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(24) Solid carbonyl compounds were dissolved in the minimum amount of pentane or benzene and added to the reaction mixture.
(25) Excess ethanolamine should be avoided, since it makes the precipitate of **1** sticky and renders more difficult the extraction of the products.
(26) ^{1}H NMR and infrared spectra of all the homoallylic alcohols prepared may be found in the Ph.D. Thesis of G. W. Kramer, Purdue University, 1976.

Selective Transformation of Vicinal-Disubstituted Epoxides into Ketones by Homogeneous Rhodium Catalysts[1]

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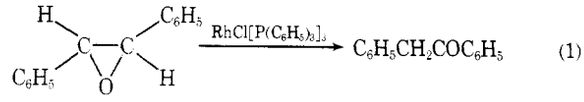
Chlorotris(triphenylphosphine)rhodium has been shown to catalyze the selective rearrangement of many vicinal-disubstituted epoxides to ketones between 150 and 210 °C. Kinetic measurements for various *trans*-1,2-diarylethylene oxides and $RhCl(PAr_3)_3$ catalysts were carried out. The reaction rate was shown to increase by introduction of electron-donating substituents into either the catalyst ligands or the substrate. The catalysis is inferred to proceed in the following order: (a) dissociation of $RhCl(PAr_3)_3$, (b) reversible nucleophilic cis addition of the epoxide to the activated catalyst to give a Rh(III) hydride, (c) intramolecular hydrogen transfer from the rhodium atom to the noncoordinated oxirane carbon, (d) reductive elimination to form the ketone and activated catalyst. The data are compatible with the expression rate = $k_1k_2[S][C]_0/(k_{-1} + k_2 + k_1[S])$ where [S] and $[C]_0$ are substrate and initial catalyst concentration, respectively. Step c is considered rate determining on the basis of kinetic isotope effect measurements. Complexes $RhCl(PAr_3)_3$ have been shown to catalyze also an unusual carbon–carbon bond cleavage in stilbene oxides having potent electron-attracting substituents to yield benzaldehydes and polymers. Epoxides in which one aromatic ring is more electron attracting than the other form aldehydes with the least electronegative groups.

Ring opening of epoxides by acids, bases, and salts has been extensively studied and reviewed.[2] In recent years some transition metal complexes have been shown to cleave catalytically C–O bonds in the oxirane system.[3] However, only in a few cases could the activities of the metal complexes be attributed to other than their acidic properties.

In this paper we present a detailed investigation on the transformation of vicinal-disubstituted ethylene oxides by the nonacidic $RhCl[P(C_6H_5)_3]_3$, including kinetic measurements and mechanistic studies on a selective isomerization of some stilbene oxides to deoxybenzoins. In addition we describe an epoxide system in which the C–C bond is cleaved in addition to the C–O linkage.

Results

Conversion of Epoxides to Ketones. While both acid- and base-catalyzed isomerization of *trans*-stilbene oxide gives usually diphenylacetaldehyde as the main product,[2c,4,5] the $RhCl[P(C_6H_5)_3]_3$-promoted reaction affords 88% deoxybenzoin, simply by heating 1 mol of the epoxide under N_2 with 2×10^{-2} mol of rhodium complex for 2 h at 210 °C. The only by-products in reaction 1 are diphenylmethane (7.9%),



(1)

trans-stilbene (2.8%), *cis*-stilbene (0.3%), and benzene (1.0%). Although $RhCl[P(C_6H_5)_3]_3$ has been assumed to liberate HCl in some other catalyses,[6] we could prove that no such decomposition is taking place in our system. The addition of a weak base to the reaction mixture that is able to remove any HCl that might have been formed, but is refractory toward the rhodium catalyst (e.g., 2,6-di-*tert*-butylpyridine), has no effect whatsoever on the results. On the other hand, addition of minute amounts of gasous hydrogen chloride causes the stilbene oxide to rearrange mainly to diphenylacetaldehyde.[7]

The high selectivity in our catalysis is conditioned by the existence of an absolutely inert atmosphere. Experiments performed under 90% N_2 and 10% O_2 gave no more than 26.5% of the ketone. *cis*-Stilbene oxide, which proved to undergo different transformations than the trans isomer by bases and acids,[5] gives the same yield of deoxybenzoin when the Wilkinson catalyst is employed.

The scope and potential synthetic application of the catalysis for selective conversion of stilbene oxides into the rearranged ketones are demonstrated by the examples listed in Table I.

While stilbene oxides with electron-donating groups give results similar to those with the unsubstituted parent compound, 4-nitrostilbene oxide forms only little of the expected ketone and 3,3′- as well as 4,4′-dinitrostilbene oxide give none at all. The negatively substituted epoxides undergo catalytic C–C bond cleavage which will be discussed below.

When two substituents of different electronic nature are being attached to the phenyl rings (one to each) the C–O bond that is closer to the more electron-donating group is expected to be the weaker one[2b] and to be cleaved preferentially. This is in fact observed in expt 5 and 6 (Table I): *trans*-4-chloro-4′-methylstilbene oxide yields $4\text{-}ClC_6H_4COCH_2C_6H_4\text{-}4\text{-}CH_3$ and $4\text{-}ClC_6H_4CH_2COC_6H_4\text{-}4\text{-}CH_3$ in ratio 7:3, and *trans*-4-

Table I. Catalytic Transformation of Stilbene Oxides $XC_6H_4\overset{O}{\overset{\diagdown\diagup}{CHCH}}C_6H_4Y$ in the Presence of $RhCl[P(C_6H_5)_3]_3$

Registry no.	Expt	Epoxide[a] X	Epoxide[a] Y	Reaction condition[b]	Products $XC_6H_4CH_2COC_6H_4Y$	Products $XC_6H_4COCH_2C_6H_4Y$	Products $(XC_6H_4)(YC_6H_4)CHCHO$	Products $(XC_6H_4)(YC_6H_4)CH_2$	Products $XC_6H_4CH=CHC_6H_4Y$ Trans	Products $XC_6H_4CH=CHC_6H_4Y$ Cis
1439-07-2	1	H	H	A	87.9		0.0	7.9	2.8	0.3
1689-71-0	2	H[c]	H[c]	B	90.6		0.0	2.1	2.8	0.9
62006-50-2	3	4-Cl	4-Cl	C	80.3		0.2	3.5	4.7	0.0
62006-51-3	4	4-CH_3	4-CH_3	B	87.7		0.0	5.1	2.3	0.0
62006-52-4	5	4-CH_3	4-Cl	A	58.3	24.5	0.0	4.6	1.8	0.0
14985-26-3	6	4-NO_2	H	A	1.8	5.9	0.0	0.0	0.0	0.0

[a] Except in expt 2 trans oxides were used. [b] A, oxide to catalyst ratio 1.2×10^{-2}; 2 h at 210°C under N_2; no solvent. B, 1.5 M solution of oxide and 3×10^{-2} M catalyst in purified 1-methylnaphthalene; 2 h at 190°C under N_2. C, as in B at 210°C. [c] *cis*-Stilbene oxide.

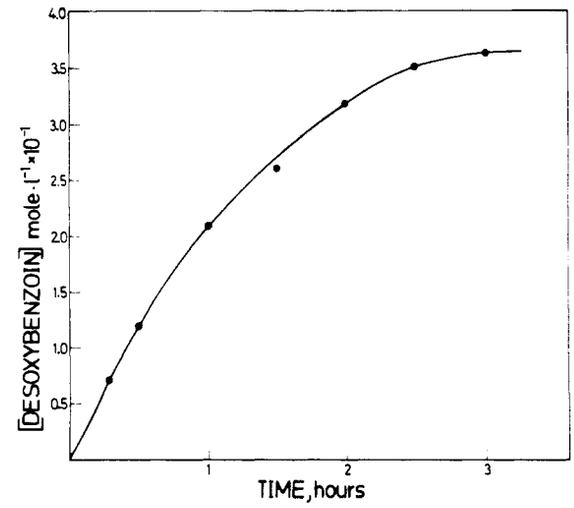


Figure 1. Concentration–time profile for deoxybenzoin formation: 0.382 M *trans*-stilbene oxide and 2.7×10^{-4} M $RhCl[P(C_6H_5)_3]_3$ in 1-methylnaphthalene at 200 °C.

nitrostilbene oxide gives 4-$NO_2C_6H_4COCH_2C_6H_5$ and 4-$NO_2C_6H_4CH_2COC_6H_5$ in ratio 13:4.

