Journal of Organometallic Chemistry, 373 (1989) 365–375
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 20026

Homogeneous and heterogeneous catalytic asymmetric reactions

II *. Asymmetric hydrogenation of steroid ketones

György Göndös, Lajos Gera, Mihály Bartók **,

Department of Organic Chemistry, József Attila University, H-6720 Szeged, Dóm tér 8 (Hungary)

and James C. Orr

Faculty of Medicine, Memorial University, St. John's Newfoundland, A1B 3V6 (Canada)

(Received April 19th, 1989)

Abstract

The asymmetric reduction of steroid 17- and 20-ketones with chiral hydrosilane-rhodium-(+)- and (−)-diop-complex catalysts allows different stereoselectivities in the formation of 17-alcohols, but not of 20-alcohols. The degree of this stereoselectivity is higher than that attained with other methods. The stereoselectivity can be explained in terms of the most preferred conformation of the α-siloxysteroid-rhodium intermediate complexes.

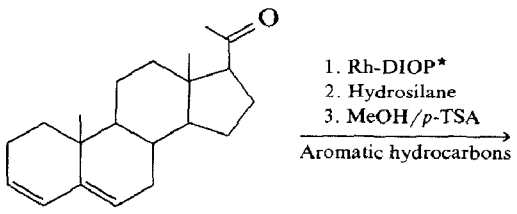
Introduction

The catalytic asymmetric hydrogenation of double bonds with transition metal complexes which contain chiral ligands and which dissolve well in organic solvents has been widely studied [1–3]. Intensive work has also been carried out on the asymmetric hydrogenation of the prochiral ketones [4–8], both enantiomeric forms of the chiral metal complexes can be used as catalysts.

A number of publications, including monographs [9,10,11] have appeared on the directions of reduction of the steroid ketones with achiral reagents. The hydrogenations of steroid 17- and 20-ketones with such achiral reducing agents have not yet led to stereoselectivities which form 17α- or 20α-alcohols in excess. We therefore

* Part I: M. Bartók, Gy. Wittmann, Gy. Göndös and G.V. Smith, J. Org. Chem., 52 (1987) 1139.
** To whom correspondence should be addressed.

0022-328X/89/$03.50



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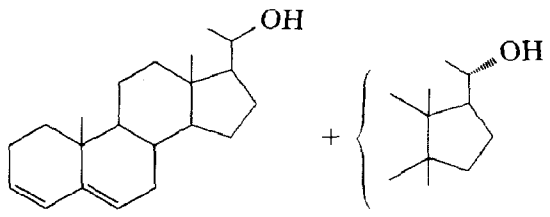

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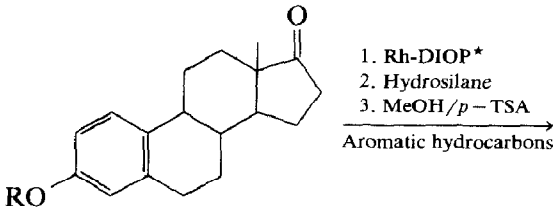
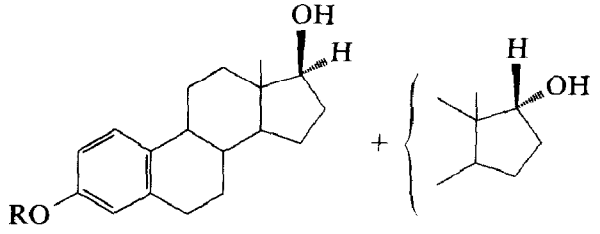


(R = H **4**;
R = CH_3 **5**)



(R = H **6**;
R = CH_3 **7**)

(R = H **8**;
R = CH_3 **9**)

Scheme 1

attempted to apply both enantiomeric forms of rhodium hydride species containing the chiral bidentate ligand (+)- or (−)-diop as chiral reducing agents for the hydrosilylation-coupled hydrogenation of steroid ketones (**1**, **4**, **5**) (Scheme 1).
A preliminary report and lecture on our experimental results has appeared [12]. In the present paper, we present a detailed discussion of the results, their interpretation being based on examinations of molecular models.

