)_2Cl]_2$ (0.006 mmol) was heated for 1 h. The resulting solution was distilled in a Buchi Kugelrohr apparatus under reduced pressure, subjected to GC analysis on a 20% SE-30 column, and the separated reaction products were collected and subjected to spectral analysis. Reaction conditions and product yields are described in Table II. No reaction was observed under the same reaction conditions but without catalyst.

Ethyl 3-benzoyl-5-hexenoate (17a): bp 128–130 °C (0.5 torr); IR (neat) $\bar{\nu}_{C=O}$ at 1730 and 1682 cm^{-1}, $\bar{\nu}_{C=C}$ at 1640 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.05–7.90 (m, 2 H), 7.60–7.25 (m, 3 H), 6.00–5.45 (m, CH=), 5.20–4.90 (m, $=CH_2$), 4.06 (q, *J* = 7.1 Hz, CH_2O), 4.15–3.80 (m, PhCOC*H*), 2.50–2.10 (m, $CH_2CH=$), 1.18 (t, *J* = 7.1 Hz, CH_3CH_2O); the CH_2COOEt absorptions are observed at δ 3.05 (d, *J* = 8.9 Hz) and 2.40 (d, *J* = 5.1 Hz) for the minor conformer and at δ 2.84 (d, *J* = 8.9 Hz) and 2.61 (d, *J* = 5.1 Hz) for the major conformer. Anal. Calcd for $C_{15}H_{18}O_3$: C, 73.15; H, 7.37. Found: C, 73.29; H, 7.46.

Ethyl 3-benzoyl-4-methyl-5-hexenoate (18a): ^{1}H NMR ($CDCl_3$) δ 8.05–7.90 (m, 2 H), 7.60–7.25 (m, 3 H), 6.00–5.45 (m, CH=), 5.20–4.85 (m, $=CH_2$), 4.06 (q, *J* = 7.1 Hz, CH_2O), 4.10–3.75 (m, PhCOC*H*), 3.25–2.25 (m, 3 H), 1.25 and 1.15 (d, *J* = 3.8 and 3.4, respectively, CH_3CH of diastereomeric pair in a ratio of 1:1.7), 0.94 (t, *J* = 7.1 Hz, CH_3CH_2O).

Ethyl 3-acetyl-5-hexenoate (19a): ^{1}H NMR ($CDCl_3$) δ 6.00–5.45 (m, CH=), 5.20–4.90 (m, $=CH_2$), 4.10 (q, *J* = 7.1 Hz, CH_2O), 3.25–2.90 (m, CH_3COCH), 2.45–2.10 (m, $=CHCH_2$), 2.23 (s, CH_3CO), 1.23 (t, *J* = 7.1 Hz, CH_3CH_2O); the CH_2COOEt absorptions are observed at δ 2.52 (d, *J* = 9.0 Hz, 1 H) and 2.44 (d, *J* = 4.6 Hz, 1 H).

Ethyl 4-oxo-7-octenoate (19b): ^{1}H NMR ($CDCl_3$) δ 6.00–5.40 (m, CH=), 5.20–4.90 (m, $=CH_2$), 4.12 (q, *J* = 7.1 Hz, CH_2O), 3.0–2.2 (m, 8 H), 1.24 (t, *J* = 7.1 Hz, CH_3CH_2O).

2-Allyl-6-(carbethoxymethyl)cyclohexanone (20a): ^{1}H NMR ($CDCl_3$) δ 6.05–5.45 (m, CH=), 5.30–4.90 (m, $=CH_2$), 4.18 (q, *J* = 7.1 Hz, CH_2O), 3.2–1.4 (m, 12 H), 1.24 (t, *J* = 7.1 Hz, CH_3CH_2O); mass spectrum, *m*/*e* (relative abundance) 225 (2.9, M + 1), 224 (18.9, M), 182 (19), 179 (46), 178 (93), 176 (7), 161 (11), 160 (6), 151 (12), 150 (26), 149 (11), 138 (12), 137 (100), 136 (82), 135 (40), 134 (18), 133 (19), 132 (8), 131 (6), 125 (8), 124 (9), 123 (7), 122 (21), 121 (27), 120 (6), 119 (36), 118 (12), 117 (12), 113 (14), 110 (10), 109 (36), 108 (28), 107 (26), 106 (11), 105 (14), 81 (72), 79 (73), 67 (95), 55 (88), 53 (51).