While many aromatic vicinal-disubstituted ethylene oxides react as smoothly as stilbene oxide in the presence of $RhCl[P(C_6H_5)_3]_3$, cycloalkene oxides open up rather slowly. Cyclohexene oxide, e.g., forms only 15, 22 and 36% of cyclohexanone when heated with the catalyst at 210 °C for 2, 3, and 15 h, respectively. (By-products in this reaction were 3.8–4.7% cyclopentane and 0.3–0.5% cyclopentanecarboxaldehyde.) This system, cleaves, however, more efficiently when $RuCl_2[P(C_6H_5)_3]_3$ is employed. (After 2 h, 1 mol of epoxide and 10^{-2} mol of catalyst give 67.8% ketone, 0.8% cyclopentane, 3.6% aldehyde, and 27.8% starting material.)

For kinetic measurements the isomerization of *trans*-stilbene oxide was chosen. A typical reaction curve for the transformation of 0.382 M epoxide by 2.7×10^{-2} M $RhCl[P(C_6H_5)_3]_3$ in 1-methylnaphthalene at 200 °C is shown in Figure 1. Changes in rate are shown to be very small in the initial stages of the reaction but become significant when the catalysis advances.

Dependence on Epoxide and Catalyst Concentration. A plot of the initial rate against epoxide concentration is shown in Figure 2. The rate is first order in the epoxide as long as the concentration does not exceed 150 mM. At higher concentrations the dependence of initial rate on concentration decreases and approaches a constant value above 1 M. Such a plot can be represented by the equation rate = $A[S]/(B + [S])$, where [S] is epoxide concentration and A and B are constants. (At high dilution $[S] \ll B$ rate = $A[S]/B$, and when $[S] \gg B$ rate = A). The reciprocal function, i.e., rate^{-1} vs. concentration^{-1}, is linear and has a positive intercept (see, e.g., Figure 4). It can thus be concluded that no higher order than 1 appear in the rate law (rate^{-1} = $\alpha/[S] + \beta$; $A = \beta^{-1}$ and $B = \alpha/\beta$).

The dependence on catalyst concentration (at 160 °C) is shown in Figure 3. In typical experiments, in which 0.877 M epoxide in 1-methylnaphthalene was treated with varying amounts of catalyst, a linear rate increase was observed for low catalyst concentration. Above 0.02 M the rate increase proved to diverge from linearity. For a 0.12 M solution the rate approached its maximum value but decreased on further addition of $RhCl[P(C_6H_5)_3]_3$ to the reaction mixture. Similar rate dependence was reported for several reactions in which rhodium- and ruthenium–phosphine complexes were used as catalysts. In $RhCl[P(C_6H_5)_3]_3$-catalyzed hydrogenation of olefins[8] or in $RuCl_2[P(C_6H_5)_3]_3$-catalyzed transfer hydroge-

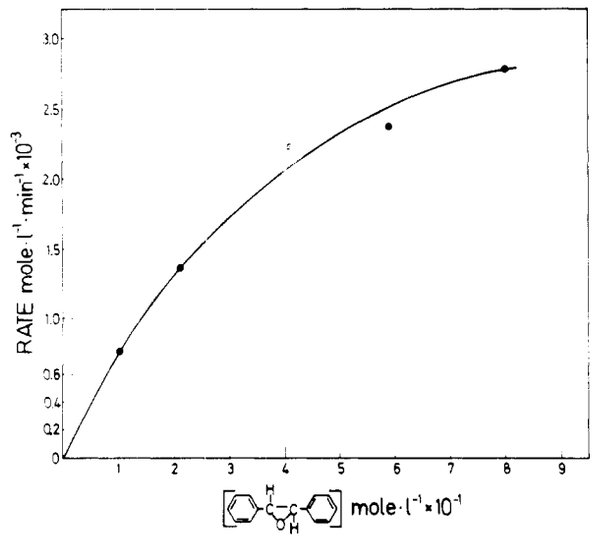


Figure 2. Dependence of initial rate of ketone formation on the concentration of *trans*-stilbene oxide in 1-methylnaphthalene at 200 °C. Catalyst concentration 1.125×10^{-4} M.

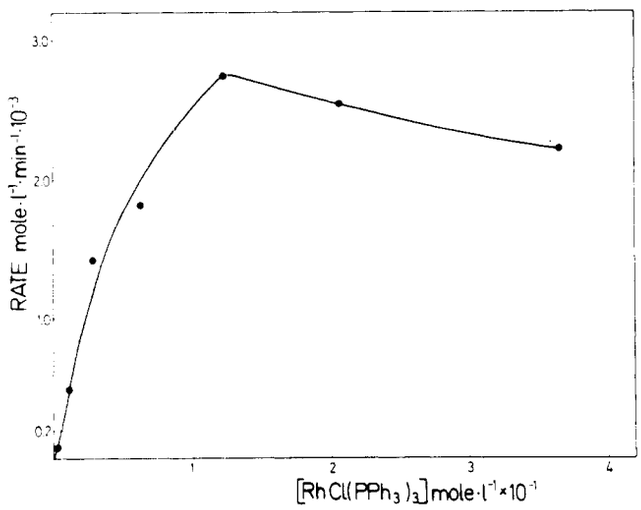


Figure 3. Rate dependence on the concentration of the rhodium catalyst at 160 °C. Initial concentration of *trans*-stilbene oxide 0.88 M.

nation of α,β-unsaturated ketones,[9] e.g., the relative slow increase in rate at high catalyst concentration was attributed to the low solubility of the catalysts[10] and to their tendency to form dimers and oligomers. Reaction 1 differs, however, from the reported ones in its *decrease* in rate after the maximum value has been reached. We assume that this phenomenon is associated with stilbene formation as a by-product (vide infra) which becomes of significance when the concentration of the phosphine-containing catalyst increases. The unsaturated hydrocarbon has been shown to react with the dissociated catalyst to give $(C_6H_5CH{=}CHC_6H_5)$-$RhCl[P(C_6H_5)_3]_2$ that has only low catalytic activity. (Cf. the inhibition of allylbenzene in $RuCl_2[P(C_6H_5)_3]_3$-catalyzed hydrogen transfer reactions.[9])

Dependence on Catalyst's Structure. The influence of the electronic structure of the catalyst was studied by utilizing complexes of the general formula $RhCl[4\text{-}X\text{-}C_6H_4)_3P]_3$ in reaction 1. The initial rates for a large range of epoxide concentration were recorded. The results of one set of experiments are listed in Table II.

Plots of the reciprocal of initial rate against the reciprocal of epoxide concentration are shown in Figure 4. The linear

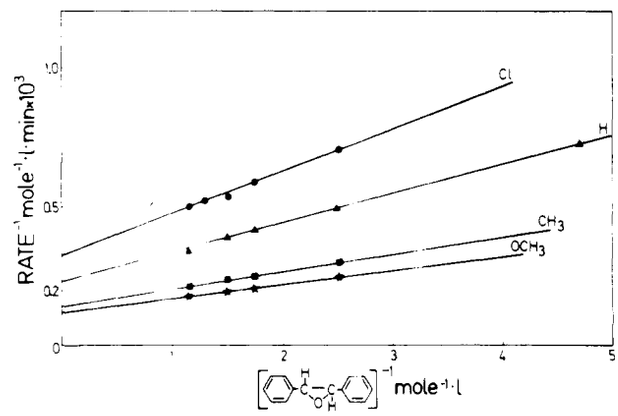


Figure 4. Plots of 1/initial rate against 1/epoxide 4-X-$C_6H_4\underline{CHOC}HC_6H_4$-4-X concentration in the presence of 1.125×10^{-4} M catalyst in 1-methylnaphthalene at 200 °C (★, X = OCH_3; ■, X = CH_3; ▲, X = H; ●, X = Cl).

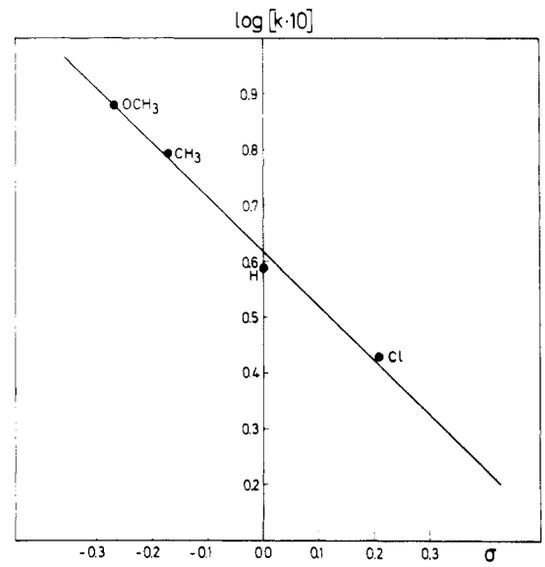


Figure 5. Hammett plot for reaction 1 using $RhCl[(4\text{-}X\text{-}C_6H_4)_3P]_3$ as catalysts. The σ values were taken from D. H. McDaniel and H. C. Brown, *J. Org. Chem.* **23,** 420 (1958).

