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Catalytic reactions of metalloporphyrins.

II *. Activation and catalytic aldol condensation of ketone with rhodium(III)-porphyrin perchlorate under neutral and mild conditions

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Abstract

Acetone and methyl ethyl ketone undergo facile and direct metalation at the methyl groups by a cationic (octaethylporphyrinato) rhodium (III) complex with a non-coordinating perchlorate counteranion, (OEP)$Rh^{III}(ClO_4)$, under mild conditions. Acetylacetone and ethyl acetoacetate are similarly metalated at the internal methylene groups. The metalation of acetone is first-order with respect to both rhodium complex and ketone, and involves the (OEP)$Rh^{III}(ClO_4)$-assisted, rate-determining enolization of the ketone. The resulting 2-oxopropyl-rhodium derivative undergoes facile cleavage of the C–Rh bond with electrophiles such as H^+ and Br_2. When cyclohexanone is used as substrate, on the other hand, (OEP)$Rh^{III}(ClO_4)$ catalyzes the aldol condensation of the ketone effectively, where the intermediate cyclohexanone enolate reacts with the ketone or other carbonyl compound present and regenerates the Rh^{III} complex. An essential aspect of the present reaction is the remarkable ability of (OEP)$Rh^{III}(ClO_4)$ to promote enolization of simple ketones by activation with charge-separated $[(OEP)Rh^{III}]^+$ (a Lewis acid) under mild and neutral conditions. The second-order rate constant of (OEP)$Rh^{III}(ClO_4)$-assisted enolization of acetone at 30 °C ($k_2 = 2.6 \times 10^{-4}\ M^{-1}\ sec^{-1}$) is 10^7 times as large as that of its spontaneous enolization in water, where water is both acid and base.

Introduction

The conversion of a carbonyl compound into the corresponding enol (enolate) is essential in many organic and biological reactions. A typical example is substitution

* For part I see ref. 1.

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at the α-position of the carbonyl group, such as in halogenation and aldol reactions with C–C bond formation. These reactions, of which the mechanisms have been extensively studied [2], are catalyzed by acids and bases. In the modern enolate chemistry [3,4], enolates are usually generated by stoichiometric reactions of strong bases [5*] as enolization reagents (not catalysts) upon carbonyl compounds possessing acidic α-hydrogens. On the other hand, the biological enolization is often catalyzed by metallo-enzymes under neutral conditions as a result of efficient cooperation between metal ion (as a Lewis acid) and basic group (as a proton acceptor) [6,7*]. We report here a new group of transformations of simple ketones using Rh^{III}-porphyrin complex with a noncoordinating counteranion. Efficient catalysis in the enolization of ketone under neutral and mild conditions was shown by this Rh^{III} complex.

Ionic organic reactions are classified into two categories; acid-base (electrophilic-nucleophilic) and oxidation-reduction (redox). Metalloporphyrins have been repeatedly shown to catalyze redox reactions chemically [8], electrochemically [9], and photochemically [10]. Here we clearly show that metalloporphyrins, together with appropriate choice of metal and counteranion, catalyze typical acid-base reactions.

Results

Direct α-metalation of ketone

In the presence of a slightly greater-than-molar amount of dissolved $AgClO_4$, (octaethylporphyrinato)rhodium(III) chloride ((OEP)Rh^{III}-Cl) readily reacts with acetone under mild conditions ($\leq 50\,^{\circ}C$) to give organometallic derivative I in good yield (eq. 1), together with microprecipitates of AgCl [11*]. The product was identified from spectral evidence [12*]. In particular, the ^1H NMR spectrum

$$(OEP)Rh^{III}\text{-}Cl \xrightarrow{AgClO_4} (OEP)Rh^{III}(ClO_4) \xrightarrow{XCH_2\overset{O}{\overset{\|}{C}}CH_2Y} (OEP)Rh^{III}\text{-}\underset{X}{\overset{}{C}}H\overset{O}{\overset{\|}{C}}CH_2Y \qquad (1)$$

I : X = Y = H
II : X = H, Y = CH_3
III : X = $COCH_3$, Y = H
IV : X = $CO_2CH_2CH_3$, Y = H

showed a doublet and a singlet at higher magnetic fields due to the porphyrin ring current effect. These were assigned to the CH_2 and CH_3 protons, respectively, of the coordinated acetone moiety from their geometrical parameters and the isoshielding map of organorhodium porphyrin derivatives [12a]. Coupling ($J = 4$ Hz) of the CH_2 protons with ^{103}Rh nucleus ($I = 1/2$) can be taken as direct evidence for Rh–CH_2 bonding. In the absence of $AgClO_4$ no reaction was detected under otherwise identical conditions. The active species in this reaction was shown to be the perchlorate complex, (OEP)$Rh^{III}(ClO_4)$, generated from the anion exchange of (OEP)Rh^{III}-Cl with $AgClO_4$. It was independently confirmed that (OEP)$Rh^{III}(ClO_4)$ reacts with acetone to give I in the absence of silver salt. The metalation of methyl ethyl ketone took place almost exclusively at the methyl position to give II.

* Reference number with asterisk indicates a note in the list of references.

Table 1

Yields, TLC R_f values, and spectral (^{1}H NMR [a], IR [b], UV-Visible [c], and Mass) and analytical data for (OEP)Rh^{III}-R

	Complex			
	I	II	III	IV
Yield [d] (%)	82	72	88	85
R_f [e]	0.18	0.30	0.24	0.03
δ ppm [f]	−5.40 (d, 2H) [g]	−5.27 (d, 2H) [g]	−4.50 (d, 1H) [g]	−4.50 (d, 1H) [g]
	−2.31 (s, 3H)	−2.54 (q, 2H)	−1.93 (s, 6H)	−1.80 (s, 3H)
		−1.00 (t, 3H)		0.16 (t, 3H)
				0.89 (q, 2H)
ν(C=O) (cm^{-1})	1680	1680	1600	1700, 1670
λ_{max}/nm (log ϵ)	387 (5.29)	386 (5.25)	387 (5.30)	394 (5.20)
	511 (4.23)	511 (4.11)	511 (4.14)	516 (4.14)
	544 (4.70)	543 (4.63)	544 (4.63)	548 (4.55)
m/e	693 (M^+)	707 (M^+)	735 (M^+)	765 (M^+)
	636 (M^+ − R)	636 (M^+ − R)	636 (M^+ − R)	636 (M^+ − R)
Anal. Found C	67.87 (67.62)	68.50 (67.98)	67.44 (67.02)	66.18 (65.96)
(calc) H	7.27 (7.13)	7.55 (7.27)	7.04 (7.00)	6.94 (6.98)
N	7.91 (7.91)	7.59 (7.93)	7.72 (7.62)	7.14 (7.33)

[a] For $CDCl_3$ solutions. [b] For KBr disks. [c] For dichloromethane solutions. [d] For chromatography-purified materials. [e] On silica gel 60 F_{254} (Merck) with dichloromethane as eluant. [f] For alkyl ligands. [g] J(Rh–H) = 4 Hz.

β-Dicarbonyl compounds such as acetylacetone and ethyl acetoacetate were metalated similarly to give the corresponding organometallic compounds III and IV, respectively (eq. 1). The ^{1}H NMR spectra indicate that the internal CH_2 group was the site of metalation. The yields, TLC R_f values, spectral (^{1}H NMR, IR, UV-VIS, and mass) and analytical data for the organorhodium complexes are summarized in Table 1.