2-Allyl-2-(carbethoxymethyl)cyclohexanone (20b): ^{1}H NMR ($CDCl_3$) δ 6.00–5.45 (m, CH=), 5.30–4.90 (m, $=CH_2$), 4.08 (q, *J* = 7.1 Hz, CH_2O), 2.62 (s, CH_2COOEt), 2.9–1.4 (m, 10 H), 1.23 (t, *J* = 7.1 Hz, CH_3CH_2O); mass spectrum, *m*/*e* (relative abundance) 225 (2.0, M + 1), 224 (10.1, M), 182 (7), 179 (30), 178 (32), 161 (21), 160 (14), 151 (14), 150 (25), 149 (12), 139 (5), 138 (12), 137 (100), 136 (40), 135 (20), 134 (29), 133 (8), 122 (9), 121 (14), 119 (15), 118 (15), 117 (5), 110 (7), 109 (51), 108 (90), 107 (33), 106 (21), 105 (13), 93 (50), 81 (71), 79 (84), 67 (80), 55 (59), 53 (42).

Synthesis of Ethyl 2-Allyl-3-benzoylpropanoate (24). Ethyl 2-methoxy-2-phenylcyclopropanecarboxylate (**1**; 8.60 g, 40.0 mmol) dissolved in 50 mL of isopentyl alcohol containing 0.100 g of $Rh_2(OAc)_4$ (0.23 mmol) was heated at reflux for 12 h. Isopentyl alcohol was then removed by distillation at atmospheric pressure, and the resulting residue was fractionally distilled under reduced pressure to produce 6.70 g of **23** (18.4 mmol, 46% yield): bp 145–155 °C (0.4 torr); ^{1}H NMR ($CDCl_3$) δ 7.6–7.2 (m, 5 H), 4.00 (q, *J* = 7.1 Hz, CH_3CH_2O), 3.33 (t, *J* = 6.5 Hz, CH_2CH_2O), 2.45–1.85 (m, CCH_2CH_2COOEt), 1.85–1.25 [m, $CH(CH_3)_2$], 1.46 (q, OCH_2CH_2CH), 1.25 (t, *J* = 7.1 Hz, CH_3CH_2O), 0.89 [*d*, *J* = 6.2 Hz, $CH(CH_3)_2$].

Ketal **23** (3.64 g, 10.0 mmol) was added over a 5-min period to 10.0 mmol of lithium diisopropylamide in 10 mL of anhydrous tetrahydrofuran, prepared from excess diisopropylamine and 6.7 mL of 1.5 M *n*-butyllithium in hexane, which was maintained in a dry ice–acetone bath at −78 °C. Allyl bromide (1.3 g, 11 mmol) in 5.2 mL of hexamethylphosphoric triamide was then added to the reaction mixture, and the resulting solution was allowed to warm to room temperature. After addition of water, the mixture was extracted with ether, the ether layer was dried over anhydrous magnesium sulfate, and the ether was then evaporated under reduced pressure. Distillation of the resulting liquid produced 2.18 g of **ethyl 2-allyl-4-(3-methyl-1-butoxy)-4-phenyl-3-butenoate** (6.9 mmol, mmol, 69% yield): bp 160 °C (0.4 torr); ^{1}H NMR ($CDCl_3$) δ 7.65–7.15 (m, 5 H), 6.05–5.40 (m, $CH_2CH=$), 5.20–4.85 (m, $=CH_2$), 5.25 and 4.73 (d, CHCH=, *Z* and *E* isomers, respectively), 4.17 and 4.16 (q, *J* = 7.1 Hz, CH_3CH_2O of *E* and *Z* isomers, respectively), 3.95–3.50 (m, 2 H), 3.50–3.00 (m, 1 H), 2.80–2.20 (m, 2 H), 2.2–1.3 (m, 3 H), 1.25 (t, *J* = 7.1 Hz, CH_3CH_2O), 0.90 and 0.85 [d, $CH(CH_3)_2$ of *Z* and *E* isomers, respectively]. Anal. Calcd for $C_{20}H_{28}O_3$: C, 75.91; H, 8.92. Found: C, 76.04; H, 9.00.

