Dimerization of Terminal Epoxides by Homogeneous Transition-Metal Complexes. A Novel Synthesis of Carboxylic Esters[1]

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Terminal epoxides have been shown to dimerize to carboxylic esters at 180 °C in the presence of some Rh(I) and Ru(II) catalysts. Mixing of two epoxides of different electronic nature gives as the main product "crossed" esters, in which the electron-donating substituents are attached to the carboxylic part and the electronegative groups to the alcoholic residue. Kinetic measurements were carried out using styrene oxide as substrate and $RuCl_2(PPh_3)_3$ as catalyst. The reaction rate proved to increase either by increasing the electron density of the metal or by introduction of electron-donating groups in the substrate. The proposed reaction mechanism includes (a) dissociation of $RuCl_2(PPh_3)_3$; (b) oxidative addition of the epoxide (through the less-substituted carbon atom) to the activated catalyst; (c) slow hydrogen transfer from the metal to the β-oxirane carbon, followed by ring cleavage of the epoxide; (d) α-hydrogen transfer and formation of a ruthenium–acyl complex; (e) addition of the second epoxide molecule to the acyl carbonyl carbon; (f) reductive elimination of ester $RCH_2CH_2OCOCH_2R$ from the rearranged ruthenium complex.

Results

Recently we reported[2] the selective conversion of vicinal-disubstituted epoxides into ketones by $RhCl(PPh_3)_3$ between 150 and 210 °C. Extension of this study to include monosubstituted compounds revealed that *terminal* oxiranes dimerize under these conditions to give carboxylic esters. Styrene oxide, e.g., forms 2-phenylethyl phenylacetate as shown in eq 1. In

$$2C_6H_5CH(O)CH_2 \xrightarrow{\text{cat.}} C_6H_5CH_2CH_2OCOCH_2C_6H_5 \quad (1)$$

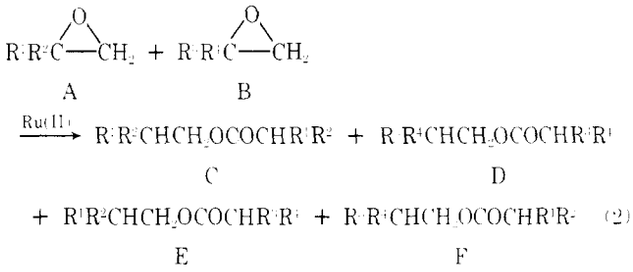
this system the rhodium catalyst can be replaced by $RuCl_2(PPh_3)_3$, though a longer reaction time is required. Other platinum–metal complexes seem to catalyze reaction 1 only to a small extent or not at all (see Table I).

By analogy to our previous study[2] one would expect terminal epoxides to rearrange into aldehydes and ketones. Therefore, it could have been assumed that reaction 1 is a two-step process, in which phenylacetaldehyde is the first intermediate that undergoes a Tischenko-like redox reaction. We have shown, however, that aldehydes do not only fail to take part in catalysis 1 but seriously interfere with the formation of the ester. Whenever any aldehyde *is* formed as a side product it must be removed during the process. The other carbonyl-free side products listed in Table I, including β-phenylethanol, result from independent routes and have no effect on the formation of the phenylacetate.

The dimerization of further terminal epoxides by $RuCl_2(PPh_3)_3$ is summarized in Table II. It is remarkable that the electronic nature of the starting oxide has hardly any influence on the yield of the ester. There exists, however, a considerable difference between the reactivity of aliphatic and aromatic oxiranes with respect to ester formation. The dimerization takes place exclusively at the terminal carbon atom. Thus, compounds $R^1R^2\overline{C-O-CH_2}$ do not give any branched ester of type $R^1R^2C(CH_3)OCOCR^1R^2$. This indicates that the hindered, rather than the unhindered, epoxide C–O bond is cleaved.

It is obvious that ester formation from two epoxide molecules must be associated with intermolecular hydrogen transfer. Since α-methylstyrene oxide, $C_6H_5\overline{C(CH_3)-O-CH_2}$, reacts almost equally as well as the nonsubstituted styrene oxide, while the β-methyl derivative, $C_6H_5\overline{CH-O-CHCH_3}$, does not dimerize at all, it can be concluded that only the terminal hydrogen atoms are essential in catalysis 1.

The hydrogen transfer may take place either between two similar or different epoxide molecules. In the latter case, the formation of "crossed" and "noncrossed" esters is observed (eq 2). Some typical examples are given in Table III.



$$\underset{A}{R^1R^2C(O)CH_2} + \underset{B}{R^3R^4C(O)CH_2} \xrightarrow{\text{Ru(II)}} \underset{C}{R^1R^2CHCH_2OCOCHR^3R^4} + \underset{D}{R^3R^4CHCH_2OCOCHR^1R^2}$$

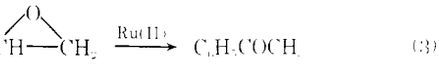
$$+ \underset{E}{R^1R^2CHCH_2OCOCHR^1R^2} + \underset{F}{R^3R^4CHCH_2OCOCHR^3R^4} \quad (2)$$

When aromatic epoxides are used, the main product is the noncrossed ester that has the most powerful electron-donating substituents. Among the "crossed" esters there prevails the one in which the better electron-attracting group is incorporated in the carbinol residue and the less-potent electron-attracting substituent in the carboxylic part. Mixtures of aliphatic and aromatic epoxides give always the "noncrossed" aromatic ester as the main product. The "crossed" ester derived from the aliphatic acid predominates over the ester of the aromatic acid. E.g., a mixture of styrene oxide and 1-hexene oxide (1:1) yields, under conditions of Table III, 36.7% $C_6H_5CH_2COO(CH_2)_2C_6H_5$, 0.6% $CH_3(CH_2)_4COO(CH_2)_5CH_3$, 1.5% $CH_3(CH_2)_4COO(CH_2)_2C_6H_5$, and 1.0% $C_6H_5CH_2COO(CH_2)_5CH_3$.

Although one epoxide molecule formally serves as the hydrogen donor and the other as the acceptor, it is essential that *both* oxiranes have one unsubstituted function. Therefore, β-methylstyrene oxide, e.g., does not only fail to dimerize, but is also unable to participate in "crossed" ester formation with unsubstituted styrene oxide: $C_6H_5\overline{CH-O-CH_2}$ and $C_6H_5\overline{CH-O-CHCH_3}$ give only $C_6H_5CH_2COO(CH_2)_2C_6H_5$ free of any $C_6H_5CH_2COOCH(CH_3)CH_2C_6H_5$.

