Journal of Organometallic Chemistry, 240 (1982) 59–63
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

ASYMMETRIC SYNTHESIS BY CHIRAL RUTHENIUM COMPLEXES

VII *. FURTHER INVESTIGATIONS ON HYDROGEN TRANSFER REACTIONS

MARIO BIANCHI, UGO MATTEOLI, PIERO FREDIANI, GLORIA MENCHI and FRANCO PIACENTI

Istituto di Chimica Organica dell'Università di Firenze, Via Gino Capponi, 9, 50121 Florence (Italy)

(Received June 1st, 1982)

Summary

There is enantioface discrimination in the hydrogen transfer from (−)-2-*exo*,3-*exo*-camphandiol or (−)-1, 2-*O*-isopropyliden-α-D-glucofuranose to acetophenone in the presence of $H_4Ru_4(CO)_8(PBu_3)_4$. This suggests the simultaneous presence of the reagents in the catalytic intermediate.

Introduction

The influence of the structure of the donor on the enantioface discrimination and of the acceptor on the enantiomer discrimination were noticed when studying the asymmetric hydrogen transfer from alcohols to ketones catalyzed by chiral cluster ruthenium complexes. These results led us to suggest that the catalytic species responsible for the stereochemical outcome of these reactions contain both donor and acceptor [1,2].

Similar effects have been noticed in the hydrogen transfer from alcohols to tiglic acid and its esters catalyzed by (−)-DIOP containing ruthenium complexes [3,4,5]. The enantioface discrimination of tiglic acid was found to be 3.9% when 1-phenylethanol is used as the alcohol. The accompanying enantiomer discrimination of the alcohol is 4.5%.

These observations suggest that the asymmetry of the catalytic intermediate does not necessarily arise from the presence of an asymmetric ligand in the catalytic precursor but may be due to its complexation with an asymmetric donor or acceptor. The results of hydrogen transfer experiments from glucides to α,β-unsaturated ketones [6] or tiglic acid [3,7] catalyzed by achiral triphenylphosphino mononuclear

* For part VI see ref. 2.

0022-328X/82/0000-0000/$02.75

TABLE I

HYDROGEN TRANSFER FROM OPTICALLY ACTIVE ALCOHOLS TO PROCHIRAL KETONES IN THE PRESENCE OF $H_4Ru_4(CO)_8(PBu_3)_4$.

Acceptor/donor molar ratio 0.5

Exp.	Donor	Acceptor (RCOR')	Solvent	T (°C)	Reaction time (h)	Conversion (%)	Alcohol formed (RCHOHR')		
							$\alpha^{25}_{D(l=1\,dm)}$	Optical purity (%)	Configuration
1	(−)(*S*)-2-Methylbutan-1-ol	$CH_3COC_6H_5$	–	120	150	6.2	0.000°	0.0	–
2	(−)-2-*exo*,3-*exo*-Camphandiol	$CH_3COC_6H_5$	Diethyl ether	140	72	59.5	+0.183°	0.4	(*S*)
3	(−)-1,2-*O*-Isopropyliden-α-D-glucofuranose	$CH_3COC_6H_5$	Diphenyl ether	120	236	7.0	−0.450°	1.0	(*R*)
4	(−)-Menthol	$C_6H_5COCH_2CH_2CH(CH_3)_2$	–	120	216	27.6	0.000°	0.0	–

complexes $H_2Ru(PPh_3)_4$ or $RuCl_2(PPh_3)_3$ seem to confirm this hypothesis, and the results of recent kinetic investigations on the hydrogen transfer from alcohols to olefins in the presence of $RuCl_2(PPh_3)_3$ are in keeping with it [8]. In order to see if intermediates containing both donor and acceptor also participate in the hydrogen transfer catalyzed by ruthenium cluster complexes we have carried out the reduction of prochiral ketones in the presence of $H_4Ru_4(CO)_8(PBu_3)_4$ using optically active donors.

Results and discussion

The results are shown in Table 1. With the (−)-menthol/1-phenyl-3-methylbutan-1-one system the reaction takes place at 120°C with no enantioface discrimination. With acetophenone the reaction takes place without asymmetric induction when (−)(*S*)-2-methylbutan-1-ol is the hydrogen donor. A low but reproducible enantioface discrimination is noticed when 2-*exo*,3-*exo*-camphandiol (0.4%) or 1,2-*O*-isopropyliden-α-D-glucofuranose (1.0%) are used. These results seem to confirm the hypothesis mentioned above.

It is very difficult to assess the nuclearity of the catalytic species but the ruthenium complex quantitatively recovered after the reaction between butan-2-one and propan-2-ol at 120°C shows IR and Raman spectra identical to those of the complex initially taken.

Activation of the reagents may in principle occur via phosphine, carbon monoxide or hydrogen substitution and, if the catalytic species is a cluster, also by metal–metal bond fission.

