Dichlorotris(triphenylphosphine)ruthenium-Catalyzed Hydrogen Transfer from Alcohols to Saturated and α,β-Unsaturated Ketones[1]

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Dichlorotris(triphenylphosphine)ruthenium has been shown to be an efficient catalyst for the selective transfer hydrogenation of α,β-unsaturated ketones by primary and secondary carbinols. Kinetic studies were carried out using 1-phenylethanol as hydrogen donor and benzylideneacetophenone as acceptor. The catalysis is inferred to proceed in the following order: (a) dissociation of $RuCl_2(PPh_3)_3$, (b) coordination of the acceptor to the metal, (c) coordination of the alcohol and the formation of a metal alkoxide, (d) hydrogen transfer from the alkoxyl ligand to the coordinated ketone, and (e) release of product. These data are compatible with the expression rate = $kK_1K_2[S^1][S^2][C]_0/(1 + K_1[S^1] + K_1K_2S^1][S^2] + K_3[S^2])$ where $[S^1]$, $[S^2]$, and $[C]_0$ are acceptor, donor, and catalyst concentration, respectively. Step d was considered rate determining on bases of kinetic isotope effect measurements. $RuCl_2(PPh_3)_3$ has been shown to catalyze also hydrogen transfer from secondary carbinols to saturated ketones provided that the ketones involved in the reaction have significantly different oxidation potentials. Kinetic studies of the reaction of dibenzyl ketone and 1-phenylethanol indicate similarity of the three intial steps to those of the former catalysis, but the following step is assumed to involve hydrogen transfer from the alkoxyl ligand to the metal. The hydride attacks then the coordinated ketone with the higher oxidation potential.

The transfer hydrogenation of olefins by carbinols and soluble transition metal catalysts has received considerable attention in recent years.[2] However, only few of the examples reported have synthetic value, and little is known about the mechanism of this process.

Among the more active catalysts studied in our laboratory is dichlorotris(triphenylphosphine)ruthenium, $RuCl_2(PPh_3)_3$ (1). It was found to promote hydrogen transfer, not only from alcohols[2k,m,3-7] but also from hydrocarbons,[3] aldehydes,[8] acids,[8,9] amides,[10] and other hydrogen donors,[9] and proved to be particularly effective in the reactions formulated in eq 1 and 2.

$$R^1R^2CHOH + R^3CH{=}CHCOR^4 \longrightarrow R^1R^2CO + R^3CH_2CH_2COR^4 \quad (1)$$

$$R^1R^2CHOH + R^3R^4CO \rightleftharpoons R^1R^2CO + R^3R^4CHOH \quad (2)$$

In this paper we describe a detailed investigation of this catalyst system, including kinetic measurements and mechanistic studies on the Ru(II)-catalyzed transfer hydrogenation of α,β-unsaturated ketones and the equilibration of *saturated* ketones and secondary carbinols.

Results

Outline of Catalysis. As described in the Experimental Section, the transfer hydrogenation of benzylideneacetophenone to 3-phenylpropiophenone is accomplished simply by heating the unsaturated ketone with benzyl alcohol and the ruthenium catalyst (molar ratio $1:1:2 \times 10^{-3}$) for 2 hr at 180°. The scope and potential synthetic application of this catalysis for the selective reduction of enones is demonstrated by the examples listed in Tables I and II and by experiments described in ref 2k, 3–5, and 7. Both primary and secondary carbinols may serve as hydrogen donors in the catalysis. The former ones, however, have the advantage of being highly selective and transfer hydrogen exclusively to the unsaturated C=C bonds. Secondary alcohols may, under suitable conditions, affect the carbonyl group as well, and therefore should be applied as reducing agents for saturated ketones (eq 2).[2m,6]

Tertiary carbinols do not donate hydrogen to unsaturated substances, but readily form ethers in the presence of 1.[11]

Ether formation from primary and secondary carbinols is exceedingly slow, except for some cases in which the generation of stable carbocations is facilitated by strong electron-donating groups [e.g., 1-(4-methoxyphenyl)ethanol]. In experiments with such carbinols large excess of the donor is required.

Although simple olefins can be used as hydrogen acceptors in the catalytic process, they have the disadvantage of being reduced very slowly by 1. On the other hand, substrates with activated double bonds react usually at high rates and give good yields. Particularly good results are obtained with α,β-unsaturated ketones (Table II). Olefinic and acetylenic bonds in $ArCH{=}CHBr$, $ArCH{=}CHNO_2$, $ArCH{=}CHSO_2CH_3$, $ArCOCH{=}CHCOAr$, $Ar(CH{=}CH)_2Ar$, and $ArC{\equiv}CCOR$ are hardly affected. These compounds form stable chelates with the ruthenium catalyst.

For kinetic measurements we chose the reduction of benzylideneacetophenone by 1-phenylethanol (eq 3). The reaction proceeds smoothly in an *irreversible* fashion (unaffected by addition of the products to the reaction mixture) and may give over 95% 3-phenylpropiophenone and acetophenone. Subsequent reduction of the saturated ketones according to eq 2 is negligible under our experimental conditions. A typical reaction curve for the transfer hydrogenation of a solution of 0.1 *M* benzylideneacetophenone by 1 *M* 1-phenylethanol and 10^{-3} *M* $RuCl_2(PPh_3)_3$ in diphenyl ether at 180° is given in Figure 1. The rate is shown to be virtually constant over the first 60% of the reaction, but the contribution of first and higher order terms becomes significant at advanced states.

$$C_6H_5CH(OH)CH_3 + C_6H_5CH{=}CHCOC_6H_5 \xrightarrow{\text{cat.}} C_6H_5COCH_3 + C_6H_5CH_2CH_2COC_6H_5 \quad (3)$$

Dependence on Donor, Acceptor, and Catalyst Concentration. Plots of the initial rate against the concentration of the hydrogen donor and of the unsaturated ketone are shown in Figures 2 and 3.

Both functions are nonlinear and the dependence of the initial rate on the concentration decreases gradually. While in the acceptor the rate becomes independent of the concentration above 0.2 *M*, in the alcohol it reaches its maximum value only in the pure substrate. Plots of the reciprocal functions, i.e., $rate^{-1}$ vs. $concentration^{-1}$, yield linear dependence with positive intercept in both cases (vide infra Figures 7 and 8). These results suggest that coordination and activation of the carbinol and of the unsaturated ketone take place prior to the rate-determining step.

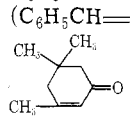
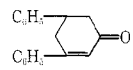
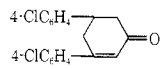
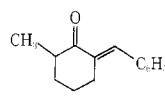
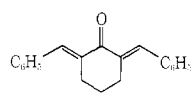
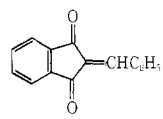
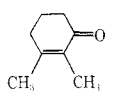
The dependence on catalyst concentration is linear

Table I
$RuCl_2(PPh_3)_3$-Catalyzed Transfer Hydrogenation of Benzylideneacetophenone by Various Carbinols at 180° [a]

Expt	Carbinol	Reaction time, min	Yield of $C_6H_5(CH_2)_2COC_6H_5$, %
1	$C_6H_5CH_2OH$	40	90
2	4-$CH_3C_6H_4CH_2OH$	40	93
3	3-$CH_3OC_6H_4CH_2OH$	40	83
4	4-$CH_3OC_6H_4CH_2OH$	15	91
5	4-$ClC_6H_4CH_2OH$	60	82
6	3-$FC_6H_4CH_2OH$	180	60
7	4-$FC_6H_4CH_2OH$	60	78
8	$C_6H_5OCH_2OH$	40	50
9	$CH_3(CH_2)_6CH_2OH$	120	68
10	4-$HOCH_2C_6H_4CH_2OH$ [b]	15	79
11	$HOCH_2CH_2OH$	60	45
12	$HOCH_2(CH_2)_4CH_2OH$ [b]	40	48
13	$HOCH_2CH_2OCH_2CH_2OH$	20	80
14	$CH_3(CH_2)_2CH(OH)CH(C_2H_5)CH_2OH$ [b]	40	23
15	$C_6H_5CH(OH)CH_3$	60	80
16	4-$CH_3C_6H_4CH(OH)CH_3$	40	96
17	4-$ClC_6H_4CH(OH)CH_3$	60	26
18	4-$FC_6H_4CH(OH)CH_3$	60	36
19	β-$C_{10}H_7CH(OH)CH_3$ [b]	20	41
20	$CH_3(CH_2)_7CH(OH)CH_3$	120	38
21	$(CH_3)_2CHCH(OH)CH(CH_3)_2$	120	25
22	c-$C_3H_5CH(OH)$-c-C_3H_5 [c]	120	30
23	$CH_3CH(OH)CH(CH_3)CH(OH)(CH_2)_2CH_3$ [b]	40	63
24	c-$C_6H_{11}OH$ [b,c]	120	34
25	3,4-Dimethylcyclohexanol [b]	120	36
26	*trans*-1,4-Dihydroxycyclohexane [b]	120	63