Kinetic measurements for the formation of I were taken in acetone, (OEP)Rh^{III}(ClO_4) was prepared in situ by a very rapid reaction of (OEP)Rh^{III}-Cl and $AgClO_4$ (1.6–2.6 equiv). The conversion of (OEp)Rh^{III}(ClO_4) into I followed first-order kinetics ($-d[(OEP)Rh^{III}(ClO_4)]/dt = k_{obs}$ [(OEP)Rh^{III}(ClO_4)]) which gave well-resolved spectra. A typical change in the spectrum in the range 500–580 nm is associated with this conversion. A set of isosbestic points indicates that there is no accumulation of intermediates. The time-course of the absorbance change at 544 nm is shown in Fig. 2. The first-order plots derived therefrom give a straight line (Fig. 2, insert) with a slope or pseudo-first-order rate constant (k_{obs}) of 3.4×10^{-3} sec^{-1} at 30.0 °C (half-life of reaction, 204 sec) and 1.9×10^{-2} sec^{-1} at 50.0 °C (half-life of reaction, 34 sec), which are independent of the initial concentrations of the rhodium complex in the range $0.72 \times 10^{-5} - 2.86 \times 10^{-5}$ M. The effect of acetone concentration on rate was investigated by use of *o*-dichlorobenzene as an inert solvent. The results are shown in Fig. 3, where k_{obs} values are linearly correlated with [acetone]; $k_{obs} = k_2$[acetone]. The slope or second-order rate constant (k_2) is 2.6×10^{-4} M^{-1} sec^{-1} at 30 °C and 1.4×10^{-3} M^{-1} sec^{-1} at 50 °C. Silver perchlorate was found to be essential for the present reaction. However, an excess of (OEP)Rh^{III} in the reaction mixture gave no further rate enhancement, and served only to inhibit the reaction; k_{obs} values of 3.4, 3.4, 2.7, 1.5, and 1.1×10^{-3}

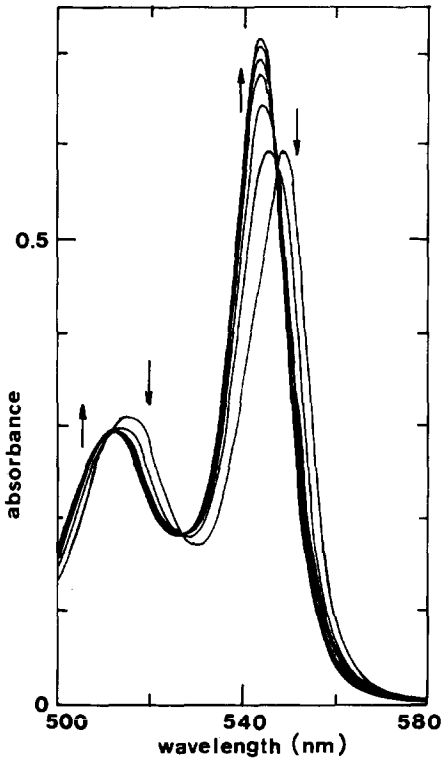


Fig. 1. Spectral change associated with the conversion of $(OEP)Rh^{III}(ClO_4)$ (1.43×10^{-5} *M*) into I in acetone at 30.0 °C; $(OEP)Rh^{III}(ClO_4)$ was prepared in situ from $(OEP)Rh^{III}$-Cl and $AgClO_4$ (3.74×10^{-5} *M*). Time interval for spectral scan was 3 min.

sec^{-1} were obtained for runs with 2.31, 3.75, 6.88, 11.37, and 22.30×10^{-5} of $AgClO_4$, respectively, and $[(OEP)Rh^{III}]$ fixed at 1.43×10^{-5} *M* in neat acetone at 30 °C.

The 2-oxopropyl-rhodium complex I was susceptible to attack by electrophiles such as H^+ and Br_2. Addition of a large excess of aqueous $HClO_4$ or HCl to an acetone solution of I resulted in rapid generation of $(OEP)Rh^{III}$ (ClO_4) or $(OEP)Rh^{III}$-Cl, suggesting that the present metalation reaction is reversible (eq. 1). The reaction of I and Br_2 also took place readily to give bromoacetone [13 *]. An important observation, on the other hand, was the lack of any carbanionic reactivity of I toward carbonyl substrate. Complex I was stable in acetone or methyl ethyl ketone and no evidence was obtained for the aldol-type reaction of I with the solvent. Furthermore, there was no exchange of the coordinated acetone in I with solvent acetone-d_6, shown by ^1H NMR spectroscopy.

Catalytic aldol condensation reaction of ketone

The reaction of $(OEP)Rh^{III}(ClO_4)$ with cyclohexanone, a representative cyclic ketone, took place differently. Instead of being converted to the corresponding organometallic derivative V, this ketone underwent efficient aldol condensation to

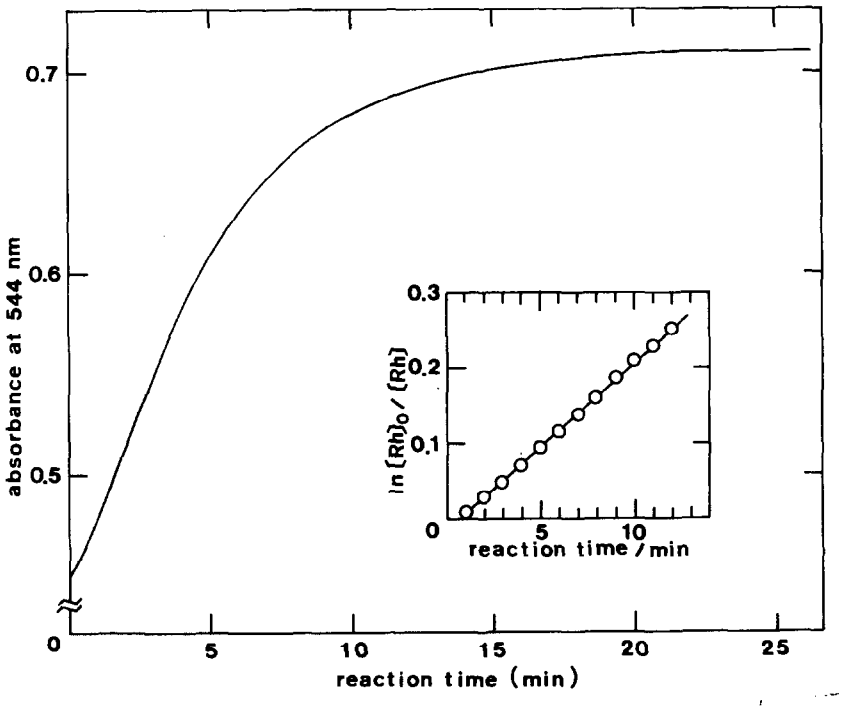


Fig. 2. Change of absorbance at 544 nm associated with the conversion of (OEP)$Rh^{III}(ClO_4)$ (1.43×10^{-5} *M*) into I in acetone at 30.0 °C with time; (OEP)$Rh^{III}(ClO_4)$ was prepared in situ from (OEP)Rh^{III}-Cl and $AgClO_4$ (3.74×10^{-5} *M*). Insert: analysis of the data according to the first-order kinetics for disappearance of (OEP)$Rh^{III}(ClO_4)$ simplified as Rh.

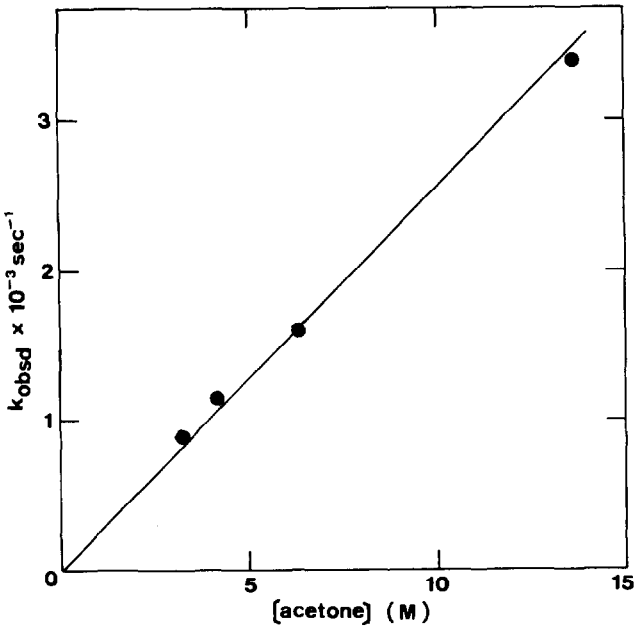


Fig. 3. Effect of acetone concentration on pseudo-first-order rate constant for the conversion of (OEP)$Rh^{III}(ClO_4)$ (3.62×10^{-5} *M*) into I in the presence of varying amounts of *o*-dichlorobenzene at 30.0 °C; (OEP)$Rh^{III}(ClO_4)$ being prepared in situ from (OEP)Rh^{III}-Cl and $AgClO_4$ (5.90×10^{-5} *M*).