Experimental

In one analytical procedure, 10 μmol steroid ketone (**1**, **4**, **5**) in benzene or other solvent, under argon, in the presence of 20 μmol hydrosilane, is allowed to react with (+)- or (−)-diop-Rh/S/Cl catalyst (0.0305 or 0.061 μmol, S = solvent) prepared in situ from $[(cycloocta\text{-}1,5\text{-}diene)RhCl]_2$. The reaction is carried out for various times and at various temperatures, and the steroid silyl ethers obtained are hydrolysed with a 0.1% methanolic solution of *p*-toluenesulfonic acid to give the corresponding free alcohols (**2**, **3**, **6**–**9**). The substrate and the products are separated by means of a high-performance liquid chromatographic procedure on a Partisil PXS 10/25 column (Whatman) [13]. UV measurements at an appropriate wavelength, with a simultaneous refractive index procedure, are used for detection. A proton nmr method too is used to check the isomer ratios (JEOL C-60-HL 60 MHz spectrometer, TMS as internal standard, $CDCl_3$ as solvent).

Results and discussion

Table 1 lists the ratios of the hydroxy isomers obtained on the hydrogenation of pregna-3,5-dien-20-one [14] (**1**), estrone (**4**) and estrone-3-methyl ether (**5**). The tabulated data show that the asymmetric hydrogenation of (**1**) with the Rh-complexes containing the ligand (+)- or (−)-diop in the presence of diphenyldihydrosilane gave the 20-hydroxy isomers (**2**, **3**) in almost the same amounts. In contrast, hydrogenation of the 17-carbonyl function of **4** or **5** led to significantly different mixtures of 17-hydroxy isomers (**6**, **7**, **8**, **9**), depending on whether the Rh-complex prepared from (+)-diop or from (−)-diop was used as the chiral catalyst in the asymmetric hydrogenation.

The data in Table 1 also reveal that, regardless of whether the substrate is **1**, **4** or **5**, the proportions of the hydroxy isomers formed are not influenced by the dihydrosilane concentration, the temperature or the catalyst concentration.

It is striking, however, that, with **4** or **5** as substrate, variation of the temperature, or of the quantity of hydrosilane or the catalyst affects the degree of conversion, though not in a clear-cut way.

It is surprising that the conversion is substantially higher for **4** than for **5**. The difference can presumably be attributed to the acidic proton of the estrone phenolic hydroxy group.

The data in Table 2 demonstrate that the type of solvent used in the hydrogenation does not essentially influence the isomer ratio with **1** as substrate. In contrast, it is clear from Table 3 that there are large differences in the ratio of the 17-hydroxy isomers in the hydrosilylation of **5**, though the yield is good in all the aromatic hydrocarbons used. The largest difference is observed in xylene, whereas there is practically no difference between the amounts of the isomers in methanol. The catalyst species presumably changes in the latter solvent. No hydrosilylation reaction was observed in tetrahydrofuran. For study of the influence of the steric effect of the hydrosilanes on the asymmetric induction, hydrosilanes with various steric structures were used in the hydrosilylation of estrone-3-methyl ether (**5**). The proportions of the 17-hydroxy isomers formed are to be seen in Table 4. When the reactions were carried out in the same solvent, it was found that the proportions of the stereoisomers were nearly the same for n-pentyl-, diphenyl- and α-naph-

Table 1

Asymmetric hydrosilylation [a] of steroid carbonyl compounds [b] (**1**, **4**, **5**) by neutral Rh-diop catalysts