Table II. Initial Rates of *trans*-Stilbene Oxide Rearrangement by Various Catalysts of Formula $RhCl[(4\text{-}X\text{-}C_6H_4)_3P]_3$ at 200 °C[a]

Registry no.	Substituent X	Initial rate, mmol L^{-1} min^{-1}
21481-17-4	OCH_3	5.60
24554-70-9	CH_3	4.67
16592-65-7	H	3.04
15008-65-8	Cl	1.89

[a] Reaction system was 0.877 M *trans*-stilbene oxide and 1.125×10^{-2} M rhodium catalyst in 1-methylnaphthalene.

dependence in all experiments suggests the same kinetics for the different catalysts employed. The rate constants k (see below) for the rate-determining step using 1.125×10^{-2} M $RhCl[(4\text{-}CH_3OC_6H_4)_3P]_3$, $RhCl[(4\text{-}CH_3C_6H_4)_3P]_3$, $RhCl[P(C_6H_5)_3]_3$, and $RhCl[(4\text{-}ClC_6H_4)_3P]_3$ at 200 °C are 0.76, 0.62, 0.39, and 0.27 min^{-1}, respectively. A quantitative representation of this electronic effect is obtained from the Hammett plot shown in Figure 5. The ρ value of −0.98 suggests partial positive charge stabilization on the rhodium atom in the rate-determining step.[11]

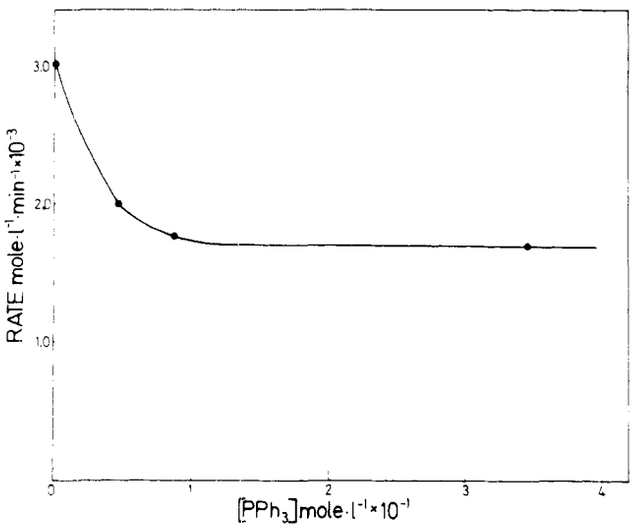


Figure 6. Effect of addition of triphenylphosphine on the initial rate. Reaction system: 0.986 M *trans*-stilbene oxide and 1.125×10^{-4} M catalyst in 1-methylnaphthalene at 200 °C.

Table III. Initial Rate of Rearrangement of Some Stilbene Oxides at 180 °C[a]

Epoxide	Initial rate, mmol L^{-1} min^{-1}
trans-4,4′-Dimethylstilbene oxide	4.77
trans-Stilbene oxide	2.46
trans-4,4′-Dichlorostilbene oxide	1.06

[a] Reaction system was 0.877 M epoxide and 2.055×10^{-2} M $RhCl[P(C_6H_5)_3]_3$ in 1-methylnaphthalene.

Dependence on Structure of the Epoxide. The data given in Table III indicate an increase in rate by introduction of electron-donating and decrease by electron-attracting substituents into the epoxide molecule. (The three epoxides listed were shown to have the same kinetics by virtue of the linear plots of rate^{-1} vs. concentration^{-1}.)

The rate constant for 4,4′-dimethyl-, unsubstituted, and 4,4′-dichlorostilbene oxide at (180 °C and 2.055×10^{-2} M rhodium catalyst) of 0.35, 0.18, and 0.07 min^{-1}, respectively, can be represented by a Hammett plot (log k vs. σ) with $\rho = -1.65$. This value suggests the formation of a *partial* positive charge rather than a real carbonium ion.[11]

The reaction rate is also affected by the *stereochemistry* of the substrate. For example, the initial rate of *cis*-stilbene oxide (0.850 M) isomerization at 170 °C by $RhCl[P(C_6H_5)_3]_3$ (2.25×10^{-2} M) in 1-methylnaphthalene is 13.8 mmol L^{-1} min^{-1}, while that of the trans isomer is only 1.50 mmol L^{-1} min^{-1} under the same conditions.

Kinetic Isotope Effect. The rates of isomerization of *trans*-stilbene oxide and of *trans*-α,α'-dideuteriostilbene oxide, $C_6H_5\underline{C}DO\underline{C}DC_6H_5$, were compared at several concentrations. At 190 °C (substrate and catalyst concentration 0.85 and 1.125×10^{-2} M, respectively), e.g., the corresponding initial rates for the deuterated and nondeuterated compounds are 0.95 and 1.96 mmol L^{-1} min^{-1}. The ratio of reaction constants of the rate-determining step $k_H/k_D = 1.93$ ($k_H = 0.27$ and $k_D = 0.14$ min^{-1}, drawn, as shown below, from plots of rate^{-1} vs. concentration^{-1}) is typical for a hydride transfer reaction.[12] (Cf. also our study on $RuCl_2[P(C_6H_5)_3]_3$-catalyzed transfer hydrogenation reactions.[9]) This value diverges from those reported for proton transfer processes which usually have larger kinetic isotope effects.[12,13]

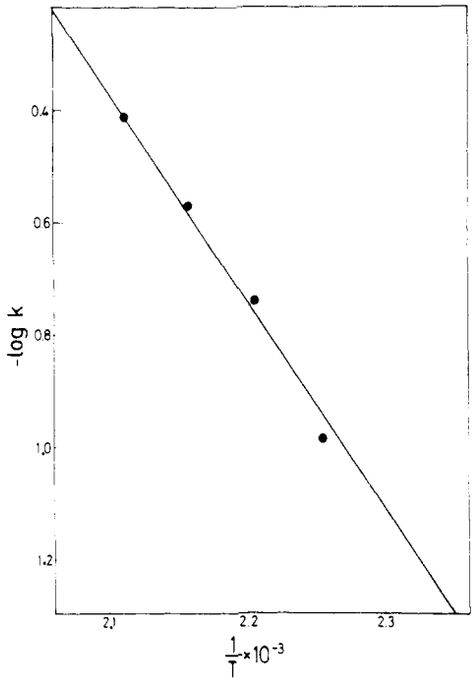


Figure 7. Arrhenius plot of *trans*-stilbene oxide rearrangement to deoxybenzoin at 170–200 °C.

Inhibition by Triphenylphosphine. The effect of addition of triphenylphosphine on the reaction rate is shown in Figure 6. The rate can be lowered to 0.56 of its original value but, in contrast to some other $RhCl[P(C_6H_5)_3]_3$-catalyzed reactions,[8,14,15] further addition of the phosphine has no effect on the catalysis.

Dependence on Temperature. Reaction 1 proved to take place under homogeneous conditions over a considerable range of temperatures, in essentially the same degree of selectivity. Initial rates were measured at 170, 180, 190, and 200 °C for several epoxide concentrations between 0.2 and 1 M. From the Arrhenius plot of log k against $1/T \times 10^{-3}$ (Figure 7) the activation energy $E_a = 17.1$ kcal mol^{-1} is obtained; $H^{\ddagger}$ (200 °C) = 16.2 kcal mol^{-1} and $S^{\ddagger}$ (200 °C) = −35.3 cal deg^{-1} mol^{-1}. Hence the general expression for $k = 5.14 \times 10^5 \cdot e^{-17.1/RT}$ s^{-1}. The greatly negative entropy of activation is uncommon for reactions in which both the starting material and the product are not polar. It may, therefore, be assumed that substantial increase in polarity and in steric strain is characteristic of the transition state of the catalysis.[16]

Side Reactions. Investigation of reaction 1 with 13 typical homogeneous catalysts (viz., $RhCl[P(C_6H_5)_3]_3$, $RhBr[P(C_6H_5)_3]_3$, $RhCl(CO)[P(C_6H_5)_3]_2$, $Rh[[(C_6H_5)_2PCH_2]_2]_2^+Cl^-$, $Rh_2(CO)_4Cl_2$, $RhCl_3[As(C_6H_5)_3]_3$, $RhCl_3 \cdot 3H_2O$, $RuCl_2[P(C_6H_5)_3]_3$, $IrCl(CO)[P(C_6H_5)_3]_2$, $PdCl_2[P(C_6H_5)_3]_2$, $PdCl_2$, $PtCl_2[P(C_6H_5)_3]_2$, and $Pt[P(C_6H_5)_3]_4$) revealed that transformation of the epoxide in high selectivity is limited to chloro- and bromotris(triphenylphosphine)rhodium(I) and chlorocarbonylbis(triphenylphosphine)rhodium(I). The other complexes gave a variety of products as shown in our preliminary report.[17]