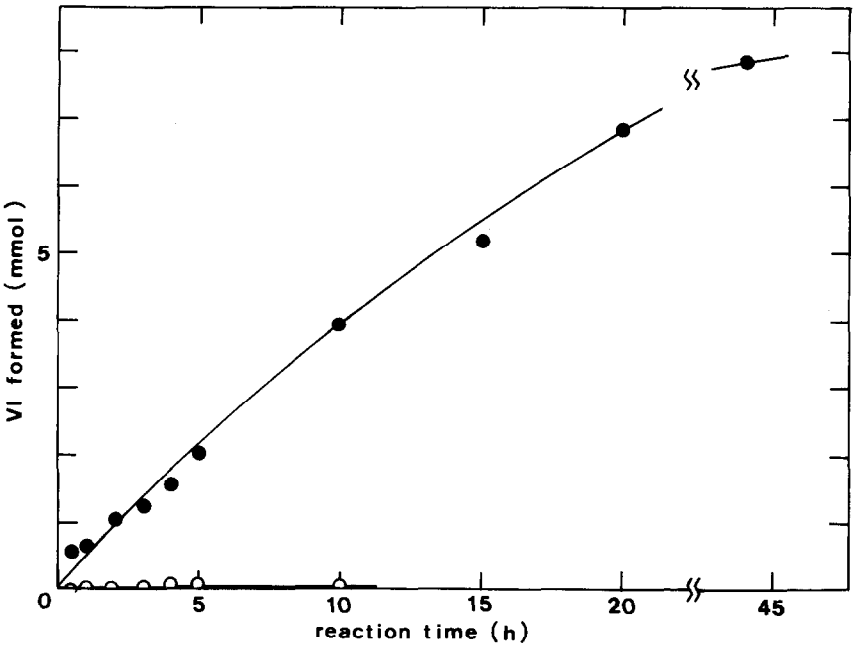
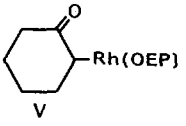
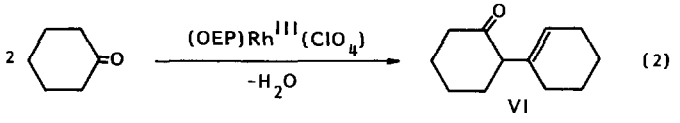


Fig. 4. Aldol condensation of cyclohexanone (3.0 g, 31 mmol) containing $AgClO_4$ (10 mg, 48 μmol) in the presence (●) and absence (○) of (OEP)Rh^{III}-Cl (4 mg 6 μmol) at 50 °C under nitrogen with time.

give VI (eq. 2), where (OEP)$Rh^{III}(ClO_4)$ was the catalyst. Under typical conditions,



V



VI (2)

1.4 g (7.9 mmol) of VI was obtained by stirring a cyclohexanone solution (3.0 g) of (OEP)$Rh^{III}(ClO_4)$ which was prepared in situ from (OEP)Rh^{III}-Cl (4 mg, 6 μmol) and $AgClO_4$ (10 mg, 48 μmol) at 50 °C under nitrogen for 40 h. The yield of VI was 1.3×10^5% based on the rhodium porphyrin catalyst, which gives a catalytic turnover number of 1.3×10^3. In marked contrast, acetone afforded only a trace amount of its aldol condensation product (mesityl oxide) under similar conditions. The rate of formation of VI, together with that for the run without rhodium complex is shown in Fig. 4. Spectroscopic and TLC monitoring of the reaction showed that the rhodium porphyrin catalyst was present as (OEP)$Rh^{III}(ClO_4)$ during the reaction.

The initial rates ($r = d[VI]/dt$) of catalyzed reactions and control runs in neat cyclohexanone or dichlorobenzene solution at 50 °C, together with the apparent catalytic rate constants (k_c, $r = k_c$[catalyst]) [14], are shown in Table 2. The

Table 2

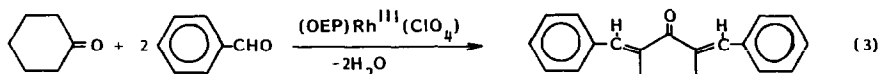
Initial rates (r) of aldol condensation of cyclohexanone at 50 °C and catalytic rate constants (k_c)

(OEP)Rh^{III}-Cl used (μmol)	$AgClO_4$ used (μmol)	Medium [a]	[cyclohexanone] (M)	r (mM/s)	k_c [b] (s^{-1})
6	48	CH	9.69	0.040	0.021
6	48	CH/DCB	4.67	0.020	0.011
6	48	CH/DCB	2.35	0.011	0.0061
6	96	CH	9.69	0.045	0.024
6	0	CH	9.69	0	0
0	48	CH	9.69	$\sim 5\times10^{-4}$	3×10^{-5}
0	$LiClO_4$ 156	CH	9.69	0	0

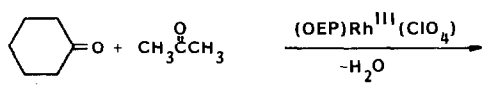
[a] CH, cyclohexanone (3.16 ml). CH-DCB, cyclohexanone/o-dichlorobenzene (3.3 ml). [b] $k_c = r/$[catalyst], where catalyst is the rhodium complex when present, and $XClO_4$ (X = Ag or Li) when rhodium complex is absent.

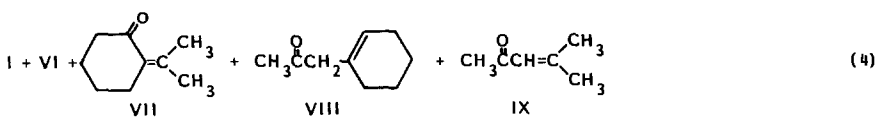
reaction catalyzed by (OEP)Rh^{III}-Cl requires $AgClO_4$ as an essential component, although simple ClO_4^- salts ($AgClO_4$ and $LiClO_4$) alone are at best only very slightly active (see Table 2). As in the metalation of acetone, an excess amount of ClO_4^- relative to [Rh^{III}] has no acceleratory effect. Furthermore, dilution of the substrate ketone with dichlorobenzene results in the corresponding decrease in the rate. These results suggest similarity of the rate-determining processes of cyclohexanone condensation and acetone metalation.

The organometallic compound V was prepared by the standard procedure [12*a] utilizing nucleophilic reaction of [(OEP)Rh^{I}]$^-$ with 2-bromocyclohexanone. Like the corresponding acetone derivative I, the authentic sample of V thus obtained showed little or no aldol reactivity, if any, toward cyclohexanone in the absence or presence of $AgClO_4$, although in its presence V as well as I underwent slow reversion to (OEP)$Rh^{III}(ClO_4)$. These facts indicate that the enolate complex and not V undergoes aldol condensation. The enolate intermediate could also be captured by other carbonyl compounds such as benzaldehyde present in the reaction mixture, leading to a cross-condensation (eq. 3). Similarly, when the reaction was carried out in a 9 : 1 mixture of acetone and cyclohexanone with (OEP)Rh^{III}-Cl (10 mg, 15 μmol) and $AgClO_4$ (13 mg, 63 μmol), I and all four condensation products were obtained; VI and VII (derived from cyclohexanone enolate), VIII and IX (from acetone enolate) in a ratio of 1 : 0.93 : 1.8 : 2.2 (eq. 4).