Both the requirement of high epoxide concentration in catalysis 1 and the existing of side reactions restricted our kinetic studies.

Typical reaction curves for 2-phenylethyl phenylacetate formation (eq 1) and for the main side reaction (eq 3) are given



$$C_6H_5CH(O)CH_2 \xrightarrow{\text{Ru(II)}} C_6H_5COCH_3 \quad (3)$$

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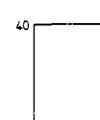
Table I. Transformation of Styrene Oxide by Various Catalysts at 180 °C[a]

Expt	Catalyst	Reaction time, h	Products, %[b]								Recovered starting material, %
			$C_6H_5CH_2COO-CH_2CH_2C_6H_5$	$C_6H_5CO-CH_3$	$C_6H_5CH_2-CHO$	$C_6H_5CH_3$	$C_6H_5CH_2-CH_2OH$	$C_6H_5CH=CH_2$	$C_6H_5C_2H_5$		
1	$RuCl_2(PPh_3)_3$	9	42.5	5.6	0.7	1.6	3.4	0.4	0.8	0.0	0.0
2	$RuCl_2(PPh_3)_3$	2	11.5	0.0	0.0	0.5	0.3	0.7	0.1	0.0	73.1
3	$RhCl(PPh_3)_3$	2	33.0	0.0	0.1	15.0	0.7	3.3	2.4	0.0	0.0
4	$Rh(CO)Cl(PPh_3)_2$	9	19.0	1.0	0.0	12.5	0.4	1.0	2.0	0.0	0.0
5	$[Rh(CO)_2Cl]_2$	2	0.0	0.0	4.8	0.7	0.0	0.4	0.0	19.4	0.0
6	$PdCl_2(PPh_3)_2$	9	3.8	0.5	0.9	35.6	0.0	0.0	4.2	0.6	0.0
7	$[Pd(CH_3COO)_2]_3$	9	1.0	0.0	0.0	33.9	0.0	0.0	0.0	21.0	0.0
8	$Ir(CO)Cl(PPh_3)_2$	9	4.5	1.6	0.0	5.0	1.9	0.0	0.0	2.4	50.3
9	$PtCl_2(PPh_3)_2$	9	2.9	5.1	0.0	1.5	2.4	0.0	0.0	1.3	63.9
10	$(C_6H_{10}PtCl_2)_2$	9	0.0	0.0	0.0	0.5	0.0	0.5	0.0	0.0	0.0
11	Rh/C (5%)	2	0.0	0.0	28.2	0.1	0.0	0.0	0.0	11.7	0.0

[a] Reaction system was 2 mmol of styrene oxide and 1.36×10^{-2} mmol of catalyst. Registry no.: styrene oxide, 96-09-3. [b] Except polymers.

Figure 1. Concentration–time profile for reaction 1 and 3. Reaction system: 0.1818 M $RuCl_2(PPh_3)_3$ at 180 °C.

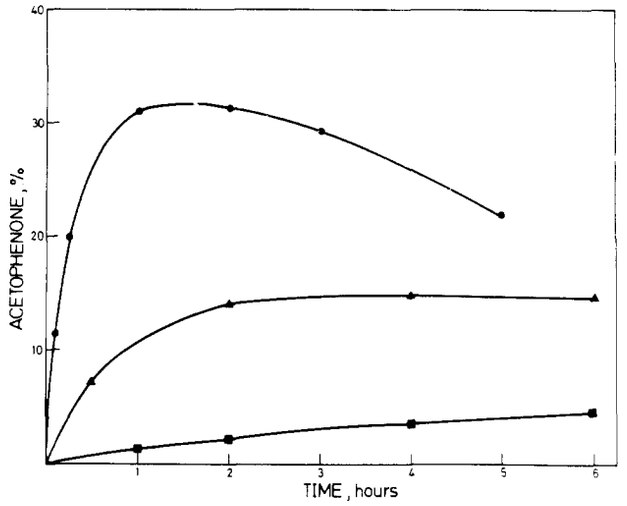


Figure 2. Dependence of acetophenone accumulation on catalyst concentration at 180 °C. ●, ▲, and ■—0.5220, 0.1818, and 0.0566 M $RuCl_2(PPh_3)_3$ in styrene oxide, respectively.

in Figure 1. While the amount of the ester increases steadily, the concentration of acetophenone starts to decrease after 2 h (or even earlier at fairly high catalyst concentration as shown in Figure 2). The partial removal of the ketone is caused by condensation with phenylacetaldehyde followed by transfer hydrogenation (eq 4).

$$C_6H_5COCH_3 + C_6H_5CH_2CHO \xrightarrow[-H_2O]{Ru(II)} C_6H_5COCH{=}CHCH_2C_6H_5 \xrightarrow[C_6H_5CH_2CH_2OH]{Ru(II)} C_6H_5(CH_2)_3COC_6H_5 \quad (4)$$

This two-step side reaction plays a crucial role in the Ru(II)-catalyzed dimerization of styrene oxide and will be discussed below.

The plot of initial rate of reaction 1 vs. catalyst concentration (Figure 3) indicates a rather complex mechanism. Rate saturation at relatively high concentration of $RuCl_2(PPh_3)_3$ is not uncommon in homogeneous catalysis (see, e.g., ref 4), and is usually attributed to both low solubility and oligomerization of the dissociated ruthenium complex. The decrease in rate above 0.2 M is associated with the competing epoxide rearrangement (to acetophenone and to its transformation

Table II. $RuCl_2(PPh_3)_3$-Catalyzed Conversion of Various Terminal Epoxides $R^1R^2\overline{C-O-CH_2}$ into Carboxylic Esters under Comparable Conditions[a]

Expt	Registry no.	Epoxide R^1	Epoxide R^2	Ester	Registry no.	Yield, %
1	2788-86-5	4-ClC_6H_4	H	4-$ClC_6H_4(CH_2)_2OCOCH_2C_6H_4$-4-Cl	22232-02-6	38.0
2	13107-39-6	4-$CH_3C_6H_4$	H	4-$CH_3C_6H_4(CH_2)_2OCOCH_2C_6H_4$-4-$CH_3$	66255-90-1	37.6
3	2085-88-3	C_6H_5	CH_3	$C_6H_5CH(CH_3)CH_2OCOCH(CH_3)C_6H_5$	66255-91-2	35.0
4	4436-24-2	$C_6H_5CH_2$	H	$C_6H_5(CH_2)_3OCO(CH_2)_2C_6H_5$	60045-27-4	4.9[b]
5	1436-34-6	$CH_3(CH_2)_3$	H	$CH_3(CH_2)_5OCO(CH_2)_4CH_3$		4.6[b]
6	106-88-7	C_2H_5	H	$CH_3(CH_2)_3OCO(CH_2)_2CH_3$		2.3[b]

[a] A mixture of 2 mmol of epoxide and 1.36×10^{-2} mmol of catalyst were heated under N_2 in a sealed ampule at 180 °C for 9 h. [b] In this experiment the ketone $R^1R^2COCH_3$ was the main product (yield 18–25%).