[a] Except in expt 10, 12, 14, 19, and 23–26, the reaction mixture consisted of a solution of 0.4 *M* benzylideneacetophenone and 10^{-3} *M* catalyst in the carbinol. [b] A solution of 0.2 *M* benzylideneacetophenone, 2 *M* carbinol, and 10^{-3} *M* catalyst in freshly purified diphenyl ether was used. [c] In a sealed tube.

Table II
$RuCl_2(PPh_3)_3$-Catalyzed Transfer Hydrogenation of Various α,β-Unsaturated Ketones by Benzyl Alcohol under Comparable Conditions[a]

Expt	Unsaturated ketone	Yield, %
1	$C_6H_5CH{=}CHCOCH_3$	95
2	$C_6H_5CH{=}CHCO(CH_3)_3$	42
3	4-$CH_3OC_6H_4CH{=}CHCOCH_3$	96
4	$C_6H_5CH{=}CHCOC_6H_5$	92
5	4-$CH_3C_6H_4CH{=}CHCOC_6H_5$	94
6	4-$CH_3OC_6H_4CH{=}CHCOC_6H_5$	93
7	4-$ClC_6H_4CH{=}CHCOC_6H_5$	90
8	4-$FC_6H_4CH{=}CHCOC_6H_5$	92
9	3,4-$(CH_3O)_2C_6H_3CH{=}CHCOC_6H_5$	89
10	4-$CH_3OC_6H_4CH{=}CHCOC_6H_4$-4-$CH_3$	89
11	4-$CH_3C_6H_4COCH{=}CHC_6H_5$	88
12	4-$CH_3OC_6H_4COCH{=}CHC_6H_5$	96
13	4-$ClC_6H_4COCH{=}CHC_6H_5$	91
14	4-$FC_6H_4COCH{=}CHC_6H_5$	94
15	$C_6H_5C(CH_3){=}CHCOC_6H_5$	45
16	$C_6H_5CH{=}C(CH_3)COC_6H_5$	44
17	$C_6H_5(CH{=}CH)_2COCH_3$	*b, c*
18	$(C_6H_5CH{=}CH)_2CO$	*b, d*
19		54
20		52[e]
21		52[e]
22		36[e]
23		*b, f*
24		45
25		0

[a] A solution of 0.4 *M* ketone and 10^{-3} *M* catalyst in benzyl alcohol was heated for 60 min at 180°, then immediately cooled to room temperature. [b] Kinetic measurements indicate that no direct conversion of dienone to the saturated ketone takes place. The monounsaturated ketone can be reduced completely to the saturated carbonyl compound upon further heating at 180°. [c] 55% $C_6H_5(CH_2)_4COCH_3$ and 40% $C_6H_5CH{=}CH(CH_2)_2COCH_3$. [d] 50% $(C_6H_5CH_2CH_2)_2CO$ and 26% $C_6H_5CH_2CH_2COCH{=}CHC_6H_5$. [e] As a mixture of cis and trans isomers. [f] 38% 2,6-dibenzylcyclohexanone and 56% 2-benzyl-6-benzylidenecyclohexanone.

below 6×10^{-4} *M* and suggests pseudo-first-order behavior. At higher concentration ($>10^{-3}$ *M*) the rate approaches a constant value, probably due to solubility limits and to the dimerization and/or polymerization[12-14] of the dissociated ruthenium catalyst (see also ref 15).

Structure–Activity Correlation. The data given in Tables I and III indicate that benzyl alcohols are more reactive than straight-chain aliphatic ones. As carbinols that are substituted by electron-releasing groups increase the activity and vice versa, it can be assumed that abstraction of a hydrogen atom, α to the hydroxyl group, as hydride is involved in the rate-determining step. This assumption is further supported by evaluation of the kinetic isotope effect measurements using deuterated 1-phenylethanol (Table IV).

Upon introduction of Cl, F, OCH_3, or CH_3 groups in the 4 and/or 4′ position in benzylideneacetophenone we found that electronic factors have no significant effect on the reaction rate and yield. The results resembled those of the unsubstituted parent compound. A decrease in rate has, however, been noted when sterically hindered hydrogen acceptors were reduced (Table V). This, once again, suggests that the coordination of the acceptor to the metal atom takes place prior to the rate-determining step. Since shielding of either the C=C double bond or the carbonyl group causes rate reduction, one may conclude also that coordination of α,β-unsaturated ketones involves *both* these functions. The reduced affinity of an α-substituted chalcone toward the ruthenium catalyst, as compared with that of the parent compound, can be derived from plots of the corresponding rate vs. ketone concentration. While, e.g., in the unsubstituted acceptor the highest rate is reached already above 0.2 *M* (Figure 3), in α-methylbenzyl-

Table III
Initial Rates of Transfer Hydrogenation of Benzylideneacetophenone by Various Carbinols[a]

Expt	Carbinol	Initial rate, mmol/min
1	Octan-1-ol	2.11
2	Decan-1-ol	1.24
3	3,4-Dimethylcyclohexanol	1.17
4	Ethylene glycol	2.95
5	Diisopropylcarbinol	0.83
6	Benzyl alcohol	8.96
7	3-Methoxybenzyl alcohol	5.00
8	4-Methoxybenzyl alcohol	30.00
9	3-Fluorobenzyl alcohol	1.38
10	4-Fluorobenzyl alcohol	4.89
11	1-Phenylethanol	5.35
12	1-(4-Tolyl)ethanol	9.67
13	1-(4-Chlorophenyl)ethanol	1.74
14	1-(4-Fluorophenyl)ethanol	2.19

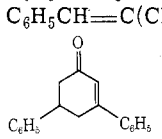
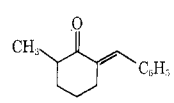
[a] Reaction system was 0.4 *M* ketone and 10^{-3} *M* catalyst in the carbinol at 180°.

Table IV
Kinetic Isotope Effect Measurements[a]

Carbinol	k_H/k_D[b]
$C_6H_5CD(OD)CH_3$	2.59
$C_6H_5CD(OH)CH_3$	2.57
$C_6H_5CH(OD)CH_3$	1.17

[a] Reaction system was 0.4 *M* benzylideneacetophenone and 10^{-3} *M* $RuCl_2(PPh_3)_3$ in deuterated 1-phenylethanol at 170°. [b] The *k* values are calculated from the reduced rate equation rate = $k[C]_0$ as described later.

Table V
Initial Rates of Transfer Hydrogenation of Some α,β-Unsaturated Ketones by Benzyl Alcohol[a]

Expt	Hydrogen accepter	Initial rate, mmol/min
1	$CH_2{=}CHCOC_2H_5$[b]	44.0
2	$C_6H_5CH{=}CHCOCH_3$	21.0
3	$C_6H_5CH{=}CHCOC_6H_5$	9.0
4	$C_6H_5CH{=}CHCOC(CH_3)_3$	3.1
5	$C_6H_5C(CH_3){=}CHCOC_6H_5$	3.2
6	$C_6H_5CH{=}C(CH_3)COC_6H_5$	3.1
7		3.5
8		2.6

[a] Reaction system was 0.4 *M* ketone and 10^{-3} *M* catalyst in benzyl alcohol at 180°. [b] In a sealed ampoule.

ideneacetophenone, $C_6H_5CH{=}C(CH_3)COC_6H_5$, this is achieved only above 1.6 *M*.