Hydrolysis of this vinyl ether (1.00 g, 3.2 mmol) in 10 mL of 96% aqueous ethanol containing 1 drop of concentrated hydrochloric acid at room temperature for 20 h produced **24** in 96% yield (0.76 g, 3.08 mmol): bp 150 °C (0.4 torr); ^{1}H NMR ($CDCl_3$) δ 8.05–7.90 (m, 2 H), 7.65–7.35 (m, 3 H), 6.05–5.55 (m, CH=), 5.22–4.93 (m, $=CH_2$), 4.15 (q, *J* = 7.1 Hz, CH_2O), 3.55–2.90 (m, 3 H), 2.55–2.30 (m, 2 H, distorted t), 1.24 (t, *J* = 7.1 Hz, CH_3CH_2O). Anal. Calcd for $C_{15}H_{18}O_3$: C, 73.15; H, 7.37. Found: C, 72.87; H, 7.58.

Rearrangement of Allyl 2-Methoxy-2-phenylcyclopropanecarboxylate (25). A mixture of 50 mg of **25** (0.22 mmol) and 4.2 mg of $PtCl_2$·2PhCN (0.011 mmol) was heated at 120 °C for 10 min. The resulting reaction mixture was subjected to GC analysis on a 20% SE-30 column; individual products were collected and subjected to spectral analysis: ^{1}H NMR ($CDCl_3$), for **25a**, δ 6.25–5.45 (m, $CH=CH_2$), 5.40–5.00 (m, $CH=CH_2$), 4.70–4.55 (m, CH_2O), remaining absorptions identical with those of **1a**; for **25b**, δ 8.10–7.95 (m, 2 H), 7.65–7.25 (m, 3 H), 6.20–5.70 (m, $CH=CH_2$), 5.45–5.05 (m, $CH=CH_2$), 4.60 (m, CH_2O), 3.30 (t, $PhCOCH_2$), 2.77 (t, CH_2COO–allyl); for **24**, δ 8.05–7.85 (m, 2 H), 7.60–7.30 (m, 3 H), 6.00–5.45 (m, $CH=CH_2$), 5.20–4.90 (m, $CH=CH_2$), 4.15–3.80 (m, PhCOC*H*), 3.62 (s, CH_3O), 2.50–2.10 (m, $CH_2CH=$); the CH_2COOMe absorptions of **26** are observed at δ 3.05 (d, *J* = 8.7 Hz) and 2.41 (d, *J* = 5.1 Hz) for the minor conformer and at δ 2.84 (d, *J* = 8.7 Hz) and 2.62 (d, *J* = 5.1 Hz) for the major conformer. Hydrolysis of **26** in 1.0 M sodium hydroxide in D_2O (reflux 1 h) produced the same product as did **17a**, 3-benzoyl-3-deuterio-5-hexenoic acid: ^{1}H NMR ($CDCl_3$) δ 8.05–7.85 (m, 2 H), 7.60–7.30 (m, 3 H), 6.00–5.45 (m, $CH=CH_2$), 5.20–4.90 (m, $CH=CH_2$), 2.50–2.10 (m, $CH_2CH=$); the CH_2COOH absorptions are observed at δ 3.09 (s) and 2.44 (s) for the minor conformer and at δ 2.87 (s) and 2.64 (s) for the major conformer.