Table III. Formation of Esters from Mixtures of Epoxides in the Presence of $RuCl_2(PPh_3)_3$[a,b]

Expt	Epoxide A R^1	Epoxide A R^2	Epoxide B R^3	Epoxide B R^4	Yields of esters, % C	D	E	F	C/D	F/E
1	C_6H_5	H	4-ClC_6H_4	H	22.8	12.0	6.0	10.8	1.9	1.8
2	4-$CH_3C_6H_4$	H	C_6H_5	H	31.3	15.6	7.0	10.6	2.0	1.5
3	4-$CH_3C_6H_4$	H	4-ClC_6H_4	H	30.1	8.2	4.5	13.5	3.7	3.0
4	C_6H_5	CH_3	C_6H_5	H	12.1	3.5	10.4	4.9	3.5	0.5

[a] A–F and R^1–R^4 as in eq 2. [b] Reaction system: 2 mmol of each epoxide and 1.4×10^{-2} mmol of catalyst heated for 9 h under N_2 at 180 °C in a sealed tube.

Table IV. Effect of Electronic Changes in the Catalyst $RuCl_2[(4\text{-}XC_6H_4)_3P]_3$ on the Rate of Reaction 1 at 180 °C[a]

Substituent X	Registry no.	Initial rate of ester formation, mmol L^{-1} min^{-1}
OCH_3	39114-24-4	61
CH_3	36733-05-8	55
H	15529-49-4	37
F	39152-69-7	34
Cl	39042-64-3	27

[a] Catalyst concentration 0.182 M in pure styrene oxide.

Table V. Initial Rate of Conversion of Some Styrene Oxides into Carboxylic Esters at 180 °C[a]

Epoxide	Initial rate, mmol L^{-1} min^{-1}
α-Methylstyrene oxide	64
4-Methylstyrene oxide	63
Styrene oxide	37
4-Chlorostyrene oxide	20

[a] Catalyst concentration: 0.182 M in the epoxide.

product) which predominates at this high concentration (see Figure 2). In a typical experiment, a 0.5 M solution of the catalyst in styrene oxide yielded after 9 h at 180 °C 15.1% of γ-phenylbutyrophenone and only 14.0% of the expected ester.

The influence of the electronic structure of the catalyst was studied utilizing complexes of the general formula $RuCl_2[(4\text{-}XC_6H_4)_3P]_3$. The initial rates of reaction 1 for various substituents X are listed in Table IV. These data show that electron-attracting groups (that decrease the electron density on the metal atom) suppress the reaction rate and vice versa, electron-donating ones stimulate the catalysis.

A similar electronic effect was observed in reaction 3. At 190 °C the initial rates of ketone formation were 70, 59, 51, 24, and 17 mmol L^{-1} min^{-1} for 0.182 M $RuCl_2[(4\text{-}CH_3OC_6H_4)_3P]_3$, $RuCl_2[(4\text{-}CH_3C_6H_4)_3P]_3$, $RuCl_2[(C_6H_5)_3P]_3$, $RuCl_2[(4\text{-}FC_6H_4)_3P]_3$, and $RuCl_2[(4\text{-}ClC_6H_4)_3P]_3$, respectively [cf. the electronic effect in $RhCl(PAr_3)_3$-catalyzed rearrangement of vicinal-disubstituted epoxides reported in our previous paper[2]].

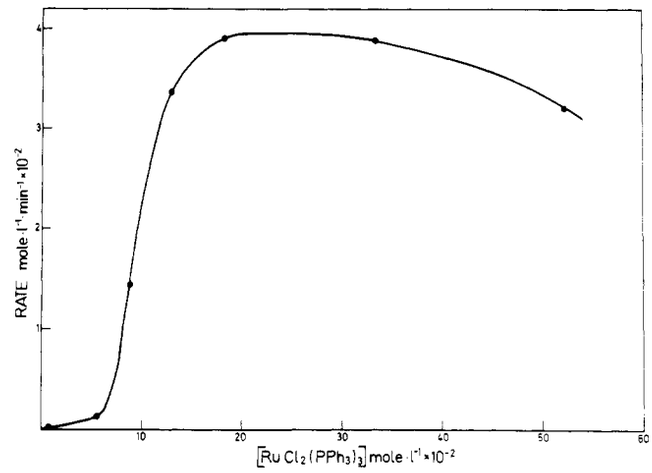


Figure 3. Rate dependence of reaction 1 on the concentration of the ruthenium catalyst at 180 °C.

The rate dependence on the structure of the epoxide is shown by some experiments listed in Table V. Introduction of an electron-donating CH_3 group, either into the phenyl ring or into the (sterically hindered) α position, leads to an increase in rate, while an electron-attracting chlorine atom slows the reaction down. As shown in Table III this electronic effect also exists in the reaction of mixtures of epoxides. However, the main side process, viz., the rearrangement $R\overline{CH-O-CH_2} \rightarrow RCOCH_3$, is practically unaffected by the electronic nature of the epoxide.

Discussion

Following the mechanisms suggested for other $RuCl_2(PPh_3)_3$-promoted reactions (see, e.g., ref 4) we assume that the major steps in catalysis 1 are: (a) activation of the catalyst; (b) oxidative addition of one molecule of epoxide; (c) rearrangement of catalyst–substrate complex; (d) reaction with a second epoxide molecule; (e) release of the product.

Activation of the Catalyst. Dichlorotris(triphenylphosphine)ruthenium has been shown to dissociate in solution to the bisphosphine complex (eq 5).[5,6]

$$RuCl_2(PPh_3)_3 \rightleftharpoons RuCl_2(PPh_3)_2 + PPh_3 \quad (5)$$

In the presence of epoxides the triphenylphosphine is quantitatively removed as Ph_3PO (Wittig deoxygenation)[2,7] and dissociation goes to completion. In fact, when a solution of $RuCl_2(PPh_3)_3$ in styrene oxide (0.2 M) is stirred under N_2 for 24 h at 25 °C a dark green complex, $[RuCl_2(PPh_3)_2]_n$, of mp 125–130 °C results.[8] It precipitates upon addition of $CHCl_3$ and petroleum ether. The oligomer, which exhibits the same kinetics as $RuCl_2(PPh_3)_3$ in conversion of styrene oxide into 2-phenylethyl phenylacetate, is assumed to dissociate and to act as the true catalyst. Since $RuCl_2(PPh_3)_3$ forms an oxido complex at ambient atmosphere that rearranges to the inactive dichlorobis(triphenylphosphine oxide)ruthenium,[9] it is essential to exclude oxygen from the reaction mixture.

