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PREDICTION OF CHIRALITY OF MAJOR PRODUCT BY MODELS OF DIOP-RHODIUM(I) COMPLEXES FOR ASYMMETRIC HYDROGENATION AND HYDROSILYLATION

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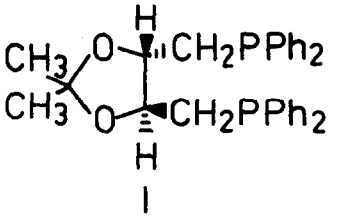
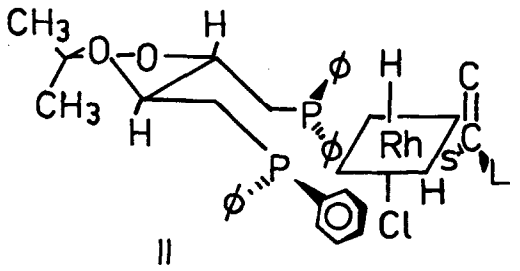
Kagan's (+) or (-) 2,3-O-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane[1,2] (DIOP) (I) ligand has been used in both rhodium-catalyzed asymmetric hydrogenation[1-5] and hydrosilylation[5-8] reactions. Space-filling CPK-type molecular models were made of (+) DIOP-Rh(I) complexes, and it was seen that the rigid dioxolan ring imposed constraints upon the conformation of the phenyl rings attached to the phosphorous atoms. Inspection of these models prompts us to suggest II and III-IV as those suffering the least steric hindrance in asymmetric hydrogenation and hydrosilylation, respectively.

As seen in V-VI, one of the sites (A) on the belt appears to suffer severe steric hindrance by the phenyl group-1 in the CPK-model, due to constraints by the rigid (+) DIOP backbone. Phenyl-1 can assume a conformation in which the P-C(Ph) bond is approximately coplanar (and the ring itself approximately perpendicular) to the belt plane of the octahedral complex. In the CPK-model, site B appears more accessible with the two phenyl rings (3&4) able to assume a conformation such that the planes intersect each other at $\sim 109^{o}$, and the belt-plane approximately bisects the Ph-P-Ph angle. The prochiral olefin can bind to the more accessible site B such that its larger substituent is closest to the hydrido ligand at site A. Non-bonded interactions between the upper apical ligand and the two pseudo-axial protons on the chelating ring can be minimized by placing the hydrido ligand and the chloro ligand in the upper and lower apical positions, respectively.

Kagan has pointed out that in the Wilkinson mechanism[9] two enantiomeric octahedral active complexes (VIIa&b) are present when achiral phosphines ($P(Ph)_3$ in $RhCl\{P(Ph)_3\}_3$) and non-prochiral olefins are used in homogeneous hydrogenation reactions.[2] When a prochiral olefin is



I



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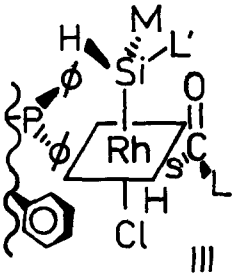

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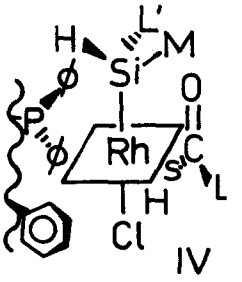

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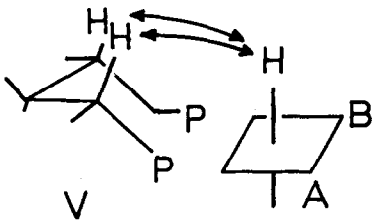

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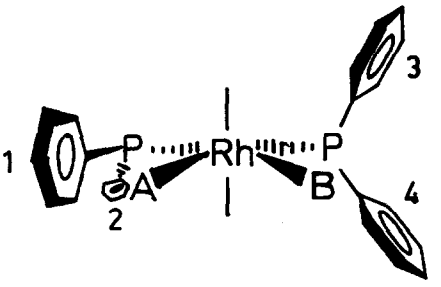

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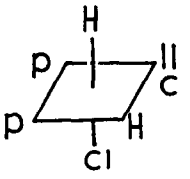
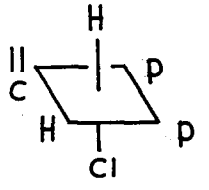
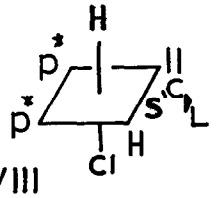


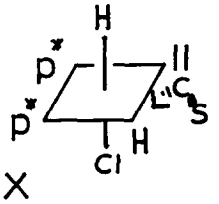
VIIa



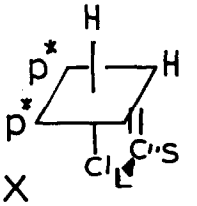
VIIb



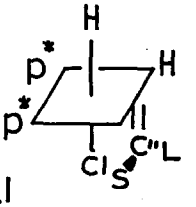
VIII



IX



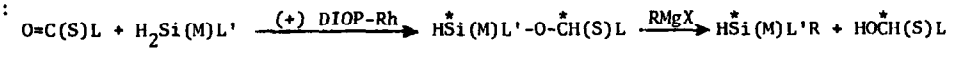
X



XI

In the above figures, S = small, M = medium, and L = L' = large in terms of steric bulk.