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Chemistry of *anti*- and *syn*-1,2:3,4-Naphthalene Dioxides and Their Potential Relevance as Metabolic Intermediates

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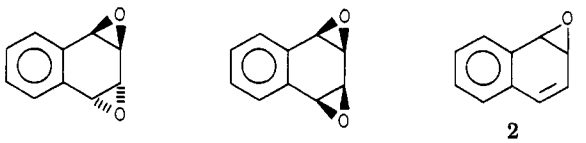
The reactivity, site of attack, and stereochemistry of reactions of a variety of nucleophiles with the *anti*- and *syn*-1,2:3,4-naphthalene dioxides have been explored. In most cases, substituted tetrahydronaphthalene products arising through attack at the C-1 and C-4 positions in the anti mode were obtained. These isomeric dioxides provide excellent precursors for a number of difficultly accessible 1,4-disubstituted naphthalene derivatives such as 1,4-diphenoxynaphthalene and 1,4-dicyanonaphthalene. Evidence is also presented that *anti*-naphthalene dioxide constitutes an intermediate metabolite in the rat.

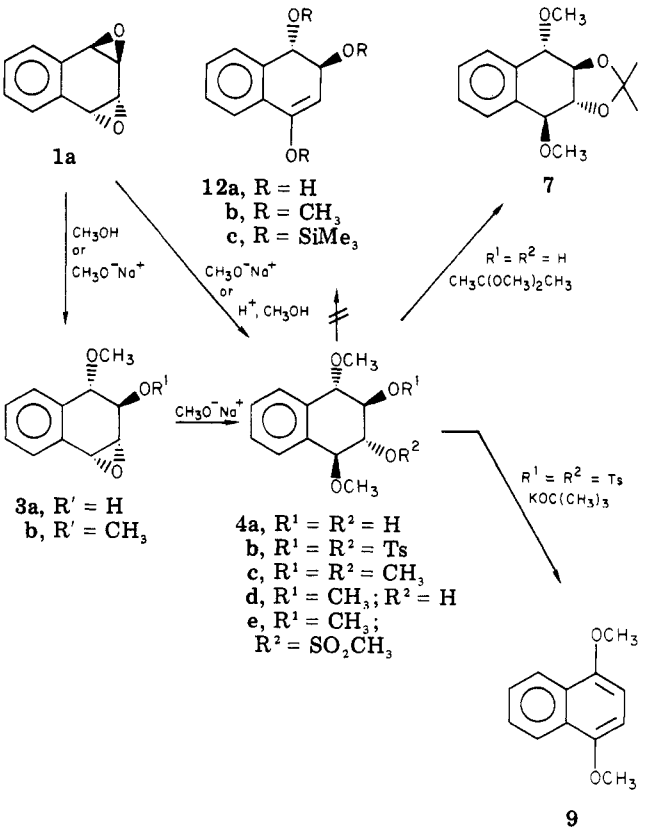
Our discovery of the direct oxidation of naphthalene to *anti*-1,2:3,4-naphthalene dioxide (**1a**)[1a,b] and the inde-



1a **1b** **2**

pendent initiation of a reinvestigation of naphthalene metabolism in rats by the Baylor group, while fortuitous, has led to a highly fruitful collaborative program.[2] As a result of these concurrent events, it became possible to characterize structurally a multitude of newly detected oxygenated and methylthio urinary metabolites of naphthalene and to define their stereochemistry. Of primary significance in this context was the revelation that the *anti*-1,2:3,4-naphthalene dioxide (**1a**), like the monoepoxide **2**,[3] is implicated as an intermediate in the metabolic processes. Heretofore, diepoxides have eluded detection as metabolites of polynuclear hydrocarbons. At this time, we report the synthetic details and structural elucidation of a number of precursors and metabolites synthesized in our laboratories, to which we have previously alluded.[2] It is our object to elaborate the conversions developed and to illustrate the potential utility of the isomeric naphthalene dioxides **1a** and **1b**[1c] for the synthesis of difficultly accessible disubstituted naphthalene derivatives. To avoid confusion, we have elected in this manuscript to employ

Scheme I



that nomenclature which has been adopted by the majority of investigators in the field of polynuclear aromatic hydrocarbon metabolism.[4]

Results and Discussion

Methanolysis of **1a** may be controlled to achieve opening of a single epoxy ring to give the monomethyl ether **3a**, which in turn may be converted to the diol diether **4a** by

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