When a mixture of $RuCl_2(PPh_3)_3$ and styrene oxide (molar ratio 0.04:1) is heated under N_2 for 9 h at 180 °C, cooled, and diluted with CCl_4, colorless (*cis*-Cl_2)Ru[*cis*-$(CO)_2$][*trans*-$(PPh_3)_2$] of mp 243–245 °C precipitates. This complex has two strong carbonyl absorptions at 1995 and 2050 cm^{-1} and rearranges on standing to the yellow all-trans isomer ($\nu_{C\equiv O}$ 2010 cm^{-1}).[10-13] Kinetic measurements revealed that none of the isomers of $RuCl_2(CO)_2(PPh_3)_2$ take part in catalyses 1. The colorless complex promotes, however, the rearrangement of styrene oxide to acetophenone in a rate comparable to $RuCl_2(PPh_3)_3$ and may, therefore, be the actual catalyst in reaction 3.

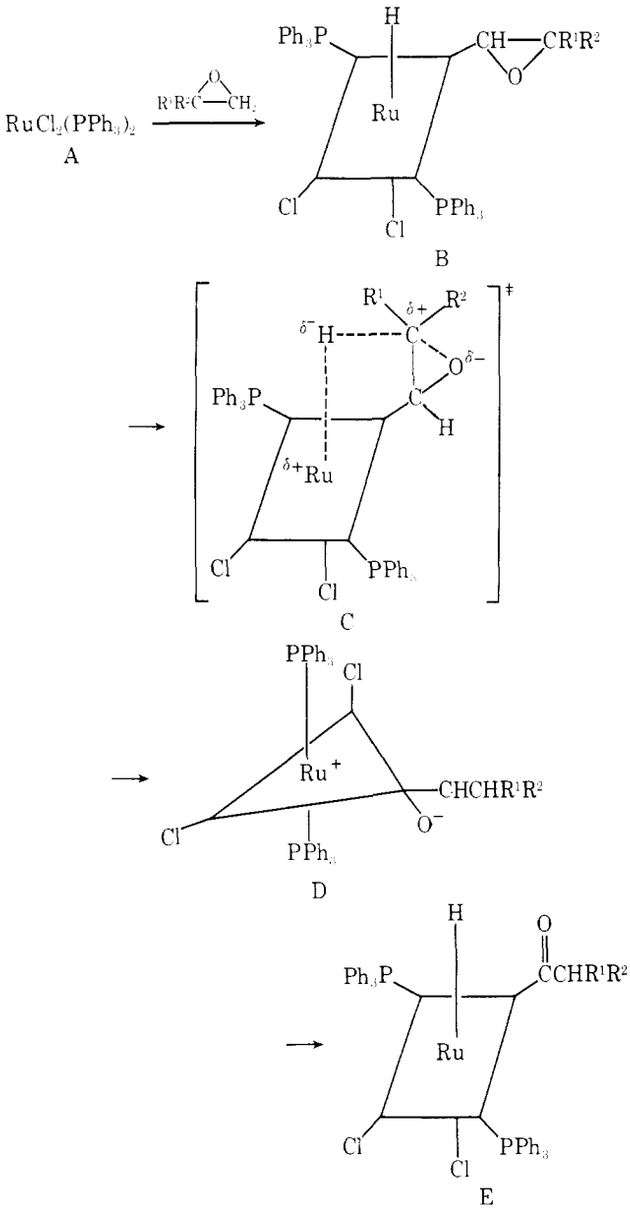
Coordination and Activation of the Epoxide. As shown previously[2] epoxides may add reversibly to Rh(I)–phosphine complexes by insertion into an oxirane σ bond. For steric reasons, the addition of terminal epoxides to the Rh(I) and Ru(II) catalysts takes place, most likely at the unsubstituted carbon atom. As a nucleophilic process it should be promoted by electron-attracting groups. However, since the rate of ester formation is increased by electron-donating substituents, epoxide activation (stage A → B) cannot be considered rate determining in catalysis 1.

Intramolecular Hydrogen Transfer. In analogy to the β-hydride transfer that occurs in $RhCl(PPh_3)_3$-catalyzed rearrangement of 1,2-disubstituted epoxides,[2] we postulate a similar hydrogen shift in B. As explained in our previous paper[2] this step can be regarded rate controlling by virtue of the observed electronic effects of both the reagent and the catalyst. Structure C represents then the activated complex in step B → D. The facts that dimerization of α-methylstyrene oxide is faster than that of the unsubstituted styrene oxide (Table IV) and the formation of 2-phenylpropyl phenylacetate, $C_6H_5CH(CH_3)CH_2OCOCH_2C_6H_5$, is greater than the other "crossed" ester (expt 4, Table III) may indicate that the positive charge stabilization on the oxirane carbon in C plays a more important role than the steric interference of the α-CH_3 group.

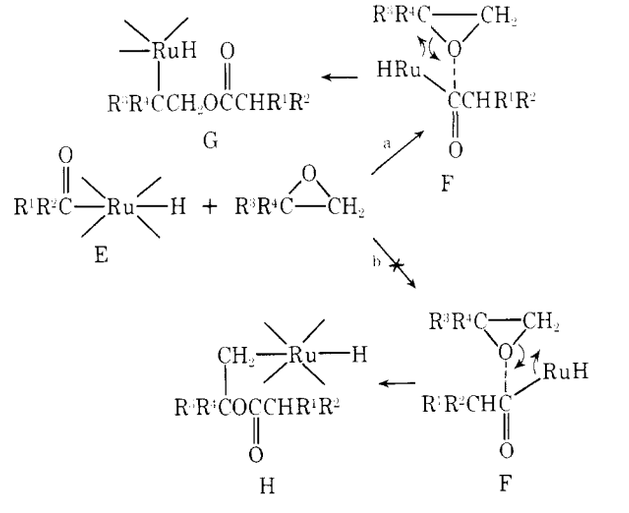
When complex D undergoes reductive elimination aldehyde R^1R^2CHCHO results. Hence varying amounts of phenylacetaldehyde and its decarbonylation product[14] are formed in the transformation of styrene oxide by $RhCl(PPh_3)_3$ and by some other catalysts listed in Table I.