A remarkable phenomenon has been observed in the transfer hydrogenation of mixtures of sterically hindered and unhindered unsaturated ketones. While, e.g., benzylideneacetophenone and α-methylbenzylidenacetophenone react separately with 1-phenylethanol in comparable velocities (ratio of initial rates was found to be 2.8:1), a *mixture* of these ketones yields no 3-phenylbutyrophenone until practically all the benzylideneacetophenone has been consumed. This can be rationalized by the "blocking" of all

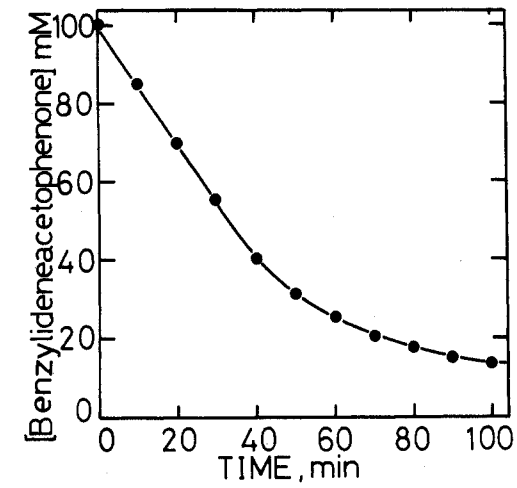


Figure 1. Plot of conversion vs. reaction time: 0.1 *M* benzylideneacetophenone, 1 *M* 1-phenylethanol, and 10^{-3} *M* $RuCl_2(PPh_3)_3$ in diphenyl ether at 180°.

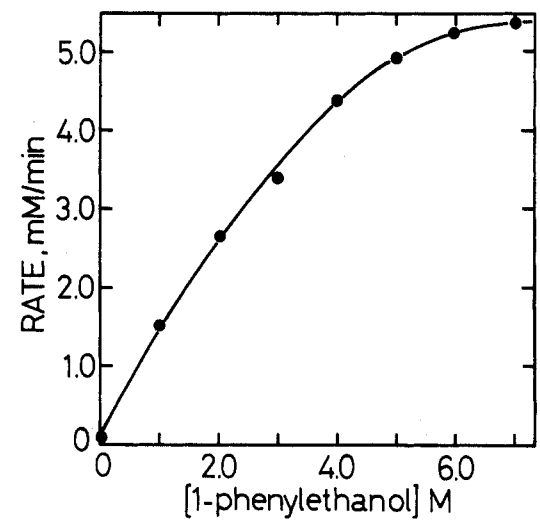


Figure 2. Dependence of initial rate on the concentration of 1-phenylethanol in diphenyl ether at 180°, with 0.4 *M* (initial concentration) benzylideneacetophenone and 10^{-3} *M* $RuCl_2(PPh_3)_3$.

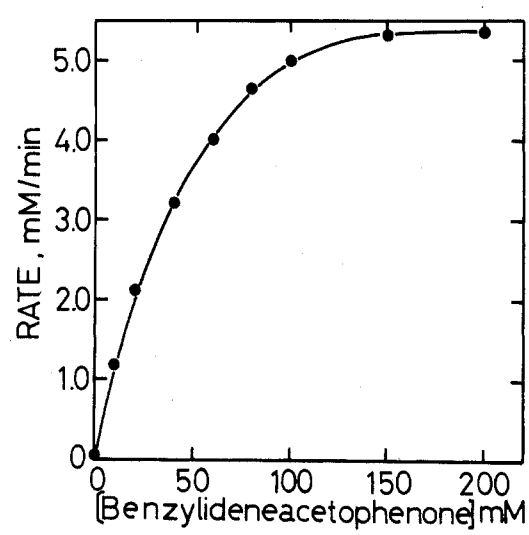


Figure 3. Dependence of initial rate on the concentration of benzylideneacetophenone at 180°. Catalyst concentration 10^{-3} *M* in 1-phenylethanol.

available active sites in the catalyst by the ketone of the higher affinity to the metal catalyst, preventing, thus, the activation of the bulky α-methyl derivative. (Cf. similar

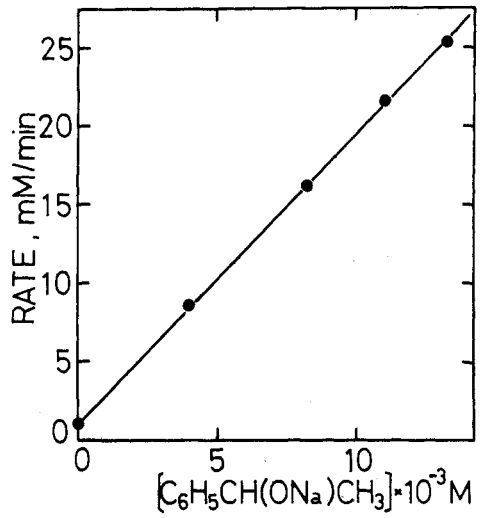


Figure 4. Influence of $C_6H_5CH(ONa)CH_3$ on the initial rate of transfer hydrogenation of benzylideneacetophenone (initial concentration 0.4 M in 1-phenylethanol) at 120°. Catalyst concentration 10^{-3} *M*.

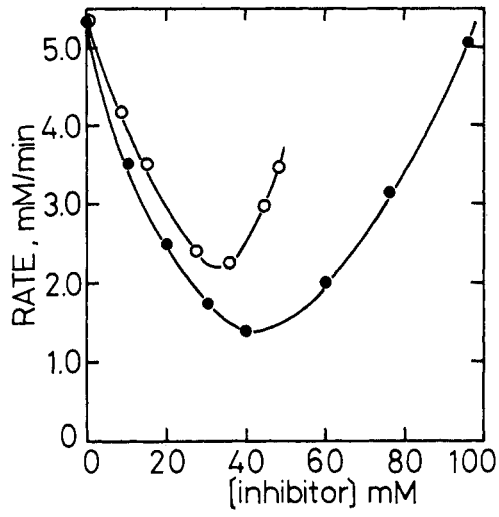


Figure 5. Effect of addition of triphenylphosphine (●) and tribenzylamine (○). Reaction system: 0.4 *M* ketone and 10^{-3} *M* $RuCl_2(PPh_3)_3$ in 1-phenylethanol at 180°.

competitive behavior in some other transition metal catalyzed reactions.[15])

The influence of the electronic structure of the catalyst upon reactivity was studied by utilizing ruthenium complexes of general formula $RuCl_2[(4\text{-}X\text{-}C_6H_4)_3P]_3$ in reaction 3. The initial rates for various substituents X are listed in Table VI. Since the formation of a metal hydride intermediate should be favored by electron-attracting groups, it is obvious that such a hydride cannot be a key step in the overall reaction.

Table VI
Reactivities of Various Catalysts of Formula $RuCl_2[(4\text{-}X\text{-}C_6H_4)_3P]_3$[a]

Registry no.	Substituent X	Initial rate, mmol/min
39042-64-3	Cl	2.05
39152-69-7	F	2.53
15529-49-4	H	2.78
36733-05-8	CH_3	4.50
39114-24-4	OCH_3	5.40

[a] Reaction system was 0.4 *M* benzylideneacetophenone and 10^{-3} *M* ruthenium catalyst in 1-phenylethanol at 170°.

Inhibitors and Cocatalysts. Reaction 3 is strongly accelerated by bases and decelerated by acids. A typical example of such an acceleration is shown in Figure 4. Although the sodium enolate, $C_6H_5CH(CH_3)O^-Na^+$, acts in this case primarily as a cocatalyst, it should be recalled that bases by themselves are capable of catalyzing hydrogen transfer from carbinols to unsaturated acceptors in the *absence* of transition-metal complexes, albeit by a different mechanism.[16] Kinetic measurements, now carried out, for the reaction of benzylideneacetophenone and 1-phenylethanol in the presence of various strong bases, free from transition-metal compounds, indicate that the reaction rate falls usually much behind that of the $RuCl_2(PPh_3)_3$-catalyzed reaction.[17]

Tertiary alcohols, which by themselves are inactive as hydrogen donors, serve as inhibitors in reaction 3. The addition of a 2 *M* solution of 2-phenylpropon-2-ol, e.g., to the reaction mixture of benzylideneacetophenone (0.4 *M*) and 1 (10^{-3} *M*) in 1-phenylethanol causes the initial rate to decrease by 45%. It seems, thus, that the tertiary carbinol competes with 1-phenylethanol for the active sites at the central ruthenium atom.