The side products obtained from *trans*-stilbene oxide in the presence of $RhCl[P(C_6H_5)_3]_3$ are diphenylmethane (7.9%) and *trans*- and *cis*-stilbene (2.8 and 0.3%, respectively). The formation of the diphenylmethane is rationalized by assuming initial rearrangement of the epoxide to diphenylacetaldehyde followed by catalytic decarbonylation (eq 2).[18]

$$C_6H_5\underset{\diagdown\,O\,\diagup}{CH}—CHC_6H_5 \longrightarrow (C_6H_5)_2CHCHO \longrightarrow (C_6H_5)_2CH_2 + CO \quad (2)$$

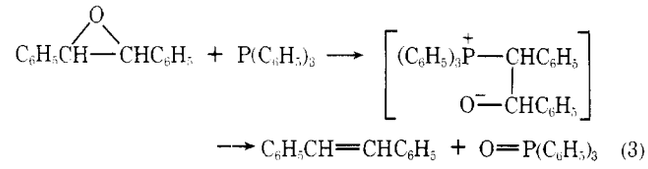
Table IV. Conversion of Some Substituted *trans*-Stilbene Oxides $XC_6H_4CHOCHC_6H_4Y$ into Benzaldehydes in the Presence of $RhCl[P(C_6H_5)_3]_3$[a]

Registry no.	Expt	Epoxide X	Epoxide Y	Products, % XC_6H_4CHO	XC_6H_5	YC_6H_4CHO	YC_6H_5
968-01-4	1	4-NO_2	4-NO_2	73.4	0.2		
	2	4-NO_2	H	5.2	0.1	0.5	25.6
13528-37-5	3	3-NO_2	3-NO_2	36.9	3.2		
	4	4-Cl	4-Cl	2.9	10.4		
	5	4-Cl	4-CH_3	0.0	0.1	0.0	5.5
	6[b]	H	H	0.0	1.0		

[a] Reaction conditions: 2 mmol of epoxide and 0.04 mmol of catalyst heated under N_2 (sealed pressure tube) at 210 °C for 2 h. [b] The cis isomer gives neither benzene nor benzaldehyde under these conditions.

In the rearrangement the rhodium catalyst is assumed to function as a weak Lewis acid. Therefore, it is not unexpected that catalysts of greater acidity than $RhCl[P(C_6H_5)_3]_3$ lead to higher yields of $(C_6H_5)_2CH_2$ and/or its precursor, $(C_6H_5)_2CHCHO$. For example, $RhCl_3[As(C_6H_5)_3]_3$, $Rh_2(CO)_4Cl_2$, $RhCl_3 \cdot 3H_2O$, and $PdCl_2$[19] give, under comparable conditions, 32.2, 36.4, 40.1, and 61.4% of $(C_6H_5)_2CH_2$ + $(C_6H_5)_2CHCHO$, respectively (see ref 17).

The formation of some stilbene along with the deoxybenzoin can be attributed to one or to several of the following processes: Wittig deoxygenation (eq 3)[20] may take place in the



presence of free triphenylphosphine liberated upon dissociation of the metal–phosphine complexes employed.[21,22]

The triphenylphosphine oxide formed may itself act as a deoxygenation agent.[23]

The stilbene obtained by the Wittig deoxygenation is expected to have the cis configuration;[24] however, the phosphine causes then isomerization to the trans compound. In a typical control experiment 1 mmol of *cis*-stilbene and 0.02 mmol of $P(C_6H_5)_3$ gave, at 210 °C (2 h, under N_2), a mixture of 96.8% *trans*- and 3.2% *cis*-stilbene. [Cf. also some other cis–trans interconversion reactions by $P(C_6H_5)_3$.[25]]

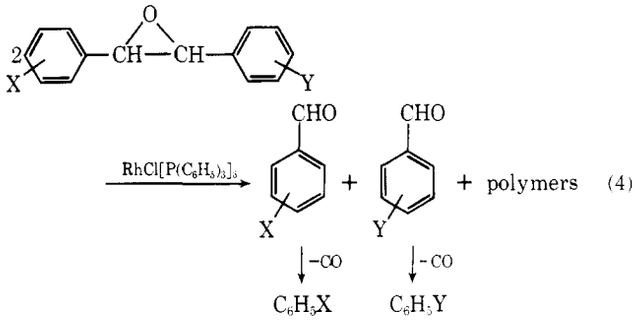
Since some complexes that do not have phosphate or arsine ligands prove also to deoxygenate stilbene oxide [$Rh_2(CO)_4Cl_2$,[17] $RhCl_3 \cdot 3H_2O$,[17] and $PdCl_2$[17] yield 12.4, 5.5, and 8.7% stilbene, respectively] it must be concluded that other than the Wittig deoxygenation takes part in olefin production as well. The formation of some CO_2 in the reaction tube suggests a mechanism which involves electrophilic attack of the metal at the epoxide oxygen, stepwise cleavage of the C–O bonds to give the olefin and a metal oxide, and oxidation of the CO [from $(C_6H_5)_2CHCHO$ decarbonylation] by the latter.[26,27]

Stilbene production by a few platinum metal complexes[17] (not $RhCl[P(C_6H_5)_3]_3$) may be attributed to their acidic properties[28] or to their ability to evolve hydrogen chloride at elevated temperatures.[6] (Cf. ref 7.)

By virtue of negative control experiments (at 210 °C) the possibility of thermal deoxygenation[29] in our catalysis must be excluded.

The most interesting side reaction is obviously a carbon–carbon bond cleavage in the oxirane ring.[30] Aldehydes and/or their decarbonylation products are formed in this process.

In stilbene oxides C–C cleavage is of significance only when electron-attracting substituents are present (see Table IV). Experiments 2 and 5 indicate that the cleavage of asymmetrically substituted epoxide yields preferentially the aldehyde with the less electronegative group. The *nitro*benzaldehydes proved to undergo least decarbonylation as expected from previous studies.[31]



In contrast to *pyrolysis* of *trans*-stilbene oxide,[29] the benzylidene residues formed in reaction 4 do not yield the corresponding stilbenes but polymerize to macromolecular compounds. In expt 2, e.g., a polymer of mp 350 °C results which has the correct elemental analysis of $(CHC_6H_4NO_2)_n$.

Discussion

Following the mechanisms suggested for some other $RhCl[P(C_6H_5)_3]_3$-promoted reactions, we assume that (a) activation of the catalyst, (b) activation and reaction of the epoxide substrate, and (c) release of products are the major steps in our catalytic process.

Activation of the Catalyst. Controversial information on the dissociation of $RhCl[P(C_6H_5)_3]_3$ has been reported in the literature.[32] While, e.g., Arai and Halpern[33] found an equilibrium constant $K_{25} = 1.4 \times 10^{-4}$ M for reaction 5 in benzene, Tolman et al.[32] reported that $RhCl[P(C_6H_5)_3]_3$ does not dissociate to $RhCl[P(C_6H_5)_3]_2$ to a spectroscopically detectable extent at 25 °C but forms the chlorine-bridged dimer $[RhCl[P(C_6H_5)_3]_2]_2$.

$$RhCl[P(C_6H_5)_3]_3 \rightleftharpoons RhCl[P(C_6H_5)_3]_2 + P(C_6H_5)_3 \quad (5)$$

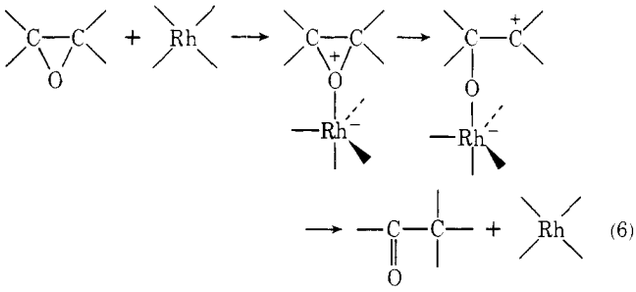
In our system, in which the trisphosphine complex is heated at ~170–220 °C *in the presence of an epoxide*, dissociation is fast and complete. The liberated $P(C_6H_5)_3$ is removed continuously as the oxide by reaction 3. On careful analysis of the reaction mixture of catalysis 1 nearly 1 mol of stilbene isomers and 1 mol of $O{=}PPh_3$ could be detected per each mol of $RhCl[P(C_6H_5)_3]_3$ employed. Owing to this phosphine–epoxide interaction even substantial quantities of added $P(C_6H_5)_3$ do not stop the catalysis (Figure 6) but cause formation of increasing amounts of stilbene which competes with the epoxide in occupying the active site in the catalyst. (Cf. the interference of ethylene in $RhCl[P(C_6H_5)_3]_3$-catalyzed hydrogenation[8] and the inhibition of catalytic transfer hydrogenation of chalcone by allylbenzene.[9])

The rhodium-containing complex formed on dissociation

of $RhCl[P(C_6H_5)_3]_3$ was subjected to molecular weight determination and found to be monomeric. We could show that no appreciable amounts of $[RhCl[P(C_6H_5)_3]_2]_2$ are formed. This observation has been confirmed by kinetic measurements which proved that in reaction 1 $RhCl[P(C_6H_5)_3]_3$ is a more active catalyst than the dimer.