(3)





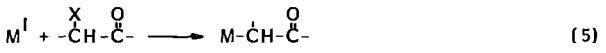
(4)

Finally, a reaction was carried out to shed light on the steric effects pertaining to I and V. The competitive alkylation of [(OEP)Rh^{I}]$^-$ with a mixture of 1-bromopro-

pane and bromocyclohexane (1 : 42) in methanol afforded n-propyl-rhodium complex almost exclusively. This result, in view of the accuracy of ^{1}H NMR spectroscopy, indicates that the open-chain bromide is at least 10^3-times more reactive than the cyclic bromide.

Discussion

The organo-transition-metal species having α-metallocarbonyl moiety or tautomeric oxo-π-allylmetal complexes are potential intermediates in synthetic reactions [15,16] and are important in the biological dehydration or 1,2-diols catalyzed by vitamin B_{12}-dependent dehydrases [17]. The synthetic procedures for these compounds require pre-activation of carbonyl substrates, usually by nucleophilic reaction of low-valent metal centers with α-haloketones (eq. 5) [15]. An alternative general method involves the electrophilic interaction of M^{III} complexes (M = Co and Rh) with alkyl [18,19] or silyl enol ethers [16] as activated ketone derivatives (eq. 6). The direct metalation of ketone, on the other hand, is rather rare



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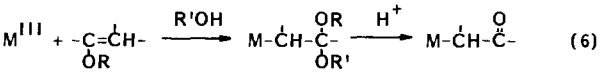
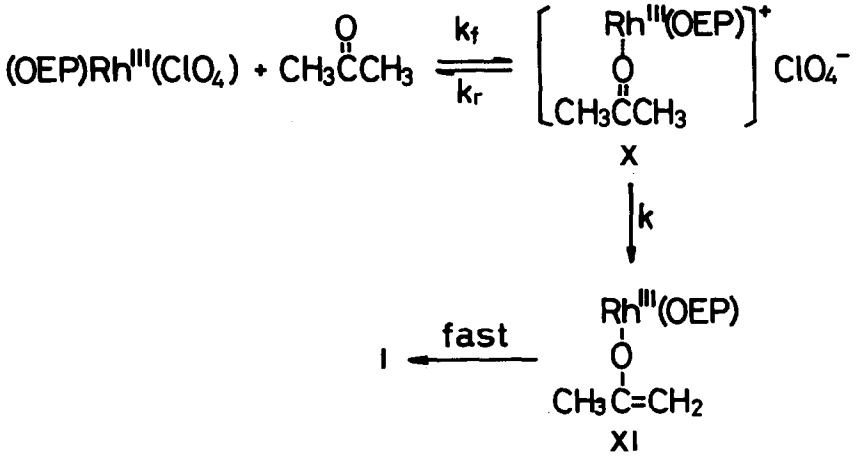


(6)

[20*]; one example is the slow metalation of ketone with cobalt(III) complexes with at least one strongly basic axial ligand or under basic conditions [21], i.e., under conditions that allow base-promoted enolization of ketone. The metalation reaction shown in eq. 1 seems to be the first example of direct, electrophilic α-metalation of ketone under neutral and mild conditions [20*]. The general mechanism of α-substitution reactions of ketone including aldol condensation, involves acid- or base-catalyzed enolization of ketone followed by capture of the thus-formed enol (enolate) by electrophiles. Contrary to the case of β-dicarbonyl compounds [22*], monoketones have a very low enol content and show very small rates for spontaneous enolization. Acetone has an enol content of 1.5×10^{-4}% [23] and the rate of enolization (in water at 25°C) of 2.8×10^{-8} min^{-1} (compared with the corresponding values of 1.0 and 0.072 min^{-1} for acetylacetone and ethyl acetoacetate, respectively) [24]. Thus, an essential point of the present reaction is the remarkable ability of $(OEP)Rh^{III}(ClO_4)$ to promote enolization of simple ketones as shown in Scheme 1, where the formation of acetone enolate (XI) is rate-determining since no accumulation of intermediate is observed. This enolization seems to follow the general mechanism of "acid"-catalyzed enolization of carbonyl compounds: coordination of Rh^{III} center to the carbonyl group to form the adduct (X), followed by removal of a proton from X by some basic species (Scheme 1). The role of the non-coordinating ClO_4^- counteranion is to generate charge-separated $[(OEP)Rh^{III}]^+$ complex with the highly electrophilic Rh^{III} center with vacant coordination sites [12*e,f]. On the other hand, the identity of actual base is not so clear, a possible candidate is ClO_4^- anion, which however, is a very weak base; the substrate ketone is probably more basic. The metalation of acetone is first-order with respect to both $(OEP)Rh^{III}(ClO_4)$ and acetone. A mechanism consistent with this involves rapid (but less-favored) (K[acetone] $\ll 1$, $K = k_f/k_r$) pre-equilibrium formation of X



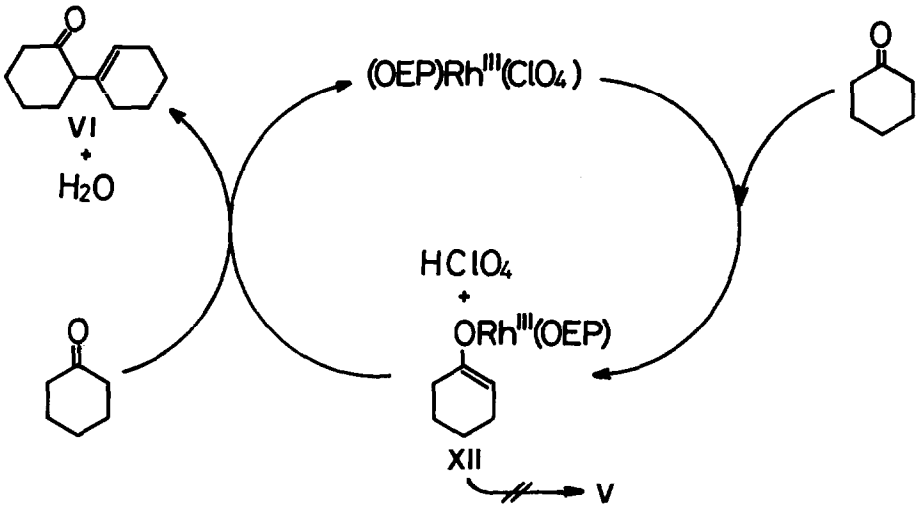
Scheme 1

followed by rate-determining removal of a proton from X by its ClO_4^- counteranion; rate = $k[X] = k_2[(OEP)Rh^{III}(ClO_4)]_t[acetone]$ ($k_2 = kK$ and t total concentration), from general expression for [X] (eq. 7) and K [acetone] $\ll 1$. This mechanism

$$[X] = \frac{K[\text{acetone}]}{K[\text{acetone}] + 1}[(OEP)Rh^{III}(ClO_4)]_t \qquad (7)$$

may account for the fact that excess ClO_4^- in bulk solution shows no rate enhancement (by not affecting the concentration of active ClO_4^- counteranion). On the other hand, ClO_4^- could also be an inert counteranion, in this case rapid and favored (K[acetone] $\gg 1$) pre-equilibrium formation of X is followed by rate-determining enolization with a second molecule of ketone as base; rate = $k[X][acetone] = k[(OEP)Rh^{III}(ClO_4)]_t[acetone]$, from eq. 7 and K[acetone] $\gg 1$. Still another mechanistic possibility is that the reaction of $(OEP)Rh^{III}(ClO_4)$ with acetone is rate-determining; rate = $k_f[(OEP)Rh^{III}(ClO_4)][acetone]$. However, this is less likely since adduct formation is usually rapid. Unfortunately these mechanisms cannot be distinguished by kinetic methods alone, resulting in ambiguity as to the proton abstraction process. Whatever the mechanistic details may be it is noteworthy that in adduct X the substrate ketone is activated with $[(OEP)Rh^{III}]^+$ to such an extent that it undergoes facile deprotonation even by a very weak base such as ClO_4^- or ketone.