Some olefins, e.g., allylbenzene, which proved to be transfer hydrogenated much slower than chalcone, interfere with the reduction of the latter. A 1 *M* solution of allylbenzene is sufficient to bring reaction 3 to a standstill.

The effect of addition of triphenylphosphine on the reaction rate is shown in Figure 5. Below 40 m*M* any addition of PPh_3 inactivates the ruthenium catalyst, probably by preventing $RuCl_2(PPh_3)_3$ from dissociation into free phosphine and the active species $RuCl_2(PPh_3)_2$ (**2**).[12,18] At higher concentration of triphenylphosphine the rate starts to increase again, possibly owing to an independent base-catalyzed reaction exerted by the addendum itself.

That considerable dissociation of $RuCl_2(PPh_3)_3$ indeed takes place under the temperature conditions of the catalysis has been proven by heating the starting catalyst in boiling oxygen-free decalin. After 20 min 80% of PPh_3 could be isolated. In addition this experiment yielded 70% of $[RuCl_2(PPh_3)_2]_x$ which catalyzes reaction 3 at similar rate recorded for the tris(triphenylphosphine) complex. In the presence of oxygen $RuCl_2(O_2)(PPh_3)_2$[19] separated. This complex does not catalyze reaction 3 at all. Another *inactive* ruthenium compound, $RuCl_2(CO)_2(PPh_3)_2$, is formed when $RuCl_2(PPh_3)_3$ is heated *in the absence* of a hydrogen acceptor above 150° in a primary alcohol solvent (e.g., benzyl alcohol).

The effect of several tertiary amines seems to be similar to that of PPh_3, although the mechanisms involved may be much more complicated. Tribenzylamine, e.g., causes the initial rate to drop from 5.35 mmol/min (zero amine concentration) to ~2.20 mmol/min on addition of 0.3 m*M*. At higher amine concentration a sharp increase in rate is noted and extensive ligand exchange occurs.

Some alkyl and aryl chlorides (e.g., chloroform, carbon tetrachloride, chlorobenzene, α-chloronaphthalene) act as powerful inhibitors. These compounds slowly coordinate with the catalyst[25] to give ruthenium complexes which are inactive in the transfer hydrogenation reaction.

Deuterium Labeling Studies. Mass spectral analyses of the 3-phenylpropiophenone obtained by transfer hydrogenation of benzylideneacetophenone using deuterated 1-phenylethanol are given in Table VII. Since $RuCl_2(PPh_3)_3$ has been shown to catalyze also internal H–D exchange in carbinols,[11,21] these figures do not give quantitative information on the chalcone transfer deuteration. They indi-

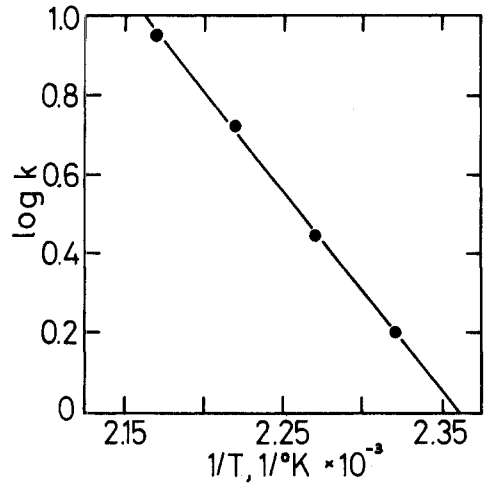


Figure 6. Arrhenius plot of transfer hydrogenation of benzylideneacetophenone by 1-phenylethanol at 160–190°.

cate, however, clearly enough, that the α hydrogen atom in the alcohol is transferred preferentially to the β carbon in the chalcone molecule and the hydroxylic proton attacks mainly at the α carbon. As the peak *m/e* 91 represents the fragment $[C_6H_5CH_2]^+$, a low ratio of intensities 91:92 indicates deuteration at the β carbon. A low ratio *m/e* 105:106 provides rough information on α-carbon labeling. (Both fragments $[C_6H_5CH_2CH_2]^+$ and $[C_6H_5CO]^+$ have similar masses.)

The last two experiments in Table VII show that the aromatic solvent exchanges part of its hydrogen atoms with the protons of the carbinol and are, in turn, transferred to the ketone.

The overall stereochemistry of the transfer hydrogenation was found to be exclusively cis addition, just as in some typical transition metal catalyzed hydrogenation reactions (see, e.g., ref 22 and 23). When, e.g., a solution of 10^{-2} *M* benzylidenepinacolone in benzyl alcohol-d_3, $C_6H_5CD_2OD$, was heated at 170° in the presence of 2.5×10^{-5} *M* $RuCl_2(PPh_3)_3$, essentially pure *threo*-4,4-dimethyl-1-phenylpentan-3-one-d_2, $C_6H_5CHDCHDCOC(CH_3)_3$, was obtained. The threo configuration (and thus cis addition) could easily be established by virtue of the low coupling constant, J = 3.9 Hz. The corresponding value for the erythro isomer is expected to be 10–14 Hz.[24]

Dependence on Temperature. Initial rates (reaction 3) were measured at four temperatures ranging from 160 to 190° for several benzylideneacetophenone concentrations between 0.01 and 0.4 *M*. From the Arrhenius plot of log k (see below) against $1/T \times 10^{-3}$ (Figure 6) a value for the activation energy, E_a, of 25.4 kcal mol^{-1} is obtained; $\Delta H^{\ddagger}$ = 24.3 kcal mol^{-1} and $\Delta S^{\ddagger} = -7.55$ ev.

Side Reactions. In order to carry out the above catalysis, free from undesired side reactions, primary alcohols, rather than secondary ones, should be utilized as hydrogen donors. The use of positively substituted primary carbinols is undesired as well, since ether formation takes place in the presence of $RuCl_2(PPh_3)_3$.[11,25]

Although dichlorotris(trisphenylphosphine)ruthenium catalyzes double-bond migration in several unsaturated systems,[10,26] it seldom promotes the isomerization of α,β-unsaturated ketones. Carvone is the only example we came across that is isomerized faster than being transfer hydrogenated.[7] Carvacrol is formed instead of dihydrocarvone.

The most undesired side reaction in process 1 is, obviously, reaction 2. Fortunately, the saturated ketone formed in reaction 1 is transferred to an alcohol only when a large *excess* of a *secondary* carbinol with high reduction potential (such as α-tetralol[27]) is used as hydrogen donor. Aldehydes and primary alcohols (that are aldehyde precursors) inhibit reaction 2 most efficiently. The side reaction can thus be completely eliminated by addition of a few drops of benzaldehyde, and the unsaturated ketone can be transfer hydrogenated exclusively at the C=C double bond. Reaction 2 may, however, have synthetic value of its own (Table VIII shows a few examples) and should deserve some attention.

Table VII
Transfer Hydrogenation of Benzylideneacetophenone by Deuterated 1-Phenylethanol[a]

Carbinol	Isotopic composition of product, % d_0	d_1	d_2	Intensities ratio of masses 91/92	105/106
$C_6H_5CD(OD)CH_3$	29	45	26	1.1	1.3
$C_6H_5CD(OH)CH_3$	46	45	9	1.1	2.7
$C_6H_5CH(OD)CH_3$	67	30	3	3.1	1.6
$C_6H_5CD(OD)CH_3$, C_6H_6[b]	46	38	16	1.4	3.4
$C_6H_5CH(OH)CH_3$, C_6D_6[b]	83	15	2	6.0	5.0

[a] Reaction system was 0.4 *M* benzylideneacetophenone and 10^{-3} *M* $RuCl_2(PPh_3)_3$ in the carbinol at 170°. [b] A 1:1 mixture of carbinol and benzene was used instead of pure carbinol.