We have found a strong inhibition by carbon monoxide and a weaker one by an excess of (−)-DIOP on the rate of the hydrogen transfer from propan-2-ol to acetophenone catalyzed by $H_4Ru_4(CO)_8[(-)\text{-DIOP}]_2$ (Table 2). Such an effect may be attributed to a suppression by these reactants of the dissociation of the catalytic complex as well as to a breakdown of metal–metal bonds by carbon monoxide or phosphine, with formation of less complex species having lower catalytic activities and different discriminating abilities. For the hydrogen transfer from benzyl alcohol to benzylidenacetone in the presence of mononuclear ruthenium species containing both carbon monoxide and triphenylphosphine, Speier and Markò favoured an

TABLE 2

HYDROGEN TRANSFER FROM PROPAN-2-OL TO ACETOPHENONE IN THE PRESENCE OF $H_4Ru_4(CO)_8[(-)\text{-DIOP}]_2$: EFFECT OF ADDED (−)-DIOP OR CARBON MONOXIDE.

Acceptor/donor molar ratio 0.5; $H_4Ru_4(CO)_8[(-)\text{-DIOP}]_2$ 1 m*M*; *T* 120°C; reaction mixture 30 ml

mole (−)-DIOP/ mole catalyst	*p*(CO) (mmHg)	Reaction time (h)	Conversion (%)
0.0	0	111	34.9 [a]
4.5	0	360	36.4 [a]
0.0	50	432	4.3
0.0	760	327	3.2

[a] Data from ref. 1.

activation mechanism involving a phosphine dissociation, which allows olefin coordination followed by an oxidative addition of the O–H bond of the alcohol on the metal as rate determining step [8].

IR investigations are in progress on the reacting systems, aimed at identifying the species present.

Experimental

Apparatus. IR spectra were recorded on a Perkin–Elmer mod. 580 instrument. Raman spectra were measured with the aid of a double monochromator Jobin–Yvon mod. HG-25, and a photomultiplier IP28. The 4759, 4880 and 5145 Å exciting lines, working at a power of 150, 300 and 300 mW respectively of a Coherent Radiation Model 52 Ar^+ laser, were used as radiation sources. GLC analyses were performed on a Perkin–Elmer Sigma 1 system. Preparative GLC separations were performed on a Perkin–Elmer mod. F21 apparatus. Rotatory powers were measured with a Perkin–Elmer mod. 241 polarimeter. Spinning band distillations were performed with a Perkin–Elmer mod. 251 instrument.

Materials. (−)(*S*)-2-methylbutan-1-ol (o.p. 99.6%) was obtained by spinning band distillation of commercial Fluka product; (−)-2-*exo*,3-*exo*-camphandiol [9] (o.p. 96%). $H_4Ru_4(CO)_8(PBu_3)_4$ [10] and $H_4Ru_4(CO)_8$ [(−)-DIOP]$_2$ [11] were prepared by standard procedures; (−)-menthol (o.p. 98%), (−)-1,2-*O*-isopropyliden-α-D-glucofuranose (o.p. 100%) and ketones were commercial products. Ketones were redistilled before use.

Experiments were carried out by the procedure previously described [1]. The extents of reaction were determined by GLC analysis. The reaction products were recovered from the crude by preparative GLC and identified through their IR spectra. No attempts were made to identify the dehydrogenation product of (−)-2-*exo*,3-*exo*-camphandiol, (−)-menthol and (−)-1,2-*O*-isopropyliden-α-D-glucofuranose. The experiments reported in Table 1 were performed using the following amounts of products:

Exp. 1: (−)(*S*)-2-methylbutan-1-ol 15.9 g, acetophenone 10.8 g, catalyst 50 mg;

Exp. 2: (−)-2-*exo*,3-*exo*-camphandiol 10 g, acetophenone 3.5 g, diethyl ether 20 ml, catalyst 100 mg;

Exp. 3: (−)-1,2-*O*-isopropyliden-α-D-glucofuranose 11 g, acetophenone 3 g, diphenyl ether 75 ml, catalyst 50 mg;

Exp. 4: (−)-menthol 15.3 g, 1-phenyl-3-methylbutan-1-one 7.9 g, catalyst 40 mg.

Recovery of the catalyst. Butan-2-one (8.9 g), propan-2-ol (14.8 g) and $H_4Ru_4(CO)_8$[(−)-DIOP]$_2$ (50 mg) were heated at 120°C for 326 h.

The reaction mixture consisted of acetone 8.9%, propan-2-ol 58.0%, butan-2-one 24.2% and butan-2-ol 8.9%. Half of the crude was evaporated to dryness under reduced pressure to leave a residue of 24.5 mg. The IR spectrum of this residue, dissolved in cyclohexane, was identical to that of $H_4Ru_4(CO)_8$[(−)-DIOP]$_2$ in the same solvent. A Raman spectrum recorded with the other half of the crude was identical to that of a solution of $H_4Ru_4(CO)_8$[(−)-DIOP]$_2$ 1 mM in the same medium.

Acknowledgements

This research was financially supported by C.N.R., Rome.

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