Substrate	Catalyst	Reaction conditions (°C, h, μmol)	Conversion %	Configuration (%)		Ratio [c]
				(**2**)	(**3**)	
1	(+)DIOP-Rh	75, 2, 0.061 diop	30	70	30	7:3
	(−)DIOP-Rh	75, 2, 0.061 diop	32	73	27	7:3
	(+)DIOP-Rh	75, 2, 0.122 diop	28	68	32	7:3
	(−)DIOP-Rh	75, 2, 0.122 diop	44	84	16	8:2
	Control	75, 2, 0.122 diop	11	67	33	7:3
1	(+)DIOP-Rh	75, 2, 35 Ph_2SiH_2	39	74	26	7:3
	(−)DIOP-Rh	75, 2, 35 Ph_2SiH_2	30	75	25	7:3
	(+)DIOP-Rh	75, 2, 55 Ph_2SiH_2	30	73	27	7:3
	(−)DIOP-Rh	75, 2, 55 Ph_2SiH^2	36	72	28	7:3
	Control	75, 2, 55 Ph_2SiH_2	16	75	25	7:3
1	(+)DIOP-Rh	22, 2, 20 Ph_2SiH_2	28	73	27	7:3
	(−)DIOP-Rh	22, 2, 20 Ph_2SiH_2	25	74	26	7:3
				(**6**)	(**8**)	
4 [d]	(+)DIOP-Rh	22, 24, 0.061 diop	79	80	20	8:2
	(−)DIOP-Rh	22, 24, 0.061 diop	89	46	54	1:1
	(+)DIOP-Rh	75, 24, 0.061 diop	92	78	22	8:2
	(−)DIOP-Rh	75, 24, 0.061 diop	96	48	52	1:1
	(+)DIOP-Rh	22, 24, 0.122 diop	78	77	23	8:2
	(−)DIOP-Rh	22, 24, 0.122 diop	81	45	55	1:1
	(+)DIOP-Rh	22, 24, 55 Ph_2SiH_2	84	77	23	8:2
	(−)DIOP-Rh	22, 24, 55 Ph_2SiH_2	88	47	53	1:1
	Control	22, 24, 55 Ph_2SiH_2	0	–	–	–
				(**7**)	(**9**)	
5	(+)DIOP-Rh	75, 3, 0.122 diop	19	83	17	8:2
	(−)DIOP-Rh	75, 3, 0.122 diop	29	63	37	6:4
	Control	75, 3, 0.122 diop	0	–	–	–
	(+)DIOP-Rh	22, 24, 0.122 diop	42	82	18	8:2
	(−)DIOP-Rh	22, 24, 0.122 diop	33	58	42	6:4
	Control	22, 24, 0.122 diop	0	–	–	–
5	(+)DIOP-Rh	22, 24, 0.061 diop	38	82	18	8:2
	(−)DIOP-Rh	22, 24, 0.061 diop	34	60	40	6:4
	(+)DIOP-Rh	22, 24, 55 Ph_2SiH_2	42	81	19	8:2
	(−)DIOP-Rh	22, 24, 55 Ph_2SiH_2	40	58	42	6:4
	Control	22, 24, 55 Ph_2SiH_2	0	–	–	–

[a] In the same reaction conditions without hydrosilane the reduction of ketones (**1**, **4**, **5**) were not carried out. [b] The steroid was 10 μmol, and normally Ph_2SiH_2 20 μmol, DIOP-Rh 0.061 μmol. [c] The ratio of stereoisomers was determined by HPLC [13]. [d] The solvent was benzene, except **4** where it was substituted xylene.

thylphenylhydrosilane (though the steric conditions of the hydrosilanes differ) with either (+)- or (−)-Rh-diop; with the (+)-Rh-diop complex as catalyst, the 17β-hydroxy isomer was observed in large excess, whereas with (−)-Rh-diop there was a mild preponderance of the 17α-hydroxy isomer.