Table VIII
Examples of $RuCl_2(PPh_3)_3$-Catalyzed Transfer Hydrogenation of Saturated Ketones by 1-Phenylethanol[a]

Starting ketone	Hydroxylic product	Yield, %
Cycloheptanone	Cycloheptanol	64
$(C_6H_5)_2CO$	$(C_6H_5)_2CHOH$	53
$C_6H_5COCH_2C_6H_5$	$C_6H_5CH(OH)CH_2C_6H_5$	60
$(C_6H_5CH_2)_2CO$	$(C_6H_5CH_2)_2CHOH$	57
4-$ClC_6H_4COCH_3$	4-$ClC_6H_4CH(OH)CH_3$	51

[a] Reaction system: 0.5 *M* ketone and 10^{-3} *M* catalyst in 1-phenylethanol at 180° for 1 hr.

The kinetic behavior of reaction 2 resembles in some, though not in all, respects that of reaction 3. The equilibration of dibenzyl ketone and 1-phenylethanol (eq 4) was chosen for the kinetic studies.

$$C_6H_5CH_2COCH_2C_6H_5 + C_6H_5CH(OH)CH_3 \rightleftharpoons C_6H_5CH_2CH(OH)CH_2C_6H_5 + C_6H_5COCH_3 \quad (4)$$

The difference between the redox potentials of the reagents and products in this system is remarkably large[26] and the reaction is, therefore, practically irreversible.

Starting with 0.5 *M* dibenzyl ketone and 10^{-3} *M* catalyst at 180°, the reaction curve is similar to that shown in Figure 1 for reaction 3. The rate is apparently constant in the first 60% of the reaction as long as terms of higher order are still small.

A plot of the initial rate vs. 1-phenylethanol concentration indicates a steady, but nonlinear, increase in rate up to 4.8 mmol/min in the pure alcohol. The dependence on dibenzyl ketone concentration is similar, but the rate reaches its highest and constant value already above 0.3 *M*. Plots of the reciprocal functions (i.e., $rate^{-1}$ vs. $concentration^{-1}$) have linear dependence as shown in Figures 7 and 8.

Rate dependence on catalyst concentration was found to be exactly the same as observed for reaction 3.

When dibenzyl ketone is substituted by 0.5 *M* solutions of cycloheptanone, benzyl phenyl ketone, benzophenone, 4-methoxy-, or 4-chloroacetophenone the initial rates are

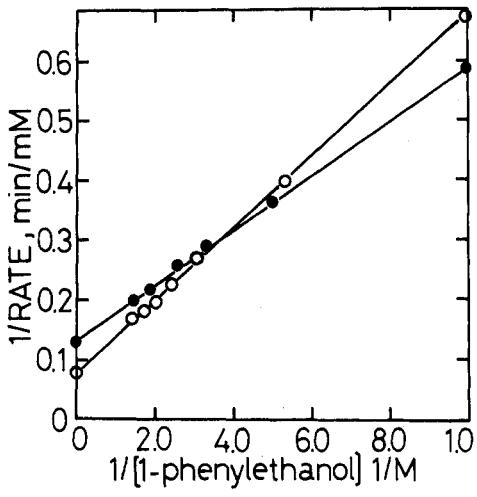


Figure 7. Plot of 1/initial rate of dibenzyl ketone (●) and benzylideneacetophenone (○) consumption against 1/1-phenylethanol concentration. (In the former system 0.5 *M* ketone and 10^{-3} *M* catalyst in 1,3-diisopropylbenzene were allowed to react at 180°; the unsaturated ketone was allowed to react in diphenyl ether under conditions of Figure 2.)

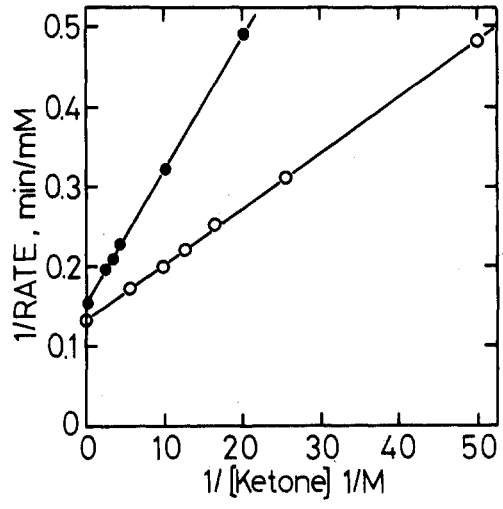


Figure 8. Plot of 1/initial rate against 1/dibenzyl ketone concentration (●) (reaction 4) and against 1/benzylideneacetophenone concentration (○) (reaction 3); catalyst concentration 10^{-3} *M* in 1-phenylethanol at 180°.

all of the same order (5.2, 5.1, 4.4, 5.0, and 4.3 mmol/min, respectively), practically independent of the nature of the ketone. Though the magnitude of the oxidation potentials should not effect the kinetics, ketones with very low oxidation potentials (e.g., α-tetralone and 2,3-dimethylcyclohexanone[27]) do not react to any measurable extent.

Electronic and steric factors in the starting carbinol exhibit a larger effect on the reaction rate. Dibenzyl ketone (0.5 *M*) is reduced at 180° by excess diisopropylcarbinol, 3,4-dimethylcyclohexanol, 1-(4-chlorophenyl)-, 1-phenyl-, and 1-(4-tolyl)ethanol at 0.8, 1.4, 3.6, 4.8, and 5.5 mmol/min (initial rates), respectively.

The k_H/k_D values for the reduction of dibenzyl ketone, under our standard conditions, using $C_6H_5CD(OD)CH_3$, $C_6H_5CD(OH)CH_3$, and $C_6H_5CH(OD)CH_3$, are 1.68, 1.52, and 1.04, respectively. These results suggest that α-hydrogen abstraction (as a metal hydride) may be involved in the rate-determining step. This assumption is further supported by the fact that electronic factors in the ruthenium catalyst provoke an influence on the reaction rate opposite to that found in the transfer hydrogenation of benzylideneacetophenone. (Compare Table VI and Table IX.)

Table IX
Effect of Electronic Changes in the Catalyst $RuCl_2[(4\text{-}X\text{-}C_6H_4)_3P]_3$ on the Rate of Reaction 4[a]

Substituent X	Initial rate, mol/min
CH_3O	3.56
CH_3	3.96
H	4.80
F	5.42
Cl	6.44

[a] Reaction system was 0.5 *M* dibenzyl ketone and 10^{-3} *M* catalyst in 1-phenylethanol at 180°.

Qualitative information on deuterium transfer from deuteriophenylethanols to dibenzyl ketone can be drawn from mass spectral analysis of the mixtures of deuterated 1,3-diphenylpropan-2-ol formed. The parent peak either loses H_2O to give $[C_6H_5CH{=}CHCH_2C_6H_5]\cdot^+$ (*m/e* 194) which, in turn, is converted into $[C_6H_5CH{=}CH]^+$ (*m/e* 103) by loss of a benzyl radical, or cleaves to $[C_6H_5CH_2CHOH]^+$ (*m/e* 121), which, by a concerted mechanism, gives $C_7H_8^+$ of mass 92. In addition moderate cleavage of both the parent peak and P − H_2O to $[C_6H_5CH_2]^+$ (*m/e* 91) and $(C_6H_5)^+$ (*m/e* 77) occurs.

Therefore, the intensity ratio of fragments *m/e* 195 to *m/e* 194 $[M^+ - H_2O]$ and of *m/e* 104 to *m/e* 103 reflect on the deuteration at the benzylic carbon, while the degree of labeling at the OH group can be estimated by the ratio of *m/e* 93 to *m/e* 92 intensities. On the ground of the 195/194 and 104/103 values given in Table X, it can be concluded that the benzylic hydrogen atom in 1-phenylethanol is transferred mainly to the α carbon in the acceptor. Likewise the transfer of the hydroxylic proton of the donor to the oxygen atom in the acceptor can be suggested by virtue of the 93/92 values that are larger when OD-containing 1-phenylethanol was used than by application of the undeuterated carbinol or $C_6H_5CD(OH)CH_3$. The ratios 123/121 and 122/121 refer to the species with both hydroxylic and benzylic hydrogen atoms and reflect only on the number of deuterium atoms transferred.