In the presence of large excess of 1-methylnapththalene (solvent) the bisphosphine complex proved, by the mass spectrum, to be a solvate. We assume, therefore, that the active catalyst is—as originally proposed for other $RhCl[P(C_6H_5)_3]_3$-catalyzed reactions[14]—the solvate $RhCl[P(C_6H_5)_3]_2$solv, where "solv" represents either a molecule of the hydrocarbon or a non-fully coordinated epoxide.

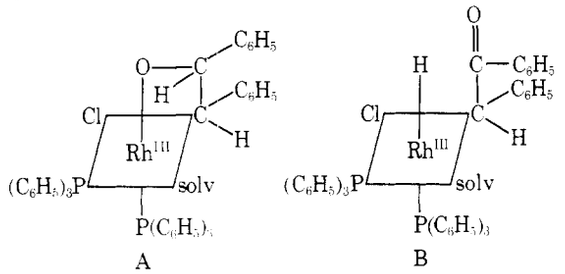
Coordination and Activation of the Epoxide. Initial coordination of the metal to the epoxide oxygen has been assumed[3n] to take place in the rearrangement of oxiranes by the Lewis acid[3k] $[Rh(CO)_2Cl]_2$ (eq 6). The intermediary of a stable



(6)

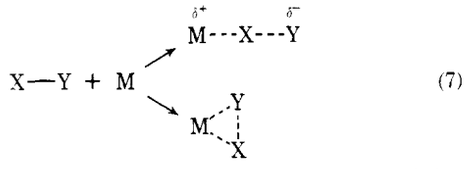
carbonium ion and migration of the most electron-releasing group to give an aldehyde can be regarded as a simple acid-catalyzed epoxide transformation. Chlorotris(triphenylphosphine)rhodium and the active solvated bisphosphine complex are, however, Lewis bases and therefore are not expected to coordinate in this manner to the epoxide heteroatom.

A second mechanism in which the relatively weak C–O bond[34] undergoes *oxidative addition* to the metal has been suggested for some iron-,[35] cobalt-,[3i] and nickel-catalyzed[30] transformations of the oxirane ring. Should $RhCl[P(C_6H_5)_3]_2$(solv) react in this way, one would expect a Rh(III) complex A to be formed that might in turn rearrange to complex B by β-hydrogen transfer. The ketone and regener-



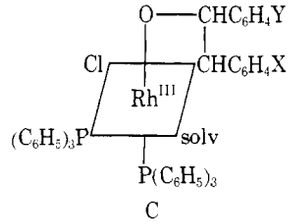
A B

ated active catalyst would then result by reductive elimination. In fact our results cannot be explained by such a mechanism. In consideration of the most probable intermediates in oxidative addition shown in eq 7,[36] the three-centered



(7)

mechanism must be ruled out right away on account of the observed electronic effect of substituents on the reaction rate. In the dipolar pathway, substituents that increase the nucleophilicity of the metal, or the electrophilicity of the substrate, should enhance the reaction rate. Assuming



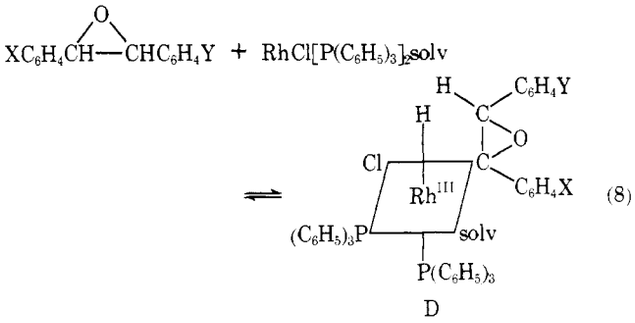
C

(X attracts electrons better than Y)

$RhCl[P(C_6H_5)_3]_2$(solv) to be a nucleophile in the oxidative addition of $XC_6H_4CHOCH_6H_4Y$ (X attracts electrons better than Y), the expected Rh(III) complex should have structure C and lead, upon reductive elimination, to $XC_6H_4CH_2CO$-C_6H_4Y and not to $XC_6H_4COCH_2C_6H_4Y$. We found, however, that the major product in the rearrangement of an asymmetrically substituted epoxide is the ketone which has the electronegative group closest to the carbonyl function (see Table I). Furthermore, Takegami et al.[35] have shown that the C–O bond in vicinal-disubstituted epoxides cannot undergo oxidative addition to iron carbonylates, owing to steric effects. It is thus obvious that C–O insertion cannot be an important step in our catalysis.

It is also improbable that insertion into the oxirane C–C bond occurs. Such oxidative addition is assumed to be the initial step in the cleavage of some stilbene oxides that form benzaldehydes as shown below.

The most probable mechanism that explains our results involves oxidative addition of an oxirane C–H bond to the rhodium catalyst.[37] Such addition to aliphatic and aromatic C–H linkages has been shown to be a nucleophilic process and to be promoted by electron-attracting groups.[37f] An oxirane C–H bond is by far a better electrophile than the corresponding aliphatic, or even aromatic, one. It can be compared in many respects to the C–H bond in aldehydes.[38] We suggest, therefore, that in our catalysis the epoxide is activated by *reversible*[37a] nucleophilic attack of the rhodium at the oxirane carbon atom having the lowest electron density as shown in eq 8.

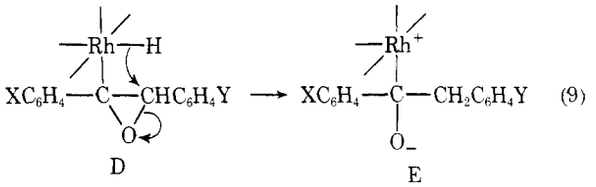


(8)

D

It should be noted, however, that while in such oxidative addition reactions the rate is expected to be increased by electron-attracting substituents, reaction 1 is accelerated by electron-releasing groups. Therefore, the epoxide activation cannot be the rate-determining step in the catalysis.

The Hydrogen Transfer Step. The rhodium intermediate D is now assumed to undergo a *slow* intramolecular β-hydride transfer from the metal to the noncoordinated oxirane carbon to yield a dipolar structure E. The observed kinetic isotope

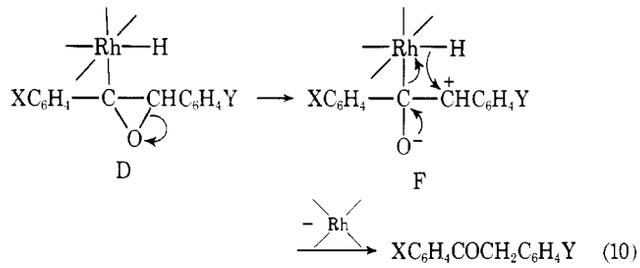


D E

(9)

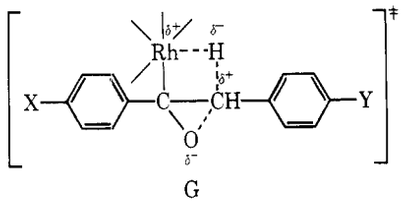
effect supports this suggestion. α-Hydride transfer seems less probable as it would not account for the preferential formation

of deoxybenzoin with the electronegative group X attached to the *aroyl* moiety, and is also disfavored for steric reasons. Neither can *initial* C–O scission and formation of carbonium ion F (eq 10) rationalize our results. In this case the electronic



nature of the epoxide substituents is expected to affect primarily the formation of F, while it has already been shown, by virtue of the kinetic isotope effect (k_H/k_D = 1.93), that the rate-determining step is associated with the cleavage of a hydrogen linkage. Furthermore, the observed rate dependence on the electronic nature of the catalyst indicates that at least one ligand–rhodium bond is modified in the rate-controlling step (which is not the case when F is being formed). Both the calculated ρ value (−1.65) and the highly negative entropy of activation ($\Delta S^{\ddagger}$ = −35.3 cal deg^{-1} mol^{-1}) are uncommon in reactions that involve oxirane cleavage to a carbonium ion in the rate-determining step.[2b,11]

Acceleration of the catalysis by electron-donating groups on the substrate could indicate a *partial* positive charge on the activated complex of the hydrogen transfer step D → E, just as in the well-known "borderline S_N2" (or "loose S_N2") mechanism in which bond breaking has progressed further in the transition state than bond making.[39] Such a mechanism has often been suggested for nucleophilic substitution reactions in epoxides,[2b,c] and was attributed to the steric strain in the oxirane ring. These activated complexes were found to be always stabilized by incorporation of electron-releasing substituents into the substrate.