Scheme 1:



used two enantiomeric sets of complexes are now possible depending on which face of the prochiral olefin faces the metal. If a chiral phosphine is used with the prochiral olefin, such that only one type of phosphine enantiomorph is present, then the two enantiomeric sets now become four diastereomers (VIII-XI). This diastereomeric mixture may now produce a preponderance of one enantiomeric product over the other.

If we suppose a similarity in the active catalytic species between hydrosilylation with $HSiR_3$ and hydrogenation, then the achiral $-SiR_3$ moity may be substituted for the apical hydrido ligand in VIII-XI. If a prochiral silane ($H_2SiR'R''$) is used (see scheme 1), then each of the structures VIII-XI may now be written in two epimeric forms (depending upon the configuration of the chiral -SiHR'R'' moity) for a total of eight diastereomers in the reaction mixture. Inspection of CPK-models reveals that at the upper apical position, the bulky tetragonal silyl moity suffers non-bonding interactions with the pseudo-axial protons on the chelating ring. However, the steric hindrance around the lower apical position appears even greater. Similar to the argument of Corriu and Moreau,[7] the configuration at silicon in III is more favorable than in epimer IV (due to interactions with phenyl-3) while the prochiral carbon center remains the same. Thus, when the ketone is at site B the carbonyl oxygen atom is staggered between the two silicon substituents M and L'. Further inspection of CPK-models reveals that carbonyl binding to crowded site A causes the silicon bound proton to assume a near eclipsed conformation with phenyl-3. When all eight diastereomers are compared, III&IV appear to suffer the least steric hindrance (III being the most favorable).

Models II-IV are first approximations to the mechanism of asymmetric hydrogenation and hydrosilylation since they are based just upon steric bulk considerations- they don't take into account polar factors (substrate hydrogen-bonding or participation of the substrate as an additional ligand). Nor do they consider cis-trans olefin geometry (under current investigation). Yet although an approximation, II-IV can be used successfully to predict the configuration of the major isomer produced (tables 1-2). While only representative examples are listed due to lack of space, all examples cited in the references were correctly predicted with only three exceptions as listed. Model II allows us to predict the configuration of the product in ex. 12 whose absolute configuration is not yet known.[4] Use of models III-IV also allows us to explain the greater optical purity at carbon relative to silicon (ex. 13-15). In addition, the higher optical purity with (-) menthyl pyruvate and (-) DIOP vs. (+) DIOP may be explained by Prelog's rule[10] and model III.

Table 1 Hydrogenation: $RCH{=}C(S)L + H_2 \xrightarrow{(+)\ DIOP\text{-}Rh^a} RCH_2\overset{*}{C}H(S)L$

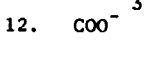
ex.	S	L	R	configuration predicted	configuration found	% enantiomeric excess	ref.
1.	COO^-	Ph	H	R	R[b]	63	1
2.	COOMe	Ph	H	R	S[b]	7	1
3.	COO^-	NHCOMe	Ph	S	S[b]	70	2
4.	COOMe	NHCOMe	Ph	S	S[b]	55	2
5.	COOH	NHCOMe	Ph	S	S[b]	72	2
6.	COOH	NHCOMe	H	S	S[b]	73	2
7.	COOH	NHCOMe	Ph-p-OH	S	S[b]	80	2
8.	NHCOMe	Ph	Me	R	R[b]	78	2
9.	Et	Ph	H	S	R	15	5
10.	Ph	$OSiMe_3$	H	S	S[b]	6	3
11.	$OSiMe_3$	t-Bu	H	R	R[b]	7	3
12.	COO^-		H	R	?[b]	88	4

Table 2 Hydrosilylation: $X{=}C(S)L + H_2SiNpPh^c \xrightarrow{(1)\ (+)\ DIOP\text{-}Rh^a \\ (2)\ MeMgX} XH\overset{*}{C}H(S)L + H\overset{*}{S}iNpPhMe$

ex.	S	L	X	configuration predicted C	configuration predicted Si	configuration found C	configuration found Si	% enantiomeric excess C	% enantiomeric excess Si	ref.
13.	Me	Ph	O	S	R	S	R	56	30	7
14.	i-Pr	Ph	O	S	-[d]	S	-	24	-	5
15.	Me	Et	O	S	R	S	R	42	40	7
16.	Me	t-Bu	O	S	R	-	R	-	35	7
17.	Me	COOn-Pr	O	S	-[d]	S	-	82	-	8
18.	H	Et	O	-	R	-	R	-	14	7
19.	Et	Et	O	-	R	-	R	-	46	7
20.	Et	Et	O	-	S[e]	-	S	-	12	7
21.	Me	COOMen[f]	O	S[g]	-[d]	S	-	62	-	8
22.	Me	COOMen[f]	O	R[g,h]	-[d]	R	-	66	-	8
23.	COOEt	Ph	O	R[g]	-[d]	S	-	1	-	8
24.	Me	Ph	NCH_2Ph	S[g]	-[d]	S	-	50	-	6

a catalyst={(olefin)$_2$RhCl}$_2$ + (+) DIOP. b (-) DIOP used, configuration converted to (+) DIOP. c Np=α-naphthyl; Ph=phenyl. d hydrolysis of silylether (or silylamine) instead of Grignard reaction. e $H_2SiNpMe$ used, Grignard=PhMgX f Men=(-) menthyl g H_2SiPh_2 used. h (-) DIOP used.

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