Table X
Mass Spectral Analysis of Labeled 1,3-Diphenylpropan-2-ols Obtained from Dibenzyl Ketone and Deuterated 1-Phenylethanol[a]

	Intensity ratio of masses				
Hydrogen donor	93/92	104/103	122/121	123/121	194/195
$C_6H_5CH(OH)CH_3$	0.15	0.23	0.22	0.03	0.19
$C_6H_5CH(OD)CH_3$	0.30	0.40	0.39	0.08	0.37
$C_6H_5CD(OH)CH_3$	0.15	1.32	1.55	0.29	0.97
$C_6H_5CD(OD)CH_3$	0.30	1.58	1.65	0.70	1.03

[a] The 1,3-diphenylpropan-2-ols were analyzed after 30 min by GC–MS on 10% Carbowax 20M on Chromosorb W. The reaction system was 0.5 *M* dibenzyl ketone and 10^{-3} *M* $RuCl_2(PPh_3)_3$ in phenylethanol at 180°.

In contrast to the effect of tribenzylamine on reaction 3, this base, and other ones, inhibits reaction 4, even at very low concentration. Triphenylphosphine, on the other hand, has the same effect on both catalyses.

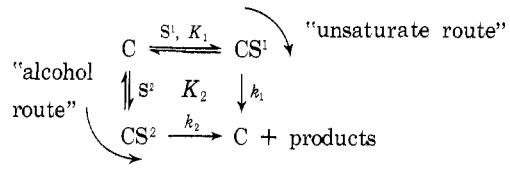
Discussion

It is obvious that both donor and acceptor are activated by the ruthenium catalyst. There rises, however, the question whether the alcohol precedes the unsaturated ketone

in coordination to the central metal atom or vice versa.

Following the mechanisms suggested for some other catalytic reactions [e.g., the homogeneous Rh(I)-catalyzed hydrogenation of olefins[15]] one might propose the formal Scheme I for the transfer hydrogenation reaction 1.

Scheme I



C, catalyst; S^1, hydrogen acceptor; S^2 hydrogen donor

The possible pathways to be considered are, thus, (a) the "unsaturate route" in which fast equilibration of the catalyst and the acceptor is followed by a slow reaction with the carbinol and (b) the "alcohol route" which requires the reversible coordination of the alcohol to the metal prior to a slow interaction of the complex, CS^2, with the acceptor. A "random mechanism" in which both routes operate simultaneously is, of course, possible as well.

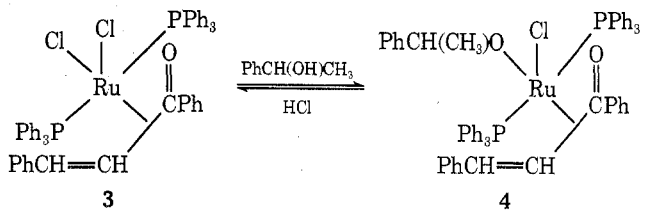
The kinetic measurements show that the catalysis follows neither a simple "alcohol route" (in which $K_2 = k_2 = 0$, and the rate law $-d[S^1]/dt = -d[S^2]/dt = k_1K_1[S^1][S^2][C]_0/(1 + K_1[S^1])$; $[C]_0$ = initial catalyst concentration), nor an isolated "unsaturate route" in which $K_1 = k_1 = 0$. The "random mechanism" for which the rate expression is $-d[S^2]/dt = (k_1K_1 + k_2)[S^1][S^2][C]_0/(1 + K_1[S^1] + K_2[S^2])$ must also be excluded on the basis of the observation that the rate dependence on the donor $[S^2]$ (in excess acceptor) is nonlinear. Further indication that the catalysis is not likely to follow the "alcohol route" or a "random mechanism" can be found in the competition experiment in which no reduction of the α-methylbenzylideneacetophenone has occurred before all the sterically unhindered chalone was consumed (cf. ref 27). In fact, the kinetic measurements can be interpreted by assuming the "unsaturate route", for which $k_2 = 0$ but $K_2 > 0$, to be the main pathway in reaction 3. The independent interaction of the catalyst with the donor, that leads to a positive value for K_2, has been demonstrated by the ability of $RuCl_2(PPh_3)_3$ to catalyze racemization,[11] H–D exchange,[11,21] ether formation,[11] and isomerization[20] in suitable carbinols even in the presence of α,β-unsaturated ketones. The dissimilarity between this suggestion and the mechanisms assigned to some other homogeneous transfer hydrogenation reactions is remarkable [cf., e.g., the recently reported reaction of cycloheptene and 2-propanol in the presence of $HRh(PPh_3)_4$[2p]].

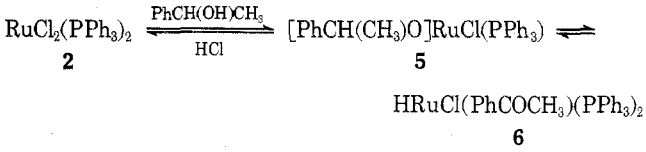
We propose, thus, reaction 1 to proceed in the following order.

A. Activation of the Catalyst. Although recent studies indicate that no more than 5% of $RuCl_2(PPh_3)_3$ (**1**) is dissociated into PPh_3 and $RuCl_2(PPh_3)_2$ (**2**) at low temperatures, we proved that above 150° dissociation is nearly complete. Under these conditions, the recombination of PPh_3 and **2** to the trisphosphine complex can be considered rather small by virtue of the relatively large amount of free phosphine needed to create a significant effect on the reaction rate. The 14-electron complex **2** forms chlorine-bridged dimers and polymers in highly concentrated solutions,[13,28] but on high dilution the monomeric species predominates (as proved by molecular weight determination) and hence the linear dependence of rate on the catalyst at least below 6×10^4 *M*.

B. Coordination and Activation of the Acceptor. As no stable ruthenium complex of α,β-unsaturated ketone could be isolated, we presume that the acceptor coordinates to the metal in the same manner as to some Pd and Pt compounds (cf., e.g., Pt complexes of mesityl oxide[29,30]). Whether the >C=C–C=O group is linked to the metal via the C=C π electrons,[31] the carbonyl bond,[19,32] or via both unsaturated functions[33] is yet uncertain. However, one can say with confidence that the adducts are unstable and decompose easily to the starting materials. The equilibrium constant K_1 is expected to be only slightly influenced by electronic variations but more severely by steric effects in the unsaturated ketone (see also ref 23).

C. Coordination of the Hydrogen Donor. The interaction of metal complexes with primary and secondary carbinols results, usually, in metal hydride formation.[34] The steps in these reactions are assumed to be conversion into a metal alkoxide complex[11,35] (rarely isolable[36]) and β-hydrogen transfer from the alkoxide ligand to the metal atom.[11,34c] Accordingly, we suggest that complex **3** formed in step B reacts with the donor to give an alkoxide **4** and a proton. This step is inhibited by acids and promoted by bases.





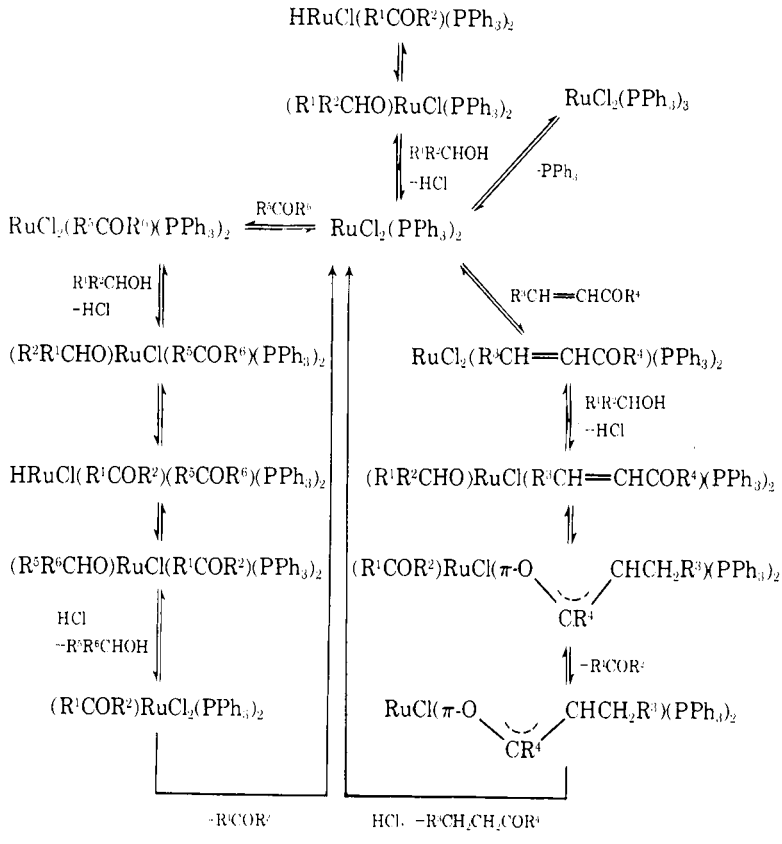
In an independent course the donor might coordinate directly to the active catalyst **2** to give alkoxide **5** which, in turn, rearranges to the pentacoordinated hydride **6**. It seems that this complex is unable to react with the acceptor to form an unfavorable heptacoordinated adduct. Therefore, **5** and **6** are not regarded as reaction intermediates in catalysis 1, but are assumed to play a part in the racemization,[11] H–D exchange,[11] ether formation,[11] and isomerization[20] of alcohols reported previously.