The aldol condensation of cyclohexanone has a number of kinetic aspects in common with the metalation of acetone; existence of only one long-lived rhodium-porphyrin intermediate $(OEP)Rh^{III}(ClO_4)$, no further rate enhancement with an excess of ClO_4^-, and linear dependence of rate on ketone concentration (Table 2). This similarity suggests that the enolization of cyclohexanone has a rate-determining profile similar to that of acetone in its metalation reaction. On the other hand, there is strong evidence against the intermediacy of the C-bound organometallic compound V in the catalytic reaction [25 *]. On these grounds a catalytic mechanism (Scheme 2) can be proposed, which involves: (i) enolization of ketone [$(OEP)Rh^{III}(ClO_4)$ + O=C–CH– → (OEP)Rh–O–C=C– + $HClO_4$] and (ii) aldol re-



Scheme 2

action of the resulting enolate complex (XII) with free ketone to give the condensation product VI (after dehydration) and the rhodium porphyrin catalyst was once more regenerated:

$$(OEP)Rh{-}O{-}C{=}C{-} + O{=}C{-}CH{-} + HClO_4 \rightarrow$$

$$(OEP)Rh^{III}(ClO_4) + O{=}C{-}C{-}C{=}C{-} + H_2O$$

The rate of reaction ($d[VI]/dt = k_c[(OEP)Rh^{III}(ClO_4)]$ is equal to that of the formation of XII ($d[XII]/dt = k_2[(OEP)Rh^{III}(ClO_4)][\text{cyclohexanone}]$, where $[(OEP)Rh^{III}(ClO_4)]$ is kept constant during the catalytic reaction. The second-order rate constant (k_2) of enolization is obtained from the relationship $k_c = k_2[\text{cyclohexanone}]$; $k_2 = 2.3 \times 10^{-3}\ M^{-1}\ \text{sec}^{-1}$ at 50 °C (see Table 2), which is reasonably consistent with that of the enolization of acetone in its metalation reaction ($k = 1.4 \times 10^{-3}\ M^{-1}\ \text{sec}^{-1}$ at 50 °C). The versatility of aldol-type processes, makes enolates one of the most important intermediates for C–C bond formation [3–5 *]. Strong bases such as alkoxides, alkyllithiums, and lithium amides are the usual enolization reagents. The generation of enolates and associated C–C bond formation are separate stoichiometric reactions. In marked contrast, $(OEP)Rh^{III}(ClO_4)$ is a catalyst for the enolization of ketone, allowing catalytic aldol condensation under neutral and mild conditions, with a rate of turnover of $k_c \cong 0.02\ \text{sec}^{-1}$ (Table 2) or 1.2 cycles per min for a run in neat ketone.

Both the α-metalation and aldol condensation of ketone involve key enolate intermediates. The striking difference in the fates of acetone enolate (XI, Scheme 1) and cyclohexanone enolate (XII, Scheme 2) needs clarification. The predominant metalation of XI is not surprising, since $(OEP)Rh^{III}(ClO_4)$ is such a powerful electrophile, and is thus capable of the direct metalation of simple arenes [12*e,f]. The aldol process of XI leading to the formation of VIII and IX may be negligible in a single turnover run, but becomes more important when reaction time is prolonged and an excess of $AgClO_4$ (eq. 4) is used; under these conditions major product I reverts to $(OEP)Rh^{III}(ClO_4)$ and hence reversibly regenerates XI. On the

other hand, selective aldol reaction of XII can be explained thus: (1) the metalation of XII to give V would be less favorable than that of XI owing to steric repulsion between the porphyrin plane and the cyclohexane ring in V. In a model alkylation reaction of $[(OEP)Rh^{I}]^{-}$ with bromocyclohexane and 1-bromopropane the reactivity difference is more than 10^3-times, although its applicability on a quantitative level to the present electrophilic reaction may be questionable. (2) Cyclohexanone is approximately one order of magnitude more reactive than acetone toward both cyclohexanone and acetone enolates, judging from the product ratios VI/VII and VIII/IX (eq. 4) after statistical correction by a factor of 9 for different concentrations of the two ketones used. Combination of these steric and electronic effects of cyclohexanone may be responsible for its selective aldol condensation.

The present study emphasizes the importance of charge separation of metal-ligand bond by using a non-coordinating counteranion to generate a highly efficient system for the enolization of simple ketones in neutral organic solutions under mild conditions. The second-order rate constant for the $(OEP)Rh^{III}(ClO_4)$-promoted enolization of acetone at 30 °C (2.6×10^{-4} M^{-1} sec^{-1}) may be compared with the apparent second-order rate constant of enolization of acetone in water at 25 °C (0.8×10^{-11} M^{-1} sec^{-1}) [26], where water serves as both acid and base. Metal-complex catalysis such as that observed here is without precedent for simple ketones, although there are some examples of metal-ion catalysis in Brönsted-base-promoted enolization in water of chelating ketones such as acetylphosphonates [27], 2-acetylpyridine [28], ethyl acetoacetate [29], and 2-oxocyclopentanecarboxylate [30]. In view of the many examples of metalloporphyrin catalysis in redox reactions [8–10] it is noteworthy that metalloporphyrin can also catalyze non-redox reactions [31*]. The efficient catalysis of C–C bond formation in the aldol reaction will enlarge the scope and versatility of metalloporphyrins as catalysts. Further functional modifications of metalloporphyrins should provide more selective catalysts. We are now trying to introduce chiral reaction field [32*,33*] or binding site for enolate acceptor.

Conclusion

Ketones undergo remarkably efficient enolization by a cationic rhodium(III)-porphyrin complex with a non-coordinating ClO_4^- counteranion. The observed activity is primarily due to the highly electrophilic nature of the central rhodium ion. The enolate complex thus formed undergoes either metalation to give organometallic derivative or aldol reaction with free ketone catalytically, depending on the steric and electronic properties of the ketones. The present study opens a way to the catalytic modification of the reactions of enolates under neutral conditions.

Experimental

General

IR spectra were recorded on a JASCO IR-810 spectrophotometer. ^1H NMR spectra were recorded in $CDCl_3$ solutions on a JEOL JNM-PMX 60 or JNM-GX 270 spectrometer using tetramethylsilane as internal reference. Electronic spectra were recorded on a Hitachi 200-10 or 320 spectrophotometer. Mass spectra were recorded with a Hitachi M-60 spectrometer. Gas-chromatographic analyses were

carried out with a Shimadzu GC-4C gas chromatograph using columns of poly(ethylene glycol) 6000 and silicone SE 30 unless otherwise indicated. Chromatographic separations were carried out in columns on silica gel (Wakogel C-200). Silica gel 60 F_{254} (Merck) was used for thin layer chromatography (TLC). Elemental analyses were performed at the Microanalysis Center of Kyoto University. (Octaethylporphyrinato)rhodium(III) chloride [(OEP)Rh^{III}-Cl] and perchlorate [(OEP)Rh^{III}-(ClO_4)] were prepared as described [12*f]. Ketones (acetone, methyl ethyl ketone, acetylacetone, ethyl acetoacetate, and cyclohexanone) were dried over $CaSO_4$ and fractionally distilled (boiling range, ± 0.2 °C). Silver perchlorate was dried at 120 °C in vacuo for 2 h just before use.