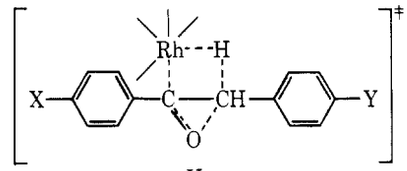
G

(X attracts electrons better than Y)

Structure G is thus the proposed transition state in step D → E. The C–O bond breaking is ahead of the C–H bond forming and, therefore, causes accumulation of a partial positive charge on the oxirane carbon atom. As expected, the formation of G is promoted by electron-releasing groups X and Y. This mechanism of hydrogen transfer in G is in full agreement with the observed kinetic isotope effect. It is known[40] that this effect results from changes in the activation energy of the process caused by differences in the zero-point energy when the reactants are converted to the activated complex, and it has been shown[8] that the zero-point energy of the C–H bond is larger than that of the Rh–H linkage by ~1.43 kcal/mol. Therefore, synchronous Rh–H breaking and C–H forming would lead to gain in zero-point energy and a reverse kinetic isotope effect (i.e., $k_H/k_D < 1$). The value k_H/k_D = 1.93 indicates that the C–H bond forming is less advanced than the Rh–H bond breaking and causes a partial negative charge location on the hydrogen. It is, however, unlikely that the hydrogen is being completely removed as H^- prior to some C–H bond formation, as this would give rise to a kinetic isotope effect of ~4 (as result of the difference of 0.86 kcal/mol in zero-point energy in Rh–H and Rh–D bonds[8]). The observed values suggests parallel, but not synchronous, formation of the C–H bond.

The assumption that a partial positive charge is formed on the rhodium atom in the rate-determining step is supported by the observation that substituents which increase the electron density on the metal accelerate the catalysis (ρ = −0.98). These groups stabilize the positive charge and facilitate hydride transfer.

An alternative five-centered mechanism for which structure H represents the transition state seems improbable. By this

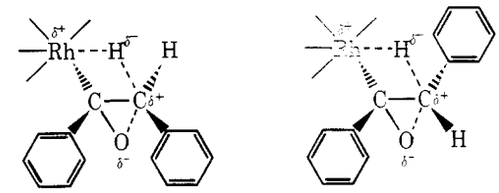


H

route the product would result by a single step reductive elimination coupled with nucleophilic attack on the oxirane ring, and groups that increase the electron density would be expected to decrease the reaction rate.

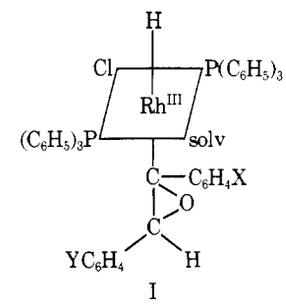
The highly negative entropy of activation ($\Delta S^{\ddagger}$ = −35.3 cal deg^{-1} mol^{-1}) may be rationalized by a combination of two factors: (a) increase in the polarity upon formation of the activated complex G from the reactants,[41] (b) the existence of a substantial steric hindrance. It must be assumed that the Rh–C bond is bent in the transition state, so that the heavily substituted rhodium atom is able to transfer its hydrogen to the oxirane carbon.

By comparison of $\Delta S^{\ddagger}$ for *trans*- and *cis*-stilbene oxide some interesting features of the stereochemistry of the corresponding activated complexes can be deduced. Since the cis oxide rearranges to deoxybenzoin 9.2 times faster than the trans isomer, it can be concluded that the activation entropy of *cis*-stilbene oxide is less negative than that of the trans compound, and the steric hindrance of the transition state of the latter is the greater one of the two. This is illustrated in structures G-c and G-t: in G-t hydrogen transfer from the substituted rhodium atom is hindered by a phenyl group; in G-c this interference does not exist. As G-c is derived from *cis*-stilbene oxide and G-t from the trans isomer, it can be concluded that the oxidative addition shown in eq 8 is cis addition, viz., hydride D is formed rather than I.



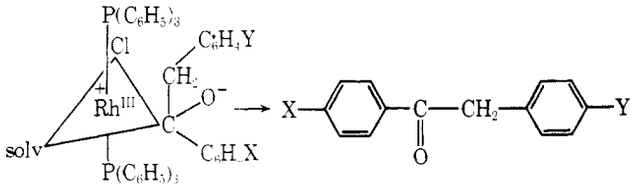
G-c

G-t



I

Release of the Product. In the final step E undergoes reductive elimination. The active Rh(I) catalyst is being reformed along with the rearranged ketone (eq 11).



E + $RhCl[P(C_6H_5)_3]_2solv$ (11)

(X attracts electrons better than Y)

The complete cycle of the catalytic rearrangement can thus be summarized by (a) fast oxidative cis addition of the epoxide to the active catalyst $RhCl[P(C_6H_5)_3]_2$, (b) slow intramolecular hydrogen transfer in D to give E, and (c) formation of product and active catalyst by fast reductive elimination.

Since under our experimental conditions $RhCl[P(C_6H_5)_3]_3$ dissociates completely in a practically irreversible fashion into the active catalyst, we can apply the kinetic Scheme I for our reaction.

Scheme I

$$C + S \underset{k_{-1}}{\overset{k_1\ (fast)}{\rightleftharpoons}} (CS)^1$$

$$(CS)^1 \xrightarrow{k_2\ (slow)} (CS)^2$$

$$(CS)^2 \xrightarrow{k_2\ (fast)} C + P$$

C, S, and P are catalyst, substrate, and product, respectively, and the rate law would be

$$\text{rate} = \frac{d[P]}{dt} = \frac{[k_2k_3/(k_2 + k_3)][C]_0[S]}{[(k_{-1} + k_2)/k_1][k_3/(k_2 + k_3)] + [S]}$$

where $[C]_0$ represents the initial concentration of $RhCl[P(C_6H_5)_3]_3$.

Since the first and final steps are much faster than the second one, i.e., $k_2 \ll k_3$ [though the relative rate of the reverse reaction $(CS)^1 \rightarrow C + S$ cannot be estimated], the rate law becomes

$$\text{rate} = \frac{k_2[C]_0[S]}{(k_{-1} + k_2)/k_1 + [S]}$$

and substituting $(k_{-1} + k_2)/k_1$ by K_A gives rate = $k_2[C]_0[S]/(K_A + [S])$. When $k_2 \ll k_1$, K_A represents the reciprocal of the equilibrium constant of the first step. This expression accounts for the observed rate dependence on the epoxide concentration shown in Figure 2. For very low concentration of the substrate ($[S] \ll K_A$) rate = $(k_2/K_A)[C]_0[S]$. This indicates that under these conditions the reaction is first order in the epoxide. When [S] increases ($[S] \gg K_A$) the rate approaches the constant $k_2[C]_0$ (see Figure 2).

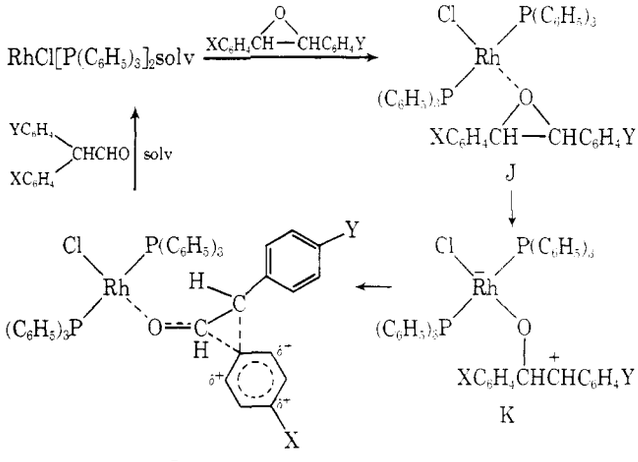
The rate expression is linear in the reciprocal form

$$\text{rate}^{-1} = [(K_A/k_2[C]_0)[S]^{-1}] + (k_2[C]_0)^{-1}$$

and $K_A/k_2[C]_0$ and $1/k_2[C]_0$ represent the corresponding terms α and β given above. The magnitude of k was thus obtained from the intercepts of the plot of rate^{-1} vs. epoxide concentration,[42] and K_A can be deduced from the gradient $K_A/k_2[C]_0$.