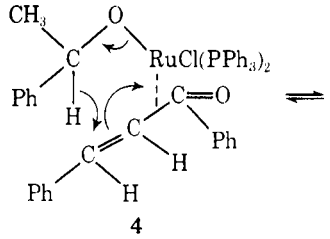
D. Hydrogen Transfer. Transformation of the alkoxide **4** to a (heptacoordinated) hydrido complex, in a similar manner as in step **5** → **6**, would be expected to be facilitated by electron-attracting substituents on the ruthenium catalyst. In fact, the experiments with $RuCl_2[(4\text{-}X\text{-}C_6H_4)_3P]_3$ proved that this is not the case and *electron-releasing* groups X increase the rate and vice versa. To rationalize our observations we assume that the β-hydrogen atom in the alkoxide moiety is transferred directly to the β carbon (as proved by deuterium labeling) in a concerted reaction. Preferential attack at the β position, due to electronic and steric effects, is the feature of many other catalytic hydrogen transfer reactions (e.g., hydrogenation of olefins by cobalt complexes[37,38]).

The kinetic isotope effect indicates that this step is rate determining in the overall reaction.

The hydride transfer yields presumably a π-oxopropenyl complex **7**.[39,40] The strong trans effect of the π-oxopropenyl ligand facilitates release of the phenethoxyl residue as acetophenone (or as the corresponding aldehyde or ketone when other carbinols are used as hydrogen donor).

Scheme II





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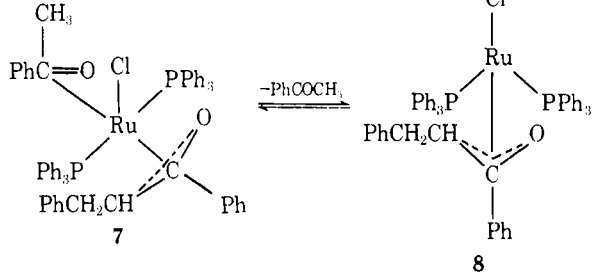

7 8

E. Release of the Product. The high electron density on the π-oxopropenyl ligand increases the sensitivity to electrophilic attack of a proton, which might occur (not necessarily in acidic media[41]) either at the oxygen atom to yield an enol or at the α carbon to give immediately the saturated ketone. Since the overall reaction proved to be stereospecific, the second possibility is the one to be preferred.

The complete cycle of the $RuCl_2(PPh_3)_3$-catalyzed transfer hydrogenation of α,β-unsaturated ketones is summarized in the right wing of Scheme II.

Since under our experimental conditions $RuCl_2(PPh_3)_3$ can be assumed to dissociate almost completely, in a practically irreversible fashion, to the active catalyst 2 (that stays mostly in the monomeric form), we can apply the kinetic Scheme III for reaction 1.

Since all the reversible steps are known to play a part in some homogeneous hydrogenation and isomerization reactions at much lower temperatures, we assume fast equilibration for these steps at 180°. The rate law for the offered scheme would then be

Scheme III

$$C + S^1 \overset{K_1}{\rightleftharpoons} CS^1$$

$$CS^1 + S^2 \overset{K_2}{\rightleftharpoons} CS^1S^2$$

$$CS^1S^2 \overset{k}{\longrightarrow} C + \text{products}$$

$$C + S^2 \overset{K_3}{\rightleftharpoons} CS^2$$

C, S^1, and S^2 have the same assignments as in Scheme I

$$\text{rate} = -\frac{d[S^1]}{dt} = \frac{kK_1K_2[S^1][S^2][C]_0}{1 + K_1[S^1] + K_1K_2[S^1][S^2] + K_3[S^2]}$$

When large excess of S^1 is present (i.e., above "saturation" concentration of 0.2 M at which the rate becomes invariable), the rate law becomes

$$\text{rate} = \frac{kK_2[S^2][C]_0}{1 + K_2[S^2]}$$

and when S^2 is in excess (i.e., >7 M) the rate can be expressed as

$$\text{rate} = \frac{kK_1K_2[S^1][C]_0}{K_3 + K_1K_2[S^1]}$$

These two simplified equations represent the observed rate dependence on the acceptor and donor, respectively, as shown in Figures 2 and 3, and which are both linear in reciprocal form (Figures 7 and 8).

When excess of both acceptor and donor are used ("total saturation") the rate expression reduces to rate = $k[C]_0$

and then the magnitude of k can be obtained directly from the initial rate of the reaction.

Finally we discuss briefly the mechanism of reaction 4, in which dibenzyl ketone is reduced to 1,3-diphenylpropan-2-ol.

For the same kinetic reasons mentioned previously for reaction 1, we propose that the acceptor is the first one to be added, reversibly, to the active catalyst **2.** Support in this assumption (on a "ketone route") can be found in the work of Stephenson and Wilkinson,[42] who prepared stable Ru(II)- and Ru(III)–acetone complexes, some by using ruthenium–carbinol adducts as starting materials. The complex $(PhCH_2COCH_2Ph)RuCl_2(PPh_3)_2$ (**9**), so formed, is assumed to react with 1-phenylpropanol to give the alkoxide $[PhCH(CH_3)O]RuCl(PhCH_2COCH_2Ph)(PPh_3)_2$ (**10**) and HCl. Unlike in **4**, an α-hydrogen atom of the alkoxyl moiety might be transferred to the metal, in the rate-determining step, to give a hexacoordinated hydride, $HRuCl(PhCOCH_3)(PhCH_2COCH_2Ph)$ (**11**). This is supported by the experiments with various catalysts $RuCl_2[(4\text{-}X\text{-}C_6H_4)_3P]_3$ (Table IX), in which electron-releasing groups X proved to decrease the reaction rate and vice versa. The hydride is now expected to attack the coordinated ketone with the higher oxidation potential to give $[PhCH_2CH(CH_2Ph)O]RuCl(PhCOCH_3)(PPh_3)_2$ (**12**), which in turn can react like **8** with a proton to form 1,3-diphenylpropan-2-ol and $RuCl_2(PhCOCH_3)(PPh_3)_2$. Elimination of acetophenone from the latter results in reforming of the active catalyst **2.**

The complete cycle of reaction 2 is summarized in the left wing of Scheme II.

Experimental Section

The catalyst $RuCl_2(PPh_3)_3$ was prepared according to Stephenson and Wilkinson.[42] The substituted triarylphosphine derivatives of this complex, $RuCl_2[(4\text{-}CH_3C_6H_4)_3P]_3$, $RuCl_2[(4\text{-}CH_3OC_6H_4)_3P]_3$, $RuCl_2[(4\text{-}ClC_6H_4)_3P]_3$, and $RuCl_2[(4\text{-}FC_6H_4)_3P]_3$ were prepared as reported previously.[43]

Dichlorobis(triphenylphosphine)ruthenium polymer, $[RuCl_2(PPh_3)_2]_x$, was obtained in 70% yield by refluxing a solution of 500 mg of $RuCl_2(PPh_3)_3$ in 20 ml of peroxide-free decalin for 30 min under argon. The black solid that separated (mp 225° dec) was not identical with the brown complex reported by Poddar and Agarwala[13a] but proved to have similar catalytic activity.