In the $RuCl_2(PPh_3)_3$-catalyzed reaction α-hydrogen transfer (from the coordinated carbon atom back to the metal) predominates, leading to E. β-Hydride transfer is of course possible as well, but by this operation the reaction would regress to B. Since at this stage the center of activity is remote from the phenyl ring and no conjugating function exists, the introduction of substituents into the aromatic moiety of styrene oxide is expected to influence transformation D → E only very little.

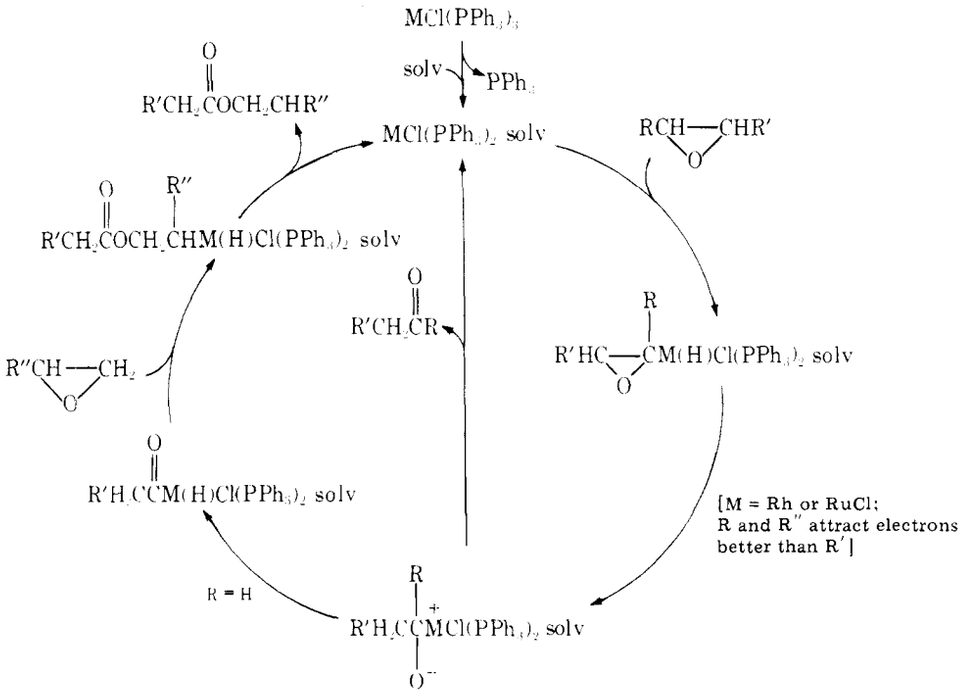
Reaction of the Second Epoxide Molecule. Electrophilic addition of a second epoxide to the active carbonyl group of E affords a hydrido–acyl–ruthenium complex F. This step



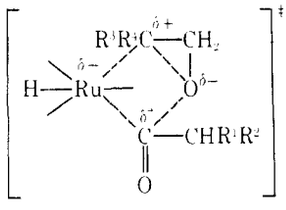
may thus resemble the well-known reaction of acid halides with oxiranes.[15] A concerted four-centered electron transfer in F may lead to either hydride G or H. The absence of any branched esters $R^1R^2CH(CH_3)OCOCHR^3R^4$ among the products suggests that such electron transfer occurs at the sterically hindered (route a) rather than at the nonhindered



Scheme I



carbon atom (route b). By this mechanism a partial positive charge accumulates on the carbon atom in the transition state when the C–O bond breaking is ahead of the Ru–C bond forming as shown in structure I. This is in agreement with the



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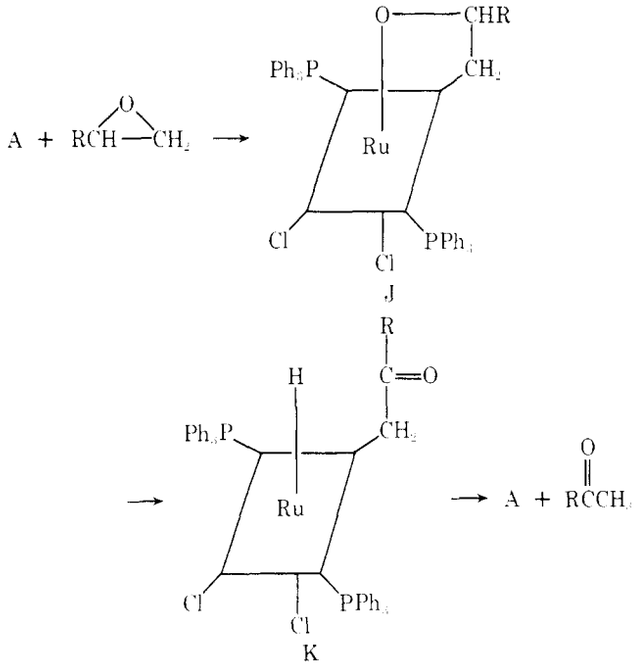
observation that an increase in electron-donating power of R^3 and/or R^4 enhances the reaction rate. An increase in the nucleophilicity of the oxirane oxygen is thus expected to have a marked effect on the rate of this step. As R^1 and R^2 are at remote positions, their influence should be much smaller than the substituents R^3 and R^4 of the second epoxide molecule. Support of this mechanism is provided by experiments with two epoxides of different electronic nature which give as the main product the noncrossed ester with the most potent electron-donating groups. The amount of the "crossed" ester having the electron-attracting substituent attached to the alcohol residue of the ester indicates that step E → G is faster than the β-hydride transfer B → D.

Release of Product. In the final step the ester is formed along with A by reductive elimination. As in oxidative addition, the reverse reaction is also facilitated by electron-attracting groups, which decrease the electron density on the metal atom. Since in the experiments with $RuCl_2[P(4\text{-}XC_6H_4)_3]_3$ electron-donating groups X proved to increase the rate, the final step also cannot be rate determining.

The similarity of A → D to the proposed reaction intermediates in the rearrangement of vicinal-disubstituted epoxides[2] suggests that both reactions may be derived from the same catalytic cycle shown in Scheme I.

Side Reactions. The main nonpolymeric side products in $RuCl_2(PPh_3)_3$- and $RhCl(PPh_3)_3$-catalyzed transformation of terminal epoxides are ketones and decarbonylated aldehydes,[14] respectively. (See expts 1 and 3 in Table I). While the formation of the aldehydes can be rationalized by the mechanism outlined for $RhCl(PPh_3)_3$-promoted rearrangement of disubstituted epoxides (see Scheme I and ref 2), the formation of ketones is best explained by the following sequence of reactions: (a) oxidative addition of the active catalyst to the oxirane C–O bond[16-18] (such addition does not take place to vicinal-disubstituted epoxides owing to steric effects[2,18]); (b) β-hydrogen abstraction;[19] (c) reductive elimination of the ketone from the hydrido complex K.