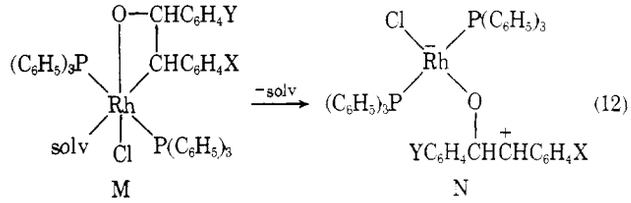
Finally we wish to comment upon the mechanisms of the main side reactions. As mentioned above the rearrangement of *trans*-stilbene oxide to diphenylacetaldehyde (eq 2) may be attributed to some Lewis acid character of the catalyst. Thus the mechanism of Grigg[3k,l,n] may be adopted: in the first step the active catalyst coordinates to the epoxide oxygen. Then the C–O bond that is closest to the electron-attracting group X is cleaved and aryl migration toward the electropositive center takes place (Scheme II).

Scheme II



(X attracts electrons better than Y)

Formation of the dipolar structure may also result via an alternative route that includes oxidative addition to the C–O bond coupled with ring opening (M → N). However, since the nucleophilic nature of the oxidative addition would take place at the carbon atom that is closest to X and the resulting carbonium ion N is less stable than K, this mechanism is disfavored.



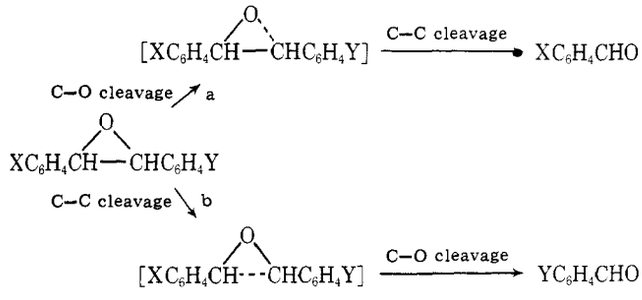
(12)

The data given in Table IV indicate that the catalytic C–C bond cleavage in stilbene oxides (eq 4) depends strongly on the ability of substituents X and Y to withdraw electrons. A Hammett ρ value of +1.76 is obtained from a plot of log percentage C–C breaking vs. the sum of the substituent constants $\sigma_X + \sigma_Y$.

We have shown that reaction 4 is independent of reaction 1. The deoxybenzoins [e.g., 4-nitro-2-(4-nitrophenyl)acetophenone, $4\text{-}NO_2C_6H_4CH_2COC_6H_4\text{-}4\text{-}NO_2$] formed by the "normal" rearrangement of the epoxides, are not converted to benzaldehydes by $RhCl[P(C_6H_5)_3]_3$.

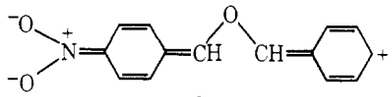
Upon transferring stilbene oxides to benzaldehydes the oxirane ring has to cleave both at the C–C and the C–O linkages. Thus, the question arises which of the two bonds is the first to break down. When it is the C–O bond the reaction follows *route* (*a*) in Scheme III and the resulting aldehyde

Scheme III

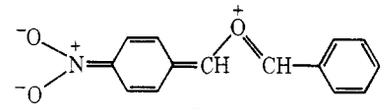


contains the utmost electron-attracting substituent X. As in fact the aldehyde with the least electron-attracting power is formed preferentially (see Table IV) it can be concluded that *route* (*b*) dominates the catalysis.

The weakness of the oxirane C–C bond in nitrostilbene has been explained by the mesomeric structures O and P.[43,44]

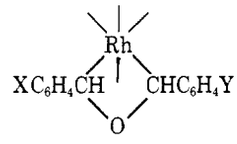


O



P

Since the analogue of P, in which a double bond is located between O^+ and the second methine group, is of low probability, the C–O bond that is closer to the nitrophenyl moiety is expected to cleave preferentially. The role of the metal catalyst in reaction 4 seems, therefore, to be associated primarily with the "trapping" or "freezing out" of the noncyclic epoxide mesomers, probably by formation of complexes of type Q. A platinum(II) analogue of Q has been isolated from the reaction of $Pt[P(C_6H_5)_3]_4$ and tetracyanoethylene oxide.[45]



Q

The C–O bond breaking is assumed to follow next; however, with the available evidence it seems premature to give the mechanism of this step.

Experimental Section

Melting points were taken on a Thomas-Hoover capillary melting point apparatus and are not corrected. Infrared and ultraviolet spectra were measured with Perkin-Elmer spectrophotometers Models 257 and 402, respectively. Proton magnetic resonance spectra were run using Varian EM-360 and HA-100 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).

The catalysts $RhCl[P(C_6H_5)_3]_3$,[8] $RhBr[P(C_6H_5)_3]_3$,[8] $RhCl[P(4\text{-}ClC_6H_4)_3]_3$,[47] $RhCl[P(4\text{-}CH_3C_6H_4)_3]_3$,[47] $RhCl[P(4\text{-}CH_3OC_6H_4)_3]_3$,[47] $RuCl_2[P(C_6H_5)_3]_3$,[48] $IrCl(CO)[P(C_6H_5)_3]_2$,[49] $PtCl_2[P(C_6H_5)_3]_2$,[50] and $Pt[P(C_6H_5)_3]_4$[50] as well as the starting and reference compounds *trans*-4-$ClC_6H_5CH{=}CHC_6H_4$-4-Cl,[51] *trans*-4-$CH_3C_6H_4CH{=}CHC_6H_4$-4-CH_3,[52] *trans*-4-Cl-$C_6H_4CH{=}CHC_6H_4$-4-CH_3,[53] *trans*-4-$NO_2C_6H_4CH{=}CHC_6H_4$-4-NO_2,[54] 4-$NO_2C_6H_4COCH_2C_6H_4$-4-NO_2,[55] 4-$NO_2C_6H_4CH_2COC_6H_5$,[55] 4-$NO_2C_6H_4COCH_2C_6H_5$,[55] $(4\text{-}ClC_6H_4)_2CHCHO$,[56] $(4\text{-}ClC_6H_4)_2CH_2$,[57] $(4\text{-}CH_3C_6H_4)_2CH_2$,[57] and 4-$ClC_6H_4CH_2C_6H_4$-4-$CH_3$[58] were prepared as previously described.

The following stilbene oxides were prepared by 3-chloroperbenzoic acid oxidation of the olefins.[59] ***trans*-Stilbene oxide:** mp 69–70 °C (lit.[60] 69–70 °C); ν_{C-O} (Nujol) 840 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.88 (s, 2), 7.38 ppm (s, 10). ***cis*-Stilbene oxide:** mp 38–39 °C (lit.[60] 37–37.5 °C); ν_{C-O} (Nujol) 892 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.37 (s, 2), 7.20 ppm (s, 10). ***trans*-4,4′-Dichlorostilbene oxide:** mp 120–121 °C (lit.[51] 123–124 °C); ν_{C-O} (Nujol) 840 cm^{-1}; ^1H NMR ($CDCl_4$) δ 3.67 (s, 2), 7.28 ppm (s, 8). ***trans*-3,3′-Dinitrostilbene oxide:** mp 157–159 °C (lit.[61] 156–158 °C); ν_{C-O} (Nujol) 850 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.03 (s, 2), 7.67 (m, 4), 8.22 ppm (m, 4).

***trans*-4,4′-Dimethylstilbene Oxide.** A solution of 2.08 g (10 mmol) of *trans*-4,4′-dimethylstilbene and 2.18 g (10.8 mmol) of 3-chloroperbenzoic acid (85%) in 40 mL of methylene chloride was stirred at 25 °C. TLC analysis [SiO_2, *n*-hexane–ethyl acetate (10:1) as eluent] indicated that the oxidation was completed after 20 h. The acids were extracted with 5% aqueous sodium bicarbonate; the organic layer was washed with water, dried, and concentrated. The residue was recrystallized (three times) from petroleum ether to yield 1.8 g (76%) of colorless needles: mp 92–93 °C; ν_{C-O} (Nujol) 875 cm^{-1}; ^1H NMR (CCl_4) δ 2.35 (s, 6), 3.65 (s, 2), 7.13 ppm (s, 8). Anal. Calcd for $C_{16}H_{16}O$: C, 85.7; H, 7.1. Found: C, 85.4; H, 7.2.

***trans*-4-Chloro-4′-methylstilbene Oxide.** A solution of 1.01 g (4.42 mmol) of *trans*-4-chloro-4′-methylstilbene and 0.99 g (4.87 mmol) of 3-chlorobenzoic acid (85%) in 40 mL of $CHCl_3$ and 5 mL of CH_2Cl_2 was stirred at 25 °C for 52 h and worked up as above to give 0.92 g (85%) of colorless plates: mp 96–97 °C; ν_{C-O} (Nujol 878 cm^{-1}; ^1H NMR ($CDCl_3$) δ 237 (s, 3), 3.83 (m, 2), 7.23 (s, 4), 7.33 ppm (s, 4). Anal. Calcd for $C_{15}H_{13}ClO$: C, 73.6; H, 5.4; Cl, 14.5. Found: C, 73.9; H, 5.4; Cl, 14.7.