Anal. Calcd for $(C_{36}H_{30}Cl_2P_2Ru)_x$: C, 62.0; H, 4.3; Cl, 10.2. Found: C, 62.3; H, 4.3; Cl, 10.3.

Dichlorocarbonylbis(triphenylphosphine)ruthenium, $RuCl_2(CO)_2(PPh_3)_2$. A solution of 100 mg of $RuCl_2(PPh_3)_3$ in 10 ml of benzyl alcohol was refluxed under argon. Upon cooling 60 mg (76%) of light yellow crystals separated: mp 160° (from benzene–hexane); $\nu_{C=O}$ (Nujul) 2000, 2070 cm^{-1}. (The NMR and ir spectra and the application of $C_6H_5CD_2OD$ proved the absence of metal-bound hydride).

Anal. Calcd for $C_{38}H_{30}Cl_2O_2P_2Ru$: C, 60.6; H, 4.0; Cl, 9.4. Found: C, 60.3; H, 4.4; Cl, 9.8.

Most carbinols and ketones were obtained from commercial sources (of highest grades available) and were freshly distilled in vacuo and degassed or recrystallyzed before use. The commercial solvents (hydrocarbons, aryl chlorides, and ethers) were purified by chromatography on alumina and distilled in vacuo. The noncommercial carbinols were prepared by the standard procedure from the corresponding esters, aldehydes, or ketones with $LiAlH_4$ ($LiAlD_4$ for deuterated compounds). Noncommercial ketones were obtained by aldol condensation of the appropriate ketones and aldehydes in basic media[44] except for 2,3-dimethyl-,[45] 3,5-diphenyl-,[46] and 3,5-di(4-chlorophenyl)cyclohex-2-enone,[47] which were prepared by other methods reported in the literature.

The products were identified by comparison of their spectral properties with those of authentic samples.

An Example of Transfer Hydrogenation of an α,β-Unsaturated Ketone. A mixture of 2.08 g (10^{-2} mol) of benzylideneacetophenone, 1.08 g (10^{-2} mol) of benzyl alcohol, and 19 mg (2×10^{-5} mol) of $RuCl_2(PPh_3)_3$ was refluxed under nitrogen for 2 hr. The catalyst was removed by flush distillation of the reaction mixture at 0.5 mm. Analysis by GC–MS (Varian 111) using both a 15% SE-30 on Chromosorb W and a 10% Carbowax 20M on Chromosorb W column indicated that 94% of the starting ketone was reduced to 3-phenylpropiophenone. The crystaline ketone of mp 72° separated on addition of ethanol to the reaction mixture.

Large-scale transfer hydrogenation of unsaturated ketones was carried out in ethylene glycol as described previously.[4]

An Example of Transfer Hydrogenation of a Saturated Ketone. A solution of 1.05 g (5×10^{-3} mol) of dibenzyl ketone and 10 mg (10^{-5} mol) of $RuCl_2(PPh_3)_3$ in 10 ml of 1-phenylethanol was heated at 180° under nitrogen for 4 hr. The mixture was flash distilled and analyzed by GC–MS on 10% Carbowax 20M on Chromosorb W. The yield of 1,3-diphenylpropan-2-ol was 93%.

The kinetic measurements were carried out in 20-ml reaction tubes equipped with gas inlets and outlets, immersed in an oil bath thermostat (accuracy ±0.2°). Samples were withdrawn and immediately frozen each 3–5 min during the first 20 min of the reaction and in intervals of 10–15 min thenceforth. GLC analysis (Packard gas chromatograph, Model 7400) was on a 1.8-m long column packed with either 3% SE-30 or 3% Carbowax 20M on Chromosorb W at 160–240° in accord with the sample injected. The initial rate was calculated in each case from the average of at least five experiments.

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Registry No.—$[RuCl_2(PPh_3)_2]_x$, 34076-51-2; $RuCl_2(CO)_2(PPh_3)_2$, 14564-35-3; benzylideneacetophenone, 94-41-7; benzyl alcohol, 100-51-6; 1-phenylethanol, 98-85-1; dibenzyl ketone, 102-04-5.

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Photochemical Reduction in the *N*-Acylketimine System

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Irradiation of a series of *N*-(α-alkylbenzylidene)benzamides in hydrogen-donating solvents results in reduction of the carbon–nitrogen double bond. The photoreduction involves an electronically excited state and does not occur by the chemical sensitization path encountered with simple *N*-alkylimines. Sensitization and emission studies show that the reaction is derived from an n–π^* triplet state. The failure of the imine nitrogen to initiate Norrish type II reactions suggests that the intermolecular hydrogen abstraction by the excited *N*-acylketimine occurs on the oxygen atom of the carbonyl group rather than on the nitrogen atom of the imine chromophore. Stern–Volmer quenching plots show that the rates of hydrogen abstraction of the *N*-acylketimines are low compared with those of aryl ketones. The low quantum efficiency of the photoreduction is attributed to both a low bimolecular hydrogen abstraction rate ($k_r = 1 \times 10^3$ l. mol^{-1} sec^{-1}) and a fast rate of triplet decay.

Aryl imines are known to undergo reduction and reductive dimerization on irradiation in 2-propanol.[1-5] Although the reaction bears analogy to aryl ketone photoreduction, the available data indicate that the reaction is quite different mechanistically in that it appears not to involve the excited state of the imine as an intermediate in the reduction.[1] The reaction has been shown to proceed via an α-amino radical formed by hydrogen atom transfer to the imine from a ketyl radical.[1] The ketyl radical is derived from carbonyl compounds present in starting material as an impurity, an added sensitizer, or as a photogenerated species (see Scheme I).

Scheme I

$$Ph_2C{=}O \xrightarrow{h\nu} Ph_2C{=}O^{*1} \longrightarrow Ph_2C{=}O^{*3}$$

$$Ph_2C{=}O^{*3} + (CH_3)_2CHOH \longrightarrow (Ph)_2\dot{C}OH + (CH_3)_2\dot{C}OH$$

$$(Ph)_2\dot{C}OH + (Ph)_2C{=}NR \longrightarrow Ph_2C{=}O + (Ph)_2\dot{C}NHR$$

$$(CH_3)_2\dot{C}OH + (Ph)_2C{=}NR \longrightarrow (CH_3)_2C{=}O + (Ph)_2\dot{C}NHR$$

$$2(Ph)_2\dot{C}NHR \longrightarrow (Ph)_2C{=}NR + (Ph)_2CHNHR$$

A number of related reports have appeared in the literature showing that reactions apparently involving sensitization by benzophenone in hydrogen-donating solvents proceed, in fact, via formation of ketyl radicals.[6-10] The term "chemical sensitization" was suggested to distinguish between such cases and sensitization involving excitation-energy transfer.[2]

Recently, Okada, Nozaki, Toshima, and coworkers reported that the photoreduction of *N*-(α-phenylbenzylidene)benzamide (1) in 2-propanol proceeds via an electronically excited triplet state (i.e., intramolecular chemical sensitization), in contrast with other diarylketimine photoreductions.[11-14] Similar results were reported by Fraser-Reid and coworkers with related compounds.[15]

$$(Ph)_2C{=}NCOPh \xrightarrow{h\nu} [(Ph)_2C{=}NCOPh]^*$$

$$[(Ph)_2C{=}NCOPh]^* + (CH_3)_2CHOH \longrightarrow$$

$$(Ph)_2C{=}N\dot{C}(OH)Ph + (CH_3)_2\dot{C}OH$$

$$2[(Ph)_2C{=}N\dot{C}(OH)Ph \longleftrightarrow (Ph)_2\dot{C}N{=}C(OH)Ph] \longrightarrow$$

$$Ph_2C{=}NCOPh + Ph_2CHNHCOPh$$

1 2

The Japanese workers also reported that the excited triplet state of *N*-acyldiphenylmethylenimine (3) can abstract the allylic hydrogens of cyclic and acyclic olefins and produce photochemical addition products (i.e., 4). The photoreduction and addition reactions were completely