Metalation of ketone

A solution of $AgClO_4$ (40 mg) and (OEP)Rh^{III}-Cl (50 mg) in acetone (10 ml) was stirred at 50 °C under nitrogen for 10–15 min, poured into water, and extracted with dichloromethane. The extract was quickly washed with water, dried over Na_2SO_4, and evaporated to dryness. The residue was chromatographed with dichloromethane as eluant to afford the 2-oxopropylrhodium derivative (I) (40 mg, 82%), which was recrystallized from benzene/petroleum ether. The metalation of methyl ethyl ketone, acetylacetone, and ethyl acetoacetate was carried out similarly. The products (2-oxobutyl- (II), 2,4-dioxo-3-pentyl- (III), and 1-ethoxycarbonyl-2-oxopropyl-(IV) rhodium compounds) were isolated in essentially the same way as for I. The yields of organorhodium complexes listed in Table 1 are for the chromatography-purified materials. The metalation of acetone under air indicated that dioxygen had practically no inhibitory effects on the formation of I. Acetone was also shown to undergo facile metalation with (OEP)Rh^{III}(ClO_4), but no reaction was detected between acetone and (OEP)Rh^{III}-Cl without $AgClO_4$ under otherwise identical conditions.

Kinetic measurements of the metalation of acetone were carried out as follows: an argon-purged acetone solution (5.0 ml) of (OEP)Rh^{III}-Cl (1.44×10^{-5} M) was prepared in a sealed, 1-cm quartz cell thermostatted at 30.0 °C or 50.0 °C in the spectrophotometer. To initiate the reaction, 20 μl of a degassed solution of $AgClO_4$ in acetone (5.79 mM) was added with a microsyringe through the rubber septum. The final concentrations of rhodium complex and perchlorate ion were 1.43×10^{-5} M and 2.31×10^{-5} M (1.6 equiv), respectively. The progress of the reaction was monitored spectrophotometrically. The pseudo-first-order rate constants (k_{obs}) were obtained as slopes of the plots of $\ln[Rh]_0/[Rh]$, i.e., $\ln(A_\infty - A_0)/(A_\infty - A)$, vs. t, where Rh = (OEP)Rh^{III}(ClO_4) and A is absorbance at 544 nm. The kinetic measurements were carried out similarly on solutions of varying concentrations of rhodium complex in the range $0.72–2.86 \times 10^{-5}$ M while keeping the [$AgClO_4$]/[(OEP)Rh^{III}-Cl] ratio constant at 1.6; and also for solutions of varying concentrations of $AgClO_4$ in the range $2.31–22.3 \times 10^{-5}$ M while keeping [(OEP)Rh^{III}-Cl] constant at 1.43×10^{-5} M. The effect of acetone concentration on the reaction rate was investigated at 30.0 °C by using *o*-dichlorobenzene as diluent while keeping [(OEP)Rh^{III}-Cl] and [$AgClO_4$] constant at 3.62×10^{-5} and 5.90×10^{-5} M, respectively ([Rh]/[ClO_4^-] = 1.6), [acetone] was 13.6 (with no dichlorobenzene added), 6.35, 4.19, and 3.29 M.

Reactivity of I

A solution of I (20 mg) and bromine (freshly distilled, 50 μl) in dichloromethane (10 ml) was stirred under nitrogen at room temperature for 30 min. The mixture was

washed with aqueous $Na_2S_2O_4$ and then with water, dried over Na_2SO_4, and concentrated to a volume of 2 ml. Gas chromatographic analysis indicated the formation of monobromoacetone (yield, ca. 20%) which was identified on the basis of coinjection with the authentic sample on columns of silicone DC QF-1 and poly(ethylene glycol) 6000. To a solution of I (9.74×10^{-6} *M*) in acetone (5 ml) was added 5 μl of aqueous $HClO_4$ (60%) to give a final [$HClO_4$] of 9.98×10^{-3} *M* and [H_2O] of 37×10^{-3} *M*, respectively. The electronic spectrum indicated rapid conversion of I into (OEP)$Rh^{III}(ClO_4)$. A similar experiment with 5 μl of aqueous HCl (35%) also gave (OEP)Rh^{III}-Cl. However, no transformation of I was detected when 5 μl of water (under otherwise identical conditions) was added, indicating that I is stable to H_2O.

A solution of I (4 mg) in acetone or methyl ethyl ketone (5 ml) was stirred at 50 °C under nitrogen for 6 h. The UV spectroscopy and TLC of the reaction mixture clearly showed that no chemical transformation of I had taken place. Gas chromatography also showed that *I* had not undergone aldol reaction with the solvent ketone. A degassed solution of I in acetone-d_6 in a sealed NMR tube was heated at 50 °C for 30 min, and the ^1H NMR spectrum taken. An integrated ratio of 2 : 4 of the signal of methylene protons (bound to rhodium) to that of *meso* protons (of the porphyrin skeleton) indicated that there had been no exchange of the rhodium-bound CH_2COCH_3 moiety in I for solvent acetone-d_6.

Aldol condensation

A solution of (OEP)Rh^{III}-Cl (4 mg, 6 μmol), $AgClO_4$ (10 mg, 48 μmol), and n-heptadecane as an internal standard (appropriate amount) in cyclohexanone (3.0 g) was stirred at 50 °C under nitrogen. Gas chromatographic analysis of aliquots taken at various intervals indicated a smooth increase in the amount of 2-(1-cyclohexenyl)cyclohexanone (VI) as the sole volatile product (Fig. 4). After 40 h, ca. 1.4 g (7.9 mmol) of VI was formed. The yield of VI was 51% based on the ketone used and 1.3×10^5% based on the rhodium catalyst. On the other hand, spectroscopic and TLC analyses of the aliquots showed that (OEP)$Rh^{III}(ClO_4)$ was the sole major rhodium-porphyrin species during the reaction. The reaction mixture was poured into water and extracted with dichloromethane. After washing with water and drying over Na_2SO_4, the solvent was removed in vacuo and the residue was chromatographed. Elution with benzene afforded a mixture of cyclohexanone and VI, from which VI was isolated by distillation: b.p. 105 °C/1 Torr; ^1H NMR δ 5.37 (s, 1H, CH=C), 2.80 (t, 1H, COCHC=C), 2.27 (m, 2H, CH_2CO), 1.93 (m, 4H, CH_2=C), 1.67 (m, 4H, CH_2); IR (neat) 1715 cm^{-1} [ν(CO)]; mass spectrum *m/e* 178 (M^+). The following control runs were carried out similarly: (1) without $AgClO_4$, (2) without rhodium complex, (3) without rhodium complex but with $LiClO_4$ instead of $AgClO_4$, and (4) with rhodium complex and 20 mg of $AgClO_4$. The effect of cyclohexanone concentration was investigated by using cyclohexanone concentrations of 9.69 (no dichlorobenzene added), 4.67, and 2.35 *M* with *o*-dichlorobenzene as diluent. Each run was monitored by gas chromatography.

An aldol condensation of acetone was attempted under otherwise identical conditions (for cyclohexanone). Mesityl oxide, in addition to I, was indeed formed in this reaction, but its yield was negligible compared with that of VI.

A solution of (OEP)Rh^{III}-Cl (10 mg) and $AgClO_4$ (13 mg) in 2.14 g of a mixed solvent of acetone and cyclohexanone (molar ratio, 9 : 1) was stirred at 50 °C for 15

h under nitrogen. Formation of I was confirmed by TLC analysis. Gas chromatography indicated the formation of four condensation products: VI [34 mg (0.19 mmol), 1300% based on (OEP)$Rh^{III}(ClO_4)$], 2-(2-propylidene)cyclohexanone (VII) [25 mg (0.18 mmol), 1200%], (1-cyclohexenyl)acetone (VIII) [48 mg (0.35 mmol), 2300%], and mesityl oxide (IX) [41 mg (0.42 mmol), 2800%] in a ratio of 1 : 0.93 : 1.8 : 2.2. The samples of VII and VIII were obtained pure by preparative gas chromatography. ^{1}H NMR of VII: δ 2.43 (2H, m, CH_2CO), 2.36 (2H, m, $CH_2C{=}C$), 1.96 (3H, s, CH_3), ca. 1.75 (4H, m, CH_2), 1.76 (3H, s, CH_3). ^{1}H NMR of VIII: δ 5.55 (1H, s, CH=C), 2.97 (2H, s, $C{=}CCH_2CO$), 2.10 (3H, s, CH_3), 2.02 and 1.88 (each 2H, distorted s, $CH_2C{=}C$), 1.58 (4H, m, CH_2).