In contrast with the above hydrosilanes, the proportions of the resulting 17-hydroxy isomers were nearly the same when diethyldihydrosilane was used in the

Table 2

Solvent effect on the chemical and stereochemical yield in the asymmetric hydrosilylation of pregn-3,5-dien-20-one with Rh-DIOP complex catalysts [a]

Solvent	Catalyst	Conversion (%)	Configuration (%)		Ratio [b]
			(%)		
			(2)	(3)	
Benzene	(+)DIOP-Rh	50	76	24	8:2
	(−)DIOP-Rh	50	76	24	8:2
Toluene	(+)DIOP-Rh	34	75	25	8:2
	(−)DIOP-Rh	45	80	20	8:2
Xylene	(+)DIOP-Rh	27	70	30	7:3
	(−)DIOP-Rh	29	77	23	8:2
Xylene	(+)DIOP-Rh	0	0	0	0
Control	(−)DIOP-Rh	0	0	0	0

[a] Substrate 10 μmol, Ph_2SiH_2 20 μmol, catalyst 0.061 μmol, reaction time 90 h, reaction temperature 5 °C. [b] The ratio of stereoisomers was determined by HPLC [13].

presence of the (+)- or the (−)-Rh-diop complex as catalyst. A hydrogenation reaction could not be detected when triphenylhydrosilane and triethoxyhydrosilanes were applied.

Table 3

Solvent effect on the chemical and stereochemical yield in the asymmetric hydrosilylation of estrone-methylether [a] (5) with diop-Rh complex catalysts

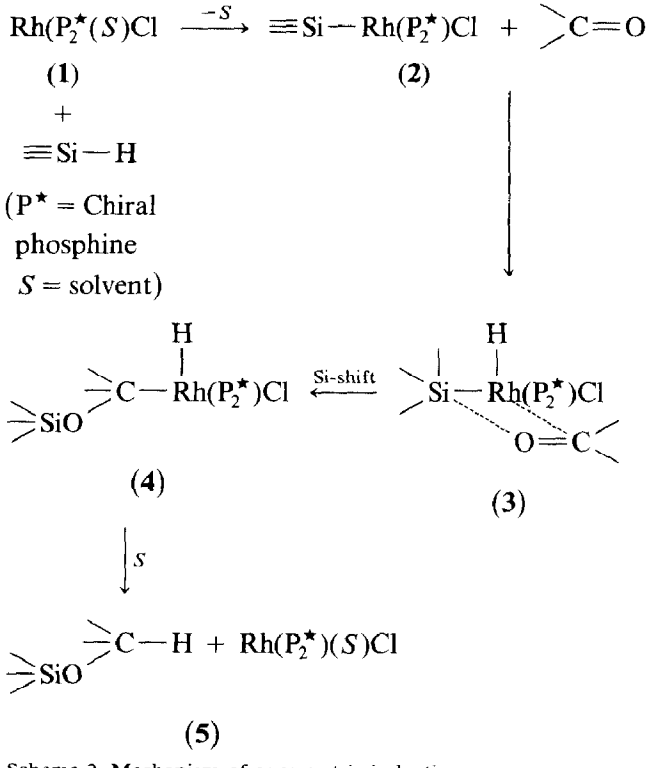
Solvent	Catalyst	Reaction temp. (°C)	Reaction time (h)	Conversion (%)	Configuration (%)		Ratio [b]
					(%)	(%)	
Benzene	(+)DIOP-Rh	5	240	60	80	20	8:2
	(−)DIOP-Rh	5	240	52	63	37	6:4
Toluene	(+)DIOP-Rh	5	240	40	79	21	8:2
	(−)DIOP-Rh	5	240	29	72	28	7:3
Xylene	(+)DIOP-Rh	5	240	42	94	6	9:1
	(−)DIOP-Rh	5	240	31	61	39	6:4
	(+)DIOP-Rh	22	24	50	80	20	8:2
	(−)DIOP-Rh	22	24	80	42	58	4:6
DXE [c]	(+)DIOP-Rh	22	24	55	79	21	8:2
	(−)DIOP-Rh	22	24	66	62	38	6:4
	(+)DIOP-Rh	22	68	83	81	19	8:2
	(−)DIOP-Rh	22	68	64	52	48	1:1
THF [d]	(+)DIOP-Rh	5	240	0	–	–	–
	(−)DIOP-Rh	5	240	0	–	–	–
Methanol	(+)DIOP-Rh	22	24	24	89	11	9:1
	(−)DIOP-Rh	22	24	12	80	20	8:2

[a] Substrate 10 μmol, Ph_2SiH_2 20 μmol, catalyst 0.061 μmol. [b] The ratio of stereoisomers was determined by HPLC. [c] DXE-diorthoxylyl-ethane. [d] THF = tetrahydrofuran.