While the main catalytic process (i.e., reaction 1) is not influenced by the accumulation (or even addition) of the ketone, the presence of aldehyde considerably reduces the rate of ester formation. Thus, when equimolar amounts of styrene oxide and phenylacetaldehyde were heated in the presence of $RuCl_2(PPh_3)_3$ for 9 h under the conditions given in Table I, only 20.8% of 2-phenylethyl phenylacetate was formed. Catalysis 1 must, therefore, be accompanied by processes which

Table VI. ^{1}H NMR Spectra of 2-(Aryl)ethyl Acetates in $CDCl_3$[a]

a b c

4-X-$C_6H_4CH_2CH_2OCOCH_2C_6H_4$-4-Y

Protons assignment	Substituent X/Y	Chemical shifts of protons a, b, and c, δ (ppm)		
		CH_3	H	Cl
a	CH_3	2.789	2.782	2.798
a	H[b]	2.834	2.833	2.844
a	Cl	2.805	2.804	2.824
b	CH_3	4.174	4.179	4.193
b	H	4.197	4.209	4.224
b	Cl	4.183	4.190	4.208
c	CH_3	3.425	3.470	3.438
c	H	3.434	3.472	3.422
c	Cl	3.425	3.474	3.451

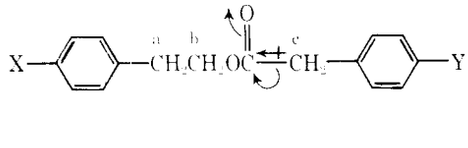
[a] Concentration of ester: 0.20 M; temperature 30.6 °C. [b] Registry no.: 102-20-5.

consume the formyl compound as soon as it is formed. In the $RhCl(PPh_3)_3$-catalyzed reaction rapid decarbonylation, RCHO → RH + CO, takes place;[20] in the $RuCl_2(PPh_3)_3$-promoted process the relatively small amount of aldehyde is removed by an aldol condensation with the ketone as shown in eq 4. We have proven, by kinetic studies using acetophenone, phenylacetaldehyde, and 2-phenylethanol, that the Ru(II) complex promotes *both* steps of reaction 4.[21] In the transfer hydrogenation of the unsaturated ketone to γ-phenylbutyrophenone, water and 2-phenylethanol (the latter formed from styrene oxide and H_2O) serve as the hydrogen donors. Since the condensation reaction is strongly inhibited by sulfur compounds, 2-vinylthiophene oxide, 2-($\overline{CH_2—O—CH_2}$)C_4H_3S, and $RuCl_2(PPh_3)_3$ give sufficient free thiophene-2-carboxaldehyde that prevents the formation of 2-(2-thienyl)ethyl (2-thienyl)acetate, 2-(C_4H_3S)-$CH_2CH_2OCOCH_2$-2-(C_4H_3S). The ester is, however, obtained when traces of $RhCl(PPh_3)_3$ (that efficiently decarbonylate thiophene aldehyde) are admixed with the Ru(II) catalyst.

Finally, we wish to comment briefly on some unexpected features of the ^{1}H NMR spectra of the arylethyl acetates obtained in reaction 1.

Table VI indicates that there is no simple correlation between the electronic nature of substituents X and Y and the chemical shifts. An increase in electron-attracting power of X in esters with the same type of Y does not cause the expected paramagnetic shift of the benzylic protons:[22] for X = Cl protons a and b are less deshielded than for X = H, though esters with X = CH_3 resonate at the highest field of this series of compounds. The effect of substituents Y on the remote protons a is, naturally, very small, although in going from compounds with Y = CH_3 or Y = H to Y = Cl a slight increase in the δ values is noted. The influence of Y on protons b is considerably larger. Protons c are least affected by X, but substituents Y have the same abnormal influence on them as X on protons a and b: the largest chemical shifts are not observed for esters with Y = Cl, but for those where Y = H.

These unexpected features of the NMR spectra can be rationalized by the net inductive effect exerted on the benzylic and homobenzylic protons in the phenethyl esters. When, e.g., Y in the following compound represents an electron-attracting chlorine atom, the inductive effect on c is composed of the effect of the ester carbonyl and that of the opposite directing Cl. (Yet the effect will still be directed toward the CO group.)



Thus, protons c in this chlorine-containing ester should be less deshielded than in the unsubstituted compound where Y = H. On the other hand the ester group does not reduce the inductive effect of the electron-releasing group and protons c in compound with Y = CH_3 are more shielded than those with Y = H or Cl. For the same reason an electron-attracting substituent X should slightly increase the δ values of protons c.

The same explanation may be applied for the "abnormality" of the chemical shifts of protons a and b.

Experimental Section

Melting points were taken on a Thomas-Hoover capillary melting point apparatus and are not corrected. Infrared spectra were measured with Perkin-Elmer spectrophotometers Models 157G and 257. Ultraviolet spectra were recorded with Perkin-Elmer Model 402 spectrometer. Proton magnetic resonance spectra were run using Varian EM-360 and HA-100D spectrometers. Mass spectra were recorded with a Varian MAT-311 spectrometer or directly from a gas chromatograph using a Varian MAT-111 instrument. Gas chromatography was performed with F & M Model 810 and Hewlett-Packard Model 7620A instruments (equipped with both thermal conductivity and flame ionization detectors) and with a Varian 920 machine (thermal conductivity detector only).

The catalysts $RuCl_2(PPh_3)_3$,[5] $RuCl_2[(4\text{-}ClC_6H_4)_3P]_3$,[23] $RuCl_2[(4\text{-}FC_6H_4)_3P]_3$,[23] $RuCl_2[(4\text{-}CH_3C_6H_4)_3P]_3$,[24] $RuCl_2[(4\text{-}CH_3OC_6H_4)_3P]_3$,[23] $RhCl(PPh_3)_3$,[25] $RhCl(CO)(PPh_3)_2$,[26] $Rh_2(CO)_4Cl_2$,[27] $IrCl(CO)(PPh_3)_2$,[28] $PdCl_2(PPh_3)_2$,[29] and $PtCl_2(PPh_3)_2$,[30] as well as the starting and reference compounds $C_6H_5CH_2\overline{CHOCH_2}$,[31] $C_6H_5\overline{C(CH_3)OCH_2}$,[32] $C_6H_5\overline{CHOCHCH_3}$,[33] 4-$CH_3C_6H_4\overline{CHOCH_2}$,[34] 2-$C_4H_3S\overline{CHOCH_2}$,[35] $CH_3(CH_2)_3OCO(CH_2)_2CH_3$,[36] and $CH_3(CH_2)_5OCO(CH_2)_4CH_3$[37] were prepared as reported in the literature.