***trans*-4,4′-Dinitrostilbene Oxide.** To a solution of 12.8 g of 4-nitrobenzaldehyde in 100 mL of benzene was added, at −70 °C, a solution of 6.8 g of tris(dimethylamino)phosphine in 15 mL of the same solvent. The mixture was brought slowly to 23 °C and stirred at this temperature for 18 h. The white precipitate (mp 203–204 °C) was recrystallized from ethyl acetate to give 5.6 g (46%) of isomerically pure trans epoxide (cf. ref 61) as colorless needles: mp 204–205 °C (lit.[61] 202–203 °C); ν_{C-O} (Nujol) 855 cm^{-1}; ^1H NMR ($AsCl_3$) δ 4.05 (s, 2), 7.88 ppm (q $A_2'B_2'$, 8).

***trans*-4-Nitrostilbene oxide** was prepared according to Bergmann and Hervey[62] from benzaldehyde and 4-nitrobenzyl chloride: mp 124.5–125.5 °C (lit.[62] 125–126 °C); ν_{C-O} ($CHCl_3$) 850, 880 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.90 (d, 1, J = 2 Hz), 4.03 (d, 1, J = 2 Hz), 7.43 (s, 5), 7.93 ppm (q $A_2'B_2'$, 4).

***trans*-α,α′-Dideuteriostilbene Oxide.** A solution of 7.12 g (0.04 mol) of diphenylacetylene in 100 mL of *n*-hexane was converted into *cis*-α,α′-dideuteriostilbene (95%) by 0.04 mol of D_2 in the presence of 0.6 g of Pd/C (10%). The catalyst was filtered off, the solvent was removed, and a crystal of iodine was added. The mixture was heated at 200 °C for 10 min and cooled to room temperature and the solid *trans*-α,α′-dideuteriostilbene was recrystallized from EtOH, yield 6.1 g (83%) of colorless prisms, mp 123–124 °C (lit.[63] 123.8–125 °C). To a solution of 4 g (22 mmol) of this compound in 100 mL of CH_2Cl_2 was added 4.8 g (24 mmol) of 3-chloroperbenzoic acid (85%) and the mixture left at 25 °C for 22 h. After neutralization with 5% aqueous $NaHCO_3$ and the usual workup the residue was chromatographed on Florisil (petroleum ether as eluent) to give 3.2 g (69%) of *trans*-α,α′-dideuteriostilbene oxide (90% d_2): mp 69–70 °C; ν_{C-O} 895 cm^{-1}; ^1H NMR (CCl_4) δ 7.30 ppm (s) (traces of ^1H compound showed up at 3.73 ppm); *m/e* 198 (M^+). Anal. Calcd for $C_{14}H_{10}D_2O$: C, 84.8; H + D,[64] 6.1. Found: C, 84.5; H + D, 6.2.

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

Reaction of *trans*-Stilbene Oxide and $RhCl[P(C_6H_5)_3]_3$. A pressure tube (wall thickness 5 mm) was carefully dried, washed with N_2, and charged with 196 mg (1 mmol) of freshly chromatographed *trans*-stilbene oxide and 18.5 mg (2×10^{-2} mmol) of $RhCl[P(C_6H_5)_3]_3$. Any traces of oxygen were removed from the reaction tube with the aid of a high vacuum line, and nitrogen was introduced at 1 atm, sealed, and immersed into an oil bath thermostat at 210 °C. The clear red-brown solution was cooled to room temperature and dissolved in CCl_4 (total volume 5 mL). GLC analysis was carried out with a 2-m long column packed with 15% stabilized DEGS on Chromosorb ST-164 operated at 228 °C, carrier gas (He) 70 mL/min. The reaction mixture proved to consist of 87.9% deoxybenzoin (retention time 490 s), 7.9% diphenylmethane (retention time 120 s), 2.8% *trans*-stilbene (retention time 370 s), and 0.3% *cis*-stilbene (retention time 145 s). The different products were isolated either by preparative GLC or by PLC on silica gel [EtOAc–*n*-hexane (1:4) as eluent].

The following substituted deoxybenzoins were isolated on 1-m long Apiezon L (20%) on Anakrom ABS (60–70 mesh) operated at 210–230 °C.

4-Chloro-α-(4′-chlorophenyl)acetophenone: mp 111–112 °C; $\nu_{C=O}$ (Nujol) 1688 cm^{-1}; ^1H NMR (CCl_4) δ 4.10 (s, 2), 7.12 (m, 4), 7.68 ppm (q $A_2'B_2'$, 4). The compound was compared with an authentic sample prepared according to Bergmann et al.[65]

4-Chloro-α-(4′-tolyl)acetophenone: mp 102–103 °C; $\nu_{C=O}$ (CCl_4) 1690 cm^{-1}; ^1H NMR (CCl_4) δ 2.30 (s, 3), 4.19 (s, 2), 7.12 ppm (s, 4). Anal. Calcd for $C_{15}H_{13}ClO$: C, 73.6; H, 5.3; Cl, 14.5. Found: C, 73.3; H, 5.1; Cl, 14.6. For comparison the ketone was prepared by the following procedure. 4-Chlorophenylacetyl chloride (prepared from 1.7 g of acid and 0.9 g of phosphorus trichloride at 100 °C) in 10 mL of dry toluene was poured, with cooling and agitation, onto 1.9 g of powdered anhydrous $AlCl_3$. The mixture was heated at 100 °C for 1 h, cooled, decomposed with ice and hydrochloric acid, and worked up in the usual manner. Upon recrystallization from MeOH (three times) there was obtained 1.95 g (80%) of the pale yellow ketone.

4-Methyl-α-(4′-chlorophenyl)acetophenone: mp 111.5–112 °C; ν_{C-O} (CCl_4) 1685 cm^{-1}; ^1H NMR (CCl_4) δ 2.39 (s, 3), 4.21 (s, 2), 7.20 (m, 6), 7.88 ppm (m, 2). Anal. Calcd for $C_{15}H_{13}ClO$: C, 73.6; H, 5.3; Cl, 14.5. Found: C, 73.4; H, 5.3; Cl, 14.3. The compound was also prepared by the Friedel–Crafts reaction described for the foregoing ketone from chlorobenzene and 4-tolylacetic acid.

α,α′-Dideuteriodeoxybenzoin: mp 59–60 °C; $\nu_{C=O}$ (CCl_4) 1680 cm^{-1}; ^1H NMR (CCl_4) δ 7.27 (s, 5), 7.37–7.60 (m, 3), 7.93–8.10 ppm

(m, 2). An authentic sample was prepared for comparison according to Corey and Schaefer.[66]

Kinetic Measurements. Typically there was prepared a 20-mL solution of the epoxide (freshly chromatographed on Florisil) and the rhodium catalyst in 1-methylnaphthalene (vacuum distilled over Na and chromatographed on alumina). Each of 19 ampules was charged with 1 mL of this solution, sealed under 1 at N_2 (purity 99.99%), and immersed into an oil bath thermostat (accuracy ±0.05 °C). During the first 1 h one ampule was withdrawn each 10 min and immediately frozen to −78 °C to await GLC analysis. The initial rate was calculated in each case from the average of at least three experiments.

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Registry No.—Bromotris(triphenylphosphine)rhodium(I), 14973-89-8; chlorocarbonylbis(triphenylphosphine)rhodium(I), 13938-94-8; *trans*-stilbene, 103-30-0; *cis*-stilbene, 645-49-8; *trans*-4,4′-dichlorostilbene, 1657-56-3; *trans*-3,3′-dinitrostilbene, 62006-53-5; *trans*-4,4′-dimethylstilbene, 18869-29-9; *trans*-4-chloro-4′-methylstilbene, 3041-83-6; 4-nitrobenzaldehyde, 555-16-8; benzaldehyde, 100-52-7; 4-nitrobenzyl chloride, 100-14-1; *trans*-α,α′-dideuteriostilbene oxide, 62006-54-6; *cis*-α,α′-dideuteriostilbene, 3947-91-9; *trans*-α,α′-dideuteriostilbene, 5284-44-6; 4-chloro-α-(4′-chlorophenyl)acetophenone, 51490-05-2; 4-chloro-α-(4′-tolyl)-acetophenone, 15221-84-8; 4-methyl-α-(4′-chlorophenyl)acetophenone, 62006-19-3; α,α′-dideuteriodeoxybenzoin, 62006-20-6.

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