A fundamental question in the interpretation of the results is the reaction step to which the asymmetric induction can be assigned. It is known from the literature [15] that the mechanism of the hydrosilylation of prochiral ketones in the presence of Rh-complex catalysts containing optically active ligands can be divided into three basically important steps, as shown in Scheme 2 [15]: (a) the oxidative addition of hydrosilane to the Rh^{I} complex, with formation of a Si–Rh bond (**2**); (b) insertion of a carbonyl group into the Si–Rh bond, with formation of the α-siloxyalkyl-Rh intermediate (**4**); (c) formation of the optically active silyl ether of the secondary alcohol, with reductive elimination (**5**).

Two basic conceptions are known in the literature [15] for the explanation of the occurrence of asymmetric induction by the mechanism in Scheme 2. In the model proposed by Ojima [16], the α-siloxy-Rh intermediate (**4**) plays a key role in the asymmetric induction, and the isomer composition of the product be formed in accordance with product development control. In the Glaser model [17], a part is played in the development of asymmetric induction by the silylhydrido-Rh intermediate (**2**), i.e. asymmetric induction occurs before carbonyl insertion, and the intermediate **2** formed chooses between the enantiotropic faces of the prochiral ketone: the isomer composition is governed by the conditions of steric approach control.

To explain the results we obtained in the hydrogenations of the various hydrosilanes, we assumed the correctness of the Ojima model. Accordingly, the key intermediate in the asymmetric induction in the hydrosilylation of estrone-3-methyl



Scheme 2. Mechanism of asymmetric induction.

Table 4

Steric effect of hydrosilanes on the chemical and stereochemical yield in the asymmetric hydrosilylation of estrone-methylether (5) with neutral Rh-diop catalysts in xylene [a]

Hydrosilane	Catalyst	Conversion (%)	Configuration (%)		Ratio
			(7)	(9)	
Et_2SiH_2	(+)DIOP-Rh	23	84	16	8:2
	(−)DIOP-Rh	24	76	24	8:2
n-PentylSiH$_3$	(+)DIOP-Rh	62	80	20	8:2
	(−)DIOP-Rh	71	53	47	1:1
Ph_2SiH_2	(+)DIOP-Rh	79	80	20	8:2
	(−)DIOP-Rh	90	46	54	1:1
α-NpPhSiH$_2$	(+)DIOP-Rh	84	82	18	8:2
	(−)DIOP-Rh	89	47	53	1:1
Ph_3SiH	(+)DIOP-Rh	0	–	–	–
	(−)DIOP-Rh	0	–	–	–
$(EtO)_3SiH$	(+)DIOP-Rh	0	–	–	–
	(−)DIOP-Rh	0	–	–	–

[a] Substrate, 10 μmol, hydrosilane 20 μmol, catalyst 0.061 μmol; reaction time 168 h., reaction temperature 22° C.

ether (5) in the presence of n-pentyl-, diphenyl- and α-naphthyl-phenylhydrosilane is the α-siloxy-estryl-Rh complex **4** (Scheme 2). For an interpretation of the results, the most preferable conformation of the chiral ligands of the Rh-diop on the intermediate complex must be compared with the configurations of the steroid alcohols formed. Although the coordinated chiral diop ligand can take several conformations [18,19], the most preferable of these in solution, based on the Dreiding model, is that in which the steric repulsion between the four phenyl substituents is the lowest (Fig. 1) [16].