The following epoxides were prepared by 3-chloroperbenzoic acid oxidation of the olefins.[38] **Hex-1-ene oxide:**[34] bp 118–120 °C; ν_{C-O} 840 cm^{-1}; ^{1}H NMR (CCl_4) δ 0.93 (m, 3), 1.43 (m, 6), 2.30 (m, 1), 2.60 (m, 2). **β,β-Dideuteriostyrene oxide** (from β,β-dideuteriostyrene[39]): bp 84–85 °C (15 mm); ν_{C-O} 850 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.90 (br s, 1), 7.30 (s, 5). **4-Chlorostyrene oxide:**[34] bp 82–84 °C (0.5 mm); ν_{C-O} 870 cm^{-1}; ^{1}H NMR (CCl_4) δ 2.60 (m, 1), 3.03 (m, 1), 3.72 (m, 1), 7.24 (m, 4).

4-Phenylbuta-1,3-diene 1,2-Oxide. A mixture of 20 g of 4-phenylbut-1-ene 1,2-oxide,[40] 24.08 g of *N*-bromosuccinimide, and 80 mL of CCl_4 was refluxed for 1 h. The succinimide was filtered off and the filtrate concentrated to yield 3-bromo-4-phenylbut-1-ene 1,2-oxide. To a solution of 8.0 g of the bromide in 50 mL of dry THF there was added at −5 °C under N_2 small portions of 1,5-diazabicyclo[4.3.0]-non-5-ene (7.00 g). After 17 h at −5 °C and 48 h at 25 °C the solvent was removed in vacuo below 0 °C, and the viscous residue treated with 20 mL of water and 100 mL of benzene. The aqueous layer was extracted with benzene and the combined organic solutions were washed with 5% aqueous KOH and water. The residue was distilled at 81–83 °C (0.8 mm) [lit.[41] 55 °C (10^{-3} mm)] to yield 2.13 g (50.5%) of colorless unsaturated epoxide: ν_{C-O} 840 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.75 (m, 1), 3.01 (m, 1), 3.49 (m, 1), 5.84 (d of d, 1, J = 16 and 7 Hz), 6.77 (d, 1, J = 16 Hz), 7.31 (s, 5).

The catalytic transformation of the various epoxides studied is illustrated by the following example.

Reaction of Styrene Oxide and $RuCl_2(PPh_3)_3$. A 3-mL pressure tube (neck length 10 cm, wall thickness 5 mm) was carefully dried, washed with N_2, and charged with 240 mg (2 mmol) of styrene oxide and 13 mg (1.36×10^{-2} mmol) of $RuCl_2(PPh_3)_3$. Any traces of oxygen were removed from the reaction tube with the aid of a high vacuum line, nitrogen was introduced at 1 atm, and the reaction tube was sealed and immersed into an oil bath thermostat at 180 °C. After 9 h, the clear orange-colored solution was cooled to room temperature and diluted with CCl_4 (total volume 5 mL). GLC analysis was carried out on a 2-m column packed with 15% stabilized DEGS on Chromosorb St-164 operated between 120 and 230 °C and a 2-m column with 20% Apiezon L on Anakrom ABS (60–70 mesh) at 70–230 °C. The reaction mixture proved to consist of 42.5% 2-phenylethyl phenylacetate, 5.6% acetophenone, 3.4% 2-phenylethanol, 1.6% toluene, 0.7% phenylacetaldehyde, 0.4% styrene, 0.3% ethylbenzene, and polymers. All these products were separated on preparative GLC columns and compared with authentic samples.

The other styrene oxides and related compounds were transformed in the same manner, but the low-boiling epoxides (1-butene oxide and 1-hexene oxide) were reacted in 1-mL ampules and treated with N_2 at −195 °C. 4-Phenylbut-1,3-diene 1,2-oxide proved to polymerize entirely under the above conditions and β,β-dideuteriostyrene oxide

underwent extensive H–D exchange in the presence of the Ru(II) catalyst[42] to give a mixture of deuterated and nondeuterated products.

The following esters were obtained in the catalytic transformation of the various epoxides. They were compared directly with authentic samples prepared by unambiguous methods.[43] (Some spectral data have already been given in Table VI.)

***n*-Hexyl phenylacetate;** bp 144–146 °C (1.8 mm); $\nu_{C=O}$ 1740 cm^{-1}, ν_{C-O} 1145, 1246 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (m, 3), 1.30 (m, 8), 3.53 (s, 2), 4.05 (t, 2, J = 6 Hz), 7.23 (s, 5); m/e 220 (M^+·). Anal. Calcd for $C_{14}H_{20}O_2$: C, 76.4; H, 9.1. Found: C, 76.5; H, 9.1.

2-Phenylpropyl phenylacetate: $\nu_{C=O}$ 1740 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.26 (d, 3, J = 7 Hz), 3.15 (q, 1, J = 7 Hz), 3.54 (s, 2), 4.18 (d, 2, J = 7 Hz), 7.19 (m, 10). Anal. Calcd for $C_{17}H_{18}O_2$: C, 80.3; H, 7.1. Found: C, 80.1; H, 7.0.

2-(4-Chlorophenyl)ethyl phenylacetate: bp 192–194 °C (1 mm); $\nu_{C=O}$ 1735 cm^{-1}, ν_{C-O} 1145, 1242 cm^{-1}. Anal. Calcd for $C_{16}H_{15}ClO_2$: C, 70.0; H, 5.5; Cl, 12.9. Found: C, 69.9; H, 5.5; Cl, 12.6.

2-(4-Tolyl)ethyl phenylacetate: $\nu_{C=O}$ 1740 cm^{-1}, ν_{C-O} 1145, 1245 cm^{-1}. Anal. Calcd for $C_{17}H_{18}O_2$: C, 80.3; H, 7.1. Found: C, 80.3; H, 7.3.

2-Phenylethyl 4-chlorophenylacetate; $\nu_{C=O}$ 1738 cm^{-1}, ν_{C-O} 1152, 1245 cm^{-1}. Anal. Calcd for $C_{16}H_{15}ClO_2$: C, 70.0; H, 5.5; Cl, 12.9. Found: C, 70.1; H, 5.5; Cl, 12.5.