A solution of (OEP)Rh^{III}-Cl (8 mg) and $AgClO_4$ (20 mg) in a mixture (3.55 g) of cyclohexanone and benzaldehyde (1 : 5) was stirred at 50 °C for 8 h under nitrogen. Pale yellow prisms of 2,6-bis(benzylidene)cyclohexanone (0.46 g, 30% based on limiting substrate, cyclohexanone) which separated when the mixture was cooled to room temperature, were recovered by filtration: m.p. 115–116 °C (from methanol); ^{1}H NMR δ 7.80 (s, 2H, CH=C), 7.43 (s, 10H, aromatic), 2.95 (m, 4H, $CH_2C{=}C$), 1.78 (m, 2H, CH_2); IR (KBr disk) 1665 [ν(CO)] and 1610 cm^{-1} [ν(C=C)]; mass spectrum *m/e* 274 (M^+).

2-Oxocyclohexyl-rhodium derivative of OEP (V)

This compound was prepared by the general procedure utilizing nucleophilic reaction of $[(OEP)Rh^I]^-$ with alkyl halide [12a]. A solution of $NaBH_4$ (17 mg) in 0.5 *N* aqueous NaOH (1 ml) was added to a solution of (OEP)Rh^{III}-Cl (50 mg) in ethanol (15 ml). The mixture was stirred under nitrogen at room temperature for 3 h to generate $[(OEP)Rh^I]^-$. α-Bromocyclohexanone (17 μl) was added and stirring was continued for 10 min. After most of the ethanol had been removed, the mixture was poured into water, and extracted with benzene. The extract was quickly washed with water, dried over Na_2SO_4, and stripped of solvent. The residue was chromatographed with benzene as eluant. The first porphyrin fraction afforded V (10 mg, 19%): ^{1}H NMR δ 10.03 (s, 4H, *meso*-H), 4.03 (8H, a pair of q, CH_2), 1.90 (24H, t, CH_3), and a set of highly shielded, well-resolved cyclohexanone ring protons at −0.88 (1H, m), −1.21 (1H, m), −1.48 (1H, m), −1.80 (1H, m), −3.75 (1H, m), −4.30 (1H, m, CH-Rh (J(H–Rh) = 4 Hz)), −4.77 (1H, m), −5.61 (1H, m); IR (KBr disk) 1720 cm^{-1} [ν(CO)]; mass spectrum *m/e* 636 ($M^+ - C_{10}H_9O$); λ_{max} (log ϵ) 386 (5.03), 510 (4.41), 542 nm (4.46). Non-alkylated porphyrin (ca. 40 mg) was recovered by further elution with benzene. A control experiment indicated no aldol reactivity of V toward cyclohexanone at 50 °C. In the presence of $AgClO_4$ (13 mg) in cyclohexanone (5 ml) of 50 °C, V (4 mg) was converted to (OEP)$Rh^{III}(ClO_4)$ which then catalyzed the aldol condensation of the ketone. However, conversion of V to the perchlorate complex was a slow process taking many hours, and the production of VI was negligible at least in the first hour of reaction.

Competitive alkylation of $[(OEP)Rh^I]^-$

A solution of $[(OEP)Rh^I]^-$ in a mixed solvent of ethanol (15 ml) and water (1 ml) was prepared as above by the reduction of (OEP)Rh^{III}-Cl (50 mg) with $NaBH_4$. To this was added ca. 3 g of a 42 : 1 mixture of bromocyclo-hexane and 1-bromopropane. The resulting solution was stirred for 1 h at room temperature. The solvent and excess alklyl bromides were removed in vacuo and the residue extracted with benzene. The extract was washed with water and then with brine, dried over

Na_2SO_4, and stripped of solvent. The ^1H NMR spectrum of the crude organorhodium complex thus obtained showed three signals at higher field δ −2.04, −4.97, and −5.51 in an integration ratio of 3 : 2 : 2. These were readily assigned to the γ- (to rhodium), α-, and β-protons, respectively, of n-propylrhodium complex by comparison with the ^1H NMR spectrum of an authentic sample [12a]. The accuracy of the NMR analysis clearly indicated that the amount of cyclohexylrhodium complex was less than 1/20 of that of n-propyl complex. 1-Bromopropane was thus more reactive than bromocyclohexane by a factor of at least $42 \times 20 \cong 10^3$.

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References

1 Y. Aoyama, T. Fujisawa, T. Watanabe, H. Toi and H. Ogoshi, J. Am. Chem. Soc., 108 (1986) 943. Preliminary accounts of a part of the present work: Y. Aoyama, T. Yoshida and H. Ogoshi, Tetrahedron Lett., 26 (1985) 6107.
2 R.P. Bell, The Proton in Chemistry (2nd ed.), Cornell University Press, Ithaca, New York, 1973.
3 (a) H.O. House, Modern Synthetic Reactions, W.A. Benjamin, Menlo Park, California, 1972; (b) J. d'Angelo, Tetrahedron, 32 (1976) 2979; (c) B.P. Mundy, Concepts of Organic Chemistry, Marcel Dekker, New York, 1979, Chapter 9.
4 (a) I. Kuwajima and E. Nakamura, Acc. Chem. Res., 18 (1985) 181; (b) T. Mukaiyama, K. Banno and K. Narasaka, J. Am. Chem. Soc., 96 (1974) 7503.
5 For enolization reagents working under more neutral conditions, see, (a) T. Mukaiyama and T. Inoue, Chem. Lett., (1976) 559; (b) T. Makaiyama, K. Saigo and O. Takazawa, ibid., (1976) 1033; (c) T. Inoue, T. Uchimaru and T. Mukaiyama, ibid., (1977) 153.
6 (a) A.S. Mildvan, in P.D. Boyer (Ed.), The Enzymes, Vol. 2, Academic Press, New York, 1970, Chapter 9; (b) M.C. Scrutton, in G.L. Eichhorn (Ed.), Inorganic Biochemistry, Vol. 1, Elsevier, Amsterdam, 1973, Chapter 14; (c) R. Kluger, in E.E. van Tamelen (Ed.), Bioorganic Chemistry, Vol. 4, Academic Press, New York, 1978, Chapter 9; (d) E.T. Kaiser and Sugimoto, J. Am. Chem. Soc., 100 (1978) 7750.
7 For the bifunctional catalysis of some primary-tertiary diamines in the α-hydrogen isotope exchange reactions of ketones, see, J. Hine, D.E. Miles and J.P. Zeigler, J. Am. Chem. Soc., 105 (1983) 4374 and references cited therein.
8 For examples, (a) B.S. Tovroy, S.E. Diamond, F. Mares and A. Szalkiewicz, J. Am. Chem. Soc., 103 (1981) 3522; (b) M.W. Nee and T.C. Bruice, ibid., 104 (1982) 6123; (c) D. Dolphin, B.R. James and T. Leung, Inorg. Chim. Acta, 79 (1983) 25; (d) J.T. Groves and T-E. Nemo, J. Am. Chem. Soc., 105 (1983) 5786; (e) Y. Aoyama, T. Watanabe, H. Onda and H. Ogoshi, Tetrahedron Lett., 24 (1983) 1183; (f) P.S. Traylor, D. Dolphin and T.G. Traylor, J. Chem. Soc., Chem. Commun., (1984) 279; (g) I. Tabushi and K. Morimitsu, J. Am. Chem. Soc., 106 (1984) 6871; (h) J.P. Collman, J.I. Brauman, B. Meunier, T. Hayashi, T. Kodadek and S.A. Raybuck, ibid., 107 (1985) 2000; (i) J.T. Groves and R. Quinn, ibid., 107 (1985) 5790.
9 For examples, (a) J.P. Collman, P. Denisevich, Y. Konai, M. Marrocco, C. Koval and F.C. Anson, J. Am. Chem. Soc., 102 (1980) 6027; (b) C.K. Chang and I. Abdalmuhdi, Angew. Chem. Int. Ed. Engl., 23 (1984) 164.
10 (a) D. Mauzerall, in D. Dolphin (Ed.), The Porphyrins, Vol. V, Academic Press, New York, 1978, Chapter 2; (b) Y. Harel and J. Manassen, J. Am. Chem. Soc., 99 (1977) 5817; (c) Y. Murakami, Y. Aoyama and K. Tokunaga, J. Chem. Soc., Chem. Commun., (1979) 1018 and references cited therein; (d) Y. Matsuda, S. Sakamoto, H. Koshima and Y. Murakami, J. Am. Chem. Soc., 107 (1985) 6415.
11 No evidence was obtained for the evolution of HCl during the course of the reaction.
12 For organorhodium derivatives of OEP, see, (a) H. Ogoshi, J. Setsune, T. Omura and Z. Yoshida, J. Am. Chem. Soc., 97 (1975) 6461; (b) H. Ogoshi, J. Setsune and Z. Yoshida, J. Chem. Soc., Chem.