Figure 2 depicts a Dreiding model of the most preferable conformation of the intermediate complex **4** after complex formation between estrone-3-methyl ether and (+)-Rh-diop. With a simpler mode of a depiction, as shown in Fig. 3, the sterically least hindered quasi-equatorial site is occupied by the bulkiest group: that

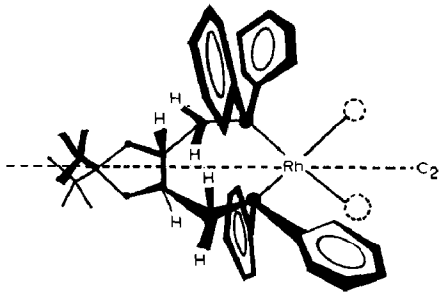


Fig. 1. Illustration of the most preferable conformation of (+)DIOP-Rh-complex in solution based on the Dreiding-model. (Before complexation).

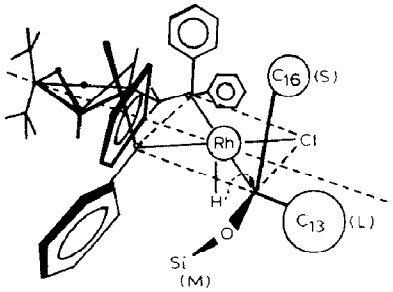


Fig. 2. Illustration of the most favorabe structure of the key intermediate complex when Estrone-3-methyl ether is chosen as substrate for the asymmetric reduction. (After complexation).

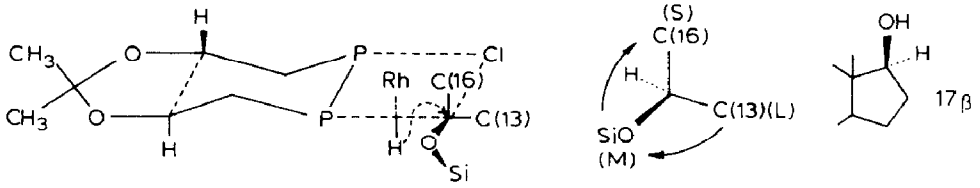


Fig. 3. Interaction of (+)(*R*,*R*)-DIOP with incipient formation of 17β-estradiol.

at $C_{(13)}$(L) * bearing virtually the whole of the sterane skeleton, while the upper apical position is occupied by the $C_{(16)}$(S) ** atom of the sterane skeleton, and the sterically most congested position by the O-silyl group (M) **. The hydride shift in this conformation should afford the (*R*) configuration, i.e. the 17β-hydroxy-estradiol-3-methyl ether. As indicated in Fig. 4, the 17β-hydroxy isomer is likewise formed when the $C_{(13)}$(L) group occupies the upper apical position, the OSi(M) group occupies the quasi-equatorial position, and the $C_{(16)}$(S) group occupies the most congested lower apical position.

In the case of the (+)-diop chiral ligand, it is difficult in principle to understand why the most preferable stereochemical arrangement leading to the 17α isomer cannot develop, i.e. with the $C_{(13)}$(L) group in the quasi-equatorial position, the OSi(M) group in the upper apical position, and the $C_{(16)}$(S) group in the most congested lower apical position (Fig. 5). Dreiding model examinations, however, clearly reveal that both the $C_{(19)}$ angular methyl group and $C_{(12)}(CH_2)$ group

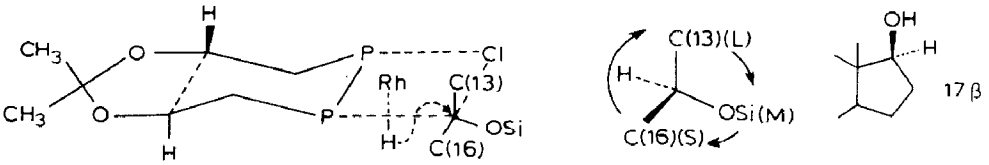


Fig. 4. Interaction of (+)(*R*,*R*)-DIOP with incipient formation of 17β-estradiol.

* L = large.