2-(4-Chlorophenyl)ethyl 4-chlorophenylacetate: bp 228–232 °C (3 mm); $\nu_{C=O}$ 1740 cm^{-1}, ν_{C-O} 1150, 1245 cm^{-1}. Anal. Calcd for $C_{16}H_{14}Cl_2O_2$: C, 62.1; H, 4.5; Cl, 23.0. Found: C, 61.8; H, 4.7; Cl, 23.3.

2-(4-Tolyl)ethyl 4-chlorophenylacetate: $\nu_{C=O}$ 1738 cm^{-1}, ν_{C-O} 1146, 1240 cm^{-1}. Anal. Calcd for $C_{17}H_{17}ClO_2$: C, 70.7; H, 5.9; Cl, 12.3. Found: C, 70.9; H, 6.0; Cl, 12.1.

2-Phenylethyl 4-tolylacetate: $\nu_{C=O}$ 1740 cm^{-1}, ν_{C-O} 1145, 1247 cm^{-1}. Anal. Calcd for $C_{17}H_{18}O_2$: C, 80.3; H, 7.1. Found: C, 80.2; H, 7.1.

2-(4-Chlorophenyl)ethyl 4-tolylacetate: bp 188–190 °C (0.2 mm); $\nu_{C=O}$ 1735 cm^{-1}, ν_{C-O} 1140, 1242 cm^{-1}. Anal. Calcd for $C_{17}H_{17}ClO_2$: C, 70.7; H, 5.9; Cl, 12.3. Found: C, 70.9; H, 5.9; Cl, 12.1.

2-(4-Tolyl)ethyl 4-tolylacetate: $\nu_{C=O}$ 1740 cm^{-1}, ν_{C-O} 1146, 1248 cm^{-1}. Anal. Calcd for $C_{18}H_{20}O_2$: C, 80.6; H, 7.5. Found: C, 80.7; H, 7.6.

2-(2-Thienyl)ethyl 2-thienylacetate: bp 135 °C (5×10^{-2} mm); $\nu_{C=O}$ 1738 cm^{-1}, $\nu_{C=C}$ 1540, 1035 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.11 (t, 2, J = 8 Hz), 3.79 (s, 2), 4.29 (t, 2, J = 8 Hz), 6.88–7.13 (m, 6). Anal. Calcd for $C_{12}H_{12}O_2S_2$: C, 57.1; H, 4.8; S, 25.4. Found: C, 57.3; H, 4.9; S, 25.9.

2-Phenylethyl 2-phenylpropionate; bp 137–139 °C (1 mm); $\nu_{C=O}$ 1738 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.48 (d, 3, J = 7 Hz), 2.82 (t, 2, J = 8 Hz), 3.67 (q, 1, J = 7 Hz), 4.24 (t, 2, J = 8 Hz), 7.18 (m, 10). Anal. Calcd for $C_{17}H_{18}O_2$: C, 80.3; H, 7.1. Found: C, 80.6; H, 7.2.

2-Phenylpropyl 2-phenylpropionate: $\nu_{C=O}$ 1735 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.16 (d, 3, J = 7 Hz), 1.41 (d, 3, J = 7 Hz), 2.99 (q, 1, J = 7 Hz), 3.64 (q, 1, J = 7 Hz), 4.18 (d, 2, J = 7 Hz), 7.17 (m, 10). Anal. Calcd for $C_{18}H_{20}O_2$: C, 80.6; H, 7.5. Found: C, 80.7; H, 7.3.

3-Phenylpropyl 3-phenylpropionate: bp 146–150 °C (0.8 mm); $\nu_{C=O}$ 1735 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.84 (m, 2), 2.54 (m, 4), 2.87 (t, 2, J = 7 Hz), 3.99 (t, 2, J = 7 Hz), 7.14 (m, 10); mass spectrum (25 eV, room temp) m/e 268 (M^+·), (70 eV, room temp) m/e (rel intensity) 151 (1.9), 150 (18.6), 133 (1.9), 119 (11.8), 118 (100), 117 (25.4), 107 (5.1), 105 (15.2), 104 (25.2), 103 (6.8), 92 (6.8), 91 (74.0), 79 (8.5), 78 (10.1), 77 (11.9), 65 (8.5), 51 (6.8). Anal. Calcd for $C_{18}H_{20}O_2$: C, 80.6; H, 7.5. Found: C, 80.4; H, 7.5.

2-Phenylethyl caproate: bp 144–146 °C (2 mm); $\nu_{C=O}$ 1740 cm^{-1}, ν_{C-O} 1165, 1240 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.90 (m, 3), 1.37 (m, 6), 2.20 (t, 2, J = 6 Hz), 2.90 (t, 2, J = 7 Hz), 4.25 (t, 2, J = 7 Hz), 7.20 (s, 5). Anal. Calcd for $C_{14}H_{20}O_2$: C, 76.4; H, 9.1. Found: C, 76.5; H, 9.0.

Kinetic Measurements. Typically, each of nine ampules was charged with 0.5 mL of a preprepared solution of the catalyst in 5 mL of degassed epoxide, sealed under 1 atm of N_2 (purity 99.99%), and immersed into an oil bath thermostat (accuracy ±0.05 °C). During the first hour one ampule was withdrawn each 15 min and immediately frozen at −78 °C. Before GLC analysis each sample was diluted with CCl_4 to a total volume of 2 mL. In order to achieve maximum accuracy, each sample was also subjected to quantitative infrared analysis (KBr cells, thickness 0.2 mm, OD 0.2–0.8). The initial rate of formation was calculated in each case from the average of at least three experiments.

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Registry No.—β,β-Dideuteriostyrene oxide, 66255-92-3; 4-phenylbuta-1,3-diene 1,2-oxide, 50901-75-2; 4-phenylbut-1-ene 1,2-oxide, 1126-76-7; 3-bromo-4-phenylbut-1-ene 1,2-oxide, 66255-93-4; *n*-hexyl phenylacetate, 5421-17-0; 2-phenylpropyl phenylacetate 66255-94-5; 2-(4-chlorophenyl)ethyl phenylacetate, 66255-95-6; 2-(4-tolyl)ethyl phenylacetate, 66255-96-7; 2-(phenyl)ethyl 4-chlorophenylacetate, 66255-97-8; 2-(4-tolyl)ethyl 4-chlorophenylacetate, 66255-98-9; 2-phenylethyl 4-tolylacetate, 66255-99-0; 2-(4-chlorophenyl)ethyl 4-tolylacetate, 66256-00-6; 2-(2-thienyl)ethyl 2-thienylacetate, 66256-01-7; 2-(phenyl)ethyl 2-phenylpropionate, 66256-02-8; 2-(phenyl)ethyl caproate, 6290-37-5; (2-thienyl)oxinane, 66256-03-9.

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