Commun., (1975) 572; (c) H. Ogoshi, J. Setsune and Z. Yoshida, J. Am. Chem. Soc., 99 (1977) 3869; (d) J. Setsune, Z. Yoshida and H. Ogoshi, J. Chem. Soc., Perkin Trans 1, (1982) 983; (e) Y. Aoyama, T. Yoshida, K. Sakurai and H. Ogoshi, J. Chem. Soc., Chem. Commun., (1983) 478; (f) idem. Organometallics, 5 (1986) 168; (g) B.B. Wayland and B.A. Woods, J. Chem. Soc., Chem. Commun., (1981) 700; (h) B.B. Wayland, B.A. Woods and V.M. Minda, ibid., (1982) 634; (i) B.B. Wayland, B.A. Woods and R. Pierce, J. Am. Chem. Soc., 104 (1982) 302; (j) B.B. Wayland, A. Duttaahmed and B.A. Woods, J. Chem. Soc., Chem. Commun., (1983) 142.

13 For examples of electrophilic cleavage of C–Rh and C–Co bonds with halogen, see, (a) ref 12f; (b) D. Dodd and M.D. Johnson, J. Chem. Soc., Chem. Commun., (1971) 571; (c) F.R. Jensen, V. Madan and D.H. Buchanan, J. Am. Chem. Soc., 93 (1971) 5283.

14 For the complete system, k_c is the turn-over rate constant of (OEP)$Rh^{III}(ClO_4)$ catalyst.

15 J.J. Doney, R.G. Bergman and C.H. Heathcock, J. Am. Chem. Soc., 107 (1985) 3724 and references cited therein.

16 (a) Y. Ito, T. Hirao and T. Saegusa, J. Org. Chem., 43 (1978) 1011; (b) Y. Ito, H. Aoyama, T. Hirao, A. Mochizuki and T. Saegusa, J. Am. Chem. Soc., 101 (1979) 494; (c) E. Nakamura and I. Kuwajima, Chem. Lett., (1983) 59; (d) idem., Tetrahedron Lett., 24 (1983) 3347.

17 (a) R.H. Abeles, in Bioinorganic Chemistry (Adv. Chem. Ser. No. 100), American Chemical Society, Washington D.C., 1971, Chapter 16; (b) R.B. Silverman and D. Dolphin, J. Am. Chem. Soc., 98 (1976) 4633.

18 (a) R.B. Silverman and D. Dolphin, J. Am. Chem. Soc., 95 (1973) 1686; (b) idem., ibid., 96 (1974) 7094; (c) idem., ibid., 96 (1974) 7096; (d) idem., ibid., 98 (1976) 4624.

19 H. Ogoshi, J. Setsune, Y. Nanbo and Z. Yoshida, J. Organomet. Chem., 159 (1978) 329.

20 The oxidative-addition reaction of bis[dicarbonylrhodium(I)] complex of porphyrin to a ketone C–H bond is known, A.M. Abeysekera, R. Grigg, J. Trocha-Grimshaw and V. Viswanatha, J. Chem. Soc., Perkin Trans. 1, (1977) 1395.

21 (a) K.L. Brown, in D. Dolphin (Ed.), B_{12}, Vol. 1, John Wiley & Sons, New York, 1982, p 280; (b) A. Bigotto, G. Costa, G. Mestroni, G. Pellizer, A. Puxeddu, E. Reisenhofer, L. Stefani and G. Tauzher, Inorg. Chim. Acta Rev., 4 (1970) 41; (c) M.E. Kastner and R. Scheidt, J. Organometal. Chem., 157 (1978) 109; (d) W.P. Schaefer, R. Walzman and B.T. Huie, J. Am. Chem. Soc., 100 (1978) 5063. Also see, (e) N.A. Bailey, B.M. Higson and E.D. McKenzie, Inorg. Nucl. Chem. Lett., 7 (1971) 591; (f) D. Cummins, B.M. Higson and E.D. McKenzie, J. Chem. Soc., Dalton Trans., (1973) 414.

22 Since the enol contents of acetylacetone (80%) and ethyl acetoacetate (13%) are very high [23], their metalation may simply involve the reaction of enol with (OEP)$Rh^{III}(ClO_4)$.

23 A. Gero, J. Org. Chem., 19 (1954) 469.

24 R.G. Pearson and R.L. Dillon, J. Am. Chem. Soc., 75 (1953) 2439.

25 α-Stannyl and α-mercurio ketones have been claimed to undergo aldol reactions with aldehydes, (a) ref 17d; (b) Y. Yamamoto and K. Maruyama, J. Am. Chem. Soc., 104 (1982) 2323. On the other hand, such reactions have not been observed with the corresponding α-transition metal species. Recently, Bergman, et al., have reported the photochemical aldol reactions for the tungsten and molybdenum complexes of this class [15].

26 M.L. Bender and A. Williams, J. Am. Chem. Soc., 88 (1966) 2502.

27 (a) R. Kluger and P. Wasserstein, J. Am. Chem. Soc., 95 (1973) 1071; (b) R. Kluger, J. Org. Chem., 38 (1973) 2721; (c) R. Kluger and A. Wayda, Can. J. Chem. 53 (1975) 2354; (d) R. Kluger, M.K. Wong and K. Dodds, J. Am. Chem. Soc., (1984) 1113.

28 B.G. Cox, J. Am. Chem. Soc., 96 (1974) 6823.

29 K.J. Pedersen, Acta Chem. Scand., 2 (1948) 252.

30 K.L. Pedersen, Acta Chem. Scand., 2 (1948) 385.

31 For examples of metalloporphyrin catalysis in non-redox reactions, see: (a) T. Aida and S. Inoue, J. Am. Chem. Soc., 105 (1983) 1304; (b) S. Asano, T. Aida and S. Inoue, J. Chem. Soc., Chem. Commun., (1985) 1148; (c) T. Aida and S. Inoue, J. Am. Chem. Soc., 107 (1985) 1358.

32 For asymmetric reactions with chiral iron porphyrins, see: (a) J.T. Groves and R.S. Myers, J. Am. Chem. Soc., (1983) 5791; (b) D. Mansuy, P. Battioni, J.-P. Renaud and P. Guerin, J. Chem. Soc., Chem. Commun., (1985) 155.

33 We have recently prepared new chiral porphyrins having asymmetric spacial arrangement of *meso* substituents, H. Ogoshi, K. Saita, K. Sakurai, T. Watanabe, H. Toi, Y. Aoyama and Y. Okamoto, Tetrahedron Lett., 27 (1986) 6365.