** S = small; M = medium.

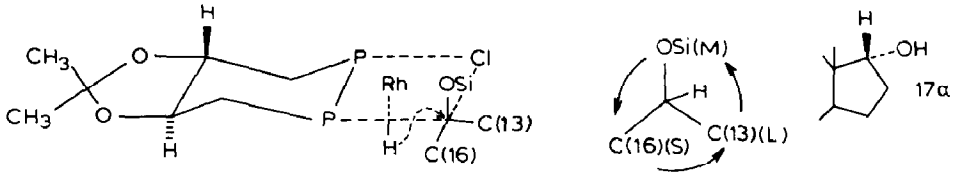


Fig. 5. Interaction of (+)(*R*,*R*)-DIOP with incipient formation of 17α-estradiol.

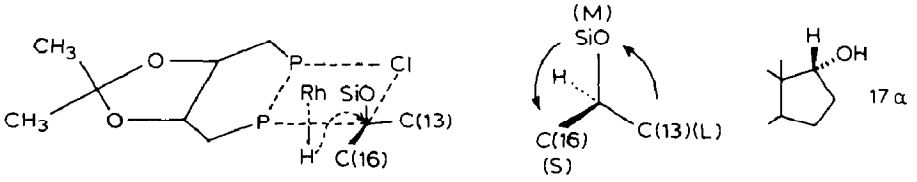


Fig. 6. Interaction of (−)(*S*,*S*)-DIOP with incipient formation of 17α-estradiol.

protons then interfere with the hydrogens of one of the upper apical phenyl groups; this is the reason why the stereochemical situations presented in Figs. 3 and 4 are preferred in the case of the (+)-diop chiral ligand.

With the (−)-diop ligand, as shown in fig. 6, the most preferable stereochemical arrangement may develop, i.e. with the $C_{(13)}$(L) group in the quasi-equatorial group, the OSi(M) group in the upper apical position, and the $C_{(16)}$(S) group in the most congested lower apical position. The steric hindrance observed with (+)-diop as ligand does not arise to prevent the development of such a stereochemical arrangement when (−)-diop is used as ligand.

The stereochemical arrangement leading to the 17β-hydroxy isomer (Fig. 7) may also be formed in the case of the intermediate obtained with (−)-diop; here, however, the most congested lower apical position is occupied by the OSi(M) group and not by the $C_{(16)}$(S) group as in the previous intermediate leading to the 17α-hydroxy isomer (Fig. 6), and therefore the formation of a slight preponderance of the 17α-hydroxy isomer can readily be interpreted.

An interpretation can also be given on the basis of model examinations for the preferred formation of the 20β-hydroxy isomer in the hydrosilylation of pregna-3,5-dien-20-one: in the intermediate leading to formation of the 20β-hydroxy isomer (Fig. 8), the bulkiest $C_{(17)}$(L) group occupies a quasi-apical position, the OSi(M) group is quasi-equatorial, and the $C_{(21)}$ group is lower apical. The formation of the 20β-hydroxy isomer with (+)-diop as ligand is therefore obvious.

Model examinations similarly provide a possibility for formation of the intermediate leading to the 20α isomer (Fig. 9), in which the bulkiest $C_{(17)}$(L) group is

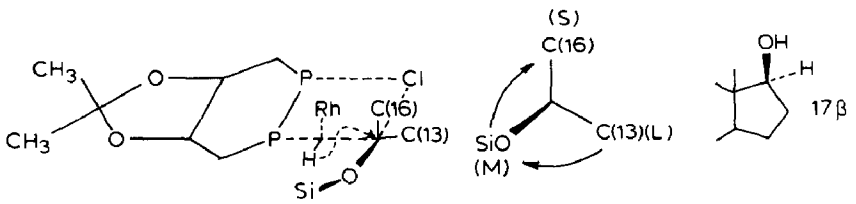


Fig. 7. Interaction of (−)(*S*,*S*)-DIOP with incipient formation formation of 17β-estradiol.

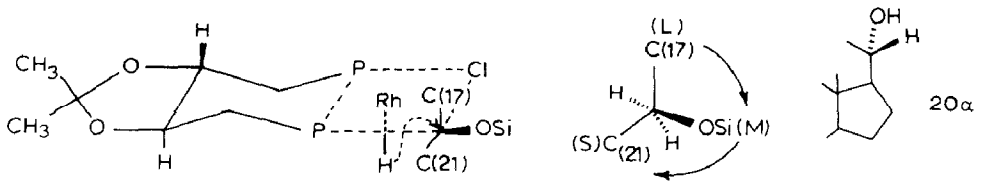


Fig. 8. Interaction of (+)(*R*,*R*)-DIOP with incipient formation of 20α-hydroxy-pregna-3,5-diene.

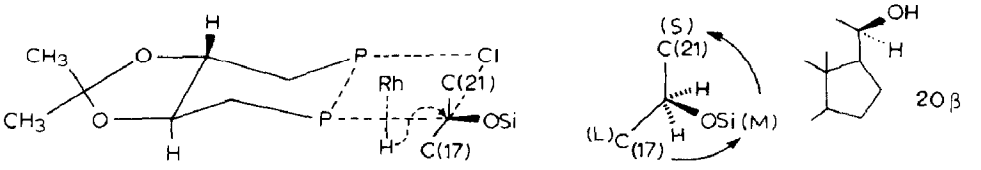


Fig. 9. Interaction of (+)(*R*,*R*)-DIOP with incipient formation of 20β-hydroxy-pregna-3,5-diene.

situated in the most congested lower apical position, the OSi(M) group is in the quasi-equatorial position, and the $C_{(21)}$(S) group in in the upper apical position. However, the free rotation around the $C_{(17)}$–$C_{(20)}$ σ-bond means that the intermediate conformer leading to the 20β-hydroxy isomer (Fig. 8) always results. The stereochemical picture is very similar for the Rh complex containing (−)-diop as ligand. Thus, the hydrosilylations in the presence of the (+)- and the (−)-Rh-diop complexes lead to the formation of mixtures of 20-hydroxy isomers with almost the same compositions.

Conclusions

Then Rh-diop complex catalysts with opposite chiralities induce opposite asymmetries in the hydrosilylations of the prochiral 17-ketones of estrone and estrone-3-methyl ether in the presence of n-pentyl-, diphenyl- or α-naphthylphenylhydrosilane. As a consequence, mixtures of the 17-hydroxy isomers in different proportions are formed. Such asymmetric induction is not observed when diethyldihydrosilane is used.

The proportions of the 17-hydroxy isomers are influenced by the nature of the solvent, but not by the temperature, the concentration of the catalyst, or the concentration of the hydrosilane. Similarly, the proportions are not affected by the steric conditions in n-pentyl-diphenyl- and α-naphthylphenylhydrosilane. Diethylsihydrosilane behaves differently from the other hydrosilanes.

The occurrence of asymmetric induction can be interpreted well in terms of the model proposed by Ojima. The asymmetric induction brought about by the ligands (+)- and (−)-diop can presumably be ascribed to the stereochemical structure of the α-silyloxy-estryl-Rh complex intermediate (**4**) in the hydrosilylation reaction. The preferable conformation of **4** presumably governs the proportions of the hydroxy isomers formed in the product mixture.

The non-occurrence of asymmetric induction in the hydrosilylation of pregna-3,5-dien-20-one under the same conditions can be attributed to the free rotation of the 20-carbonyl function around the $C_{(17)}$–$C_{(20)}$ σ-bond.

The reduction of the ketones (**1**, **4**, **5**) was not carried out under the same reaction conditions without hydrosilane.

Although our results can be interpreted well by utilizing the Ojima model, the non-occurrence of asymmetric induction when diethyldihydrosilane is used, and similarly the non-occurrence of hydrosilylation in the cases of triphenyl- and triethoxyhydrosilanes, indicate that the Glaser model cannot by neglected in the interpretation of the results.

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