Homogeneous Deuteriation of Alkenes using $[RhX(PR_3)_3]$ (X = halide, R = aryl) Catalysts

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Catalytic deuteriation of cycloalkenes using $[RhX(PR_3)_3]$ (X = halide, R = aryl) catalysts frequently gives rise to some polydeuteriation and scrambled addition of deuterium to the cycloalkene substrate. It is shown that these undesirable side reactions can be minimized by using small, electronegative aniono ligands or electron-withdrawing triarylphosphine ligands. Both these ligands inhibit the decomposition of the 16-electron intermediate rhodium(III) alkyl complex $[RhD(X)(alkyl)(PR_3)_2]$. Its decomposition by β-hydride abstraction brings about both polydeuteriation and scrambled addition of deuterium to the alkene. Acyclic, alk-1-enes give the best yields of $[^2H_2]$ products when $[RhI(PPh_3)_3]$ is the catalyst, since the formation of the less stable 2-alkyl intermediate is sterically inhibited.

Whilst it is generally agreed that $[RhCl(PPh_3)_3]$ is an excellent catalyst for the deuteriation of alkene substrates,[1–4] more searching investigations have usually revealed both a small degree of polydeuteriation (the incorporation of more than two atoms of deuterium per alkene bond in the substrate) and some scrambled addition (the incorporation of deuterium elsewhere than at the site of the original alkene bond).[5] It has been noted that both these reactions become increasingly prominent as the deuteriation reaction proceeds.[6]

The participation of these side reactions depends also on the nature of the substrate (see Table). Small cycloalkenes do not give polydeuteriated products, and it has been noted elsewhere[5] that both cycloheptene and cyclo-octene produce polydeuteriated cycloalkanes. The usual source of polydeuteriation in catalytic reactions is the participation of relatively long-lived metal–alkyl species in the catalytic cycle.[7,8] For this reason monohydrido catalysts utilizing the 'alkyl route' are unsatisfactory deuteriation catalysts.[9] As cycloalkenes can only form secondary alkyl complexes during the reaction, and since cyclo-octene had been shown to undergo a high degree of polydeuteriation,[5] it was selected as the reference substrate for the present study.

Results and Discussion

It has been shown that the species $[RhCl(PPh_3)_2]$ is an important participant in the catalytic cycle of Wilkinson's catalyst.[10] At the low deuterium and alkene concentrations encountered towards the end of the reactions this species can dimerize to $[\{RhCl(PPh_3)_2\}_2]$, which in turn can form $[\{RhD_2Cl(PPh_3)_2\}_2]$. By virtue of its *trans* deuterio ligands this latter species could follow the alkyl route and give rise to polydeuteriated products. However, experiments using the dimer as the catalytic species, and conversely experiments carried out when dimer formation had been inhibited by addition of PPh_3 to $[RhCl(PPh_3)_3]$ solutions, showed no change in the distribution of deuteriated products from those obtained when $[RhCl(PPh_3)_3]$ was used. Thus, the origin of the polydeuteriated products lay elsewhere.

Analogues of Wilkinson's catalyst containing other triarylphosphines have been employed as hydrogenation catalysts. It has been demonstrated empirically that electron-donating aryl substituents increase the rate of hydrogenation and that electron-withdrawing aryl substituents decrease the rate of hydrogenation.[2,11] Their effects on the rates of deuteriation of cyclo-octene have, with one exception, been found to be

Table. Yields of alkane isotopomers from deuteriations catalysed by $[RhX(PPh_3)_3]$ complexes

			Yield of alkane isotopomer/%					
Alkene	Solvent	X	$^2H_0$	$^2H_1$	$^2H_2$	$^2H_3$	$^2H_4$	$^2H_5$
Allylbenzene	C_7H_8	Cl			99.4	0.6		
Allyl phenyl ether	C_7H_8	Cl			100.0			
Bicyclo[2.2.1]hept-2-ene	C_7H_8	Cl			100.0			
Dec-1-ene	C_7H_8	Cl	0.9	3.3	92.6	2.3	0.9	
		I	0.5	2.3	94.4	1.9	0.9	
Hept-1-ene	C_7H_8	Cl	3.7	4.4	86.9	2.5	2.5	
		I	2.9	2.9	89.8	1.5	2.5	0.5
cis-Hept-2-ene	C_7H_8	Cl		1.7	97.1	1.2		
		I	0.5	4.4	91.1	3.0	1.0	
Hex-1-ene	C_7H_8	Cl			98.0	1.3	0.7	
2-Methylbut-2-ene	C_7H_8	Cl			97.4	2.6		
		I[a]			97.2	2.8		
Oct-1-ene	C_8H_{10}[b]	Cl	0.5	4.2	91.6	2.8	0.9	
		I	0.6	2.4	95.8	0.6	0.6	
1*R*,5*R*-Pin-2-ene[c]	C_7H_8	Cl			93.5	3.7	2.8	
		I			83.8	10.8	5.4	

[a] 40% Reduction. [b] *o*-Xylene. [c] 10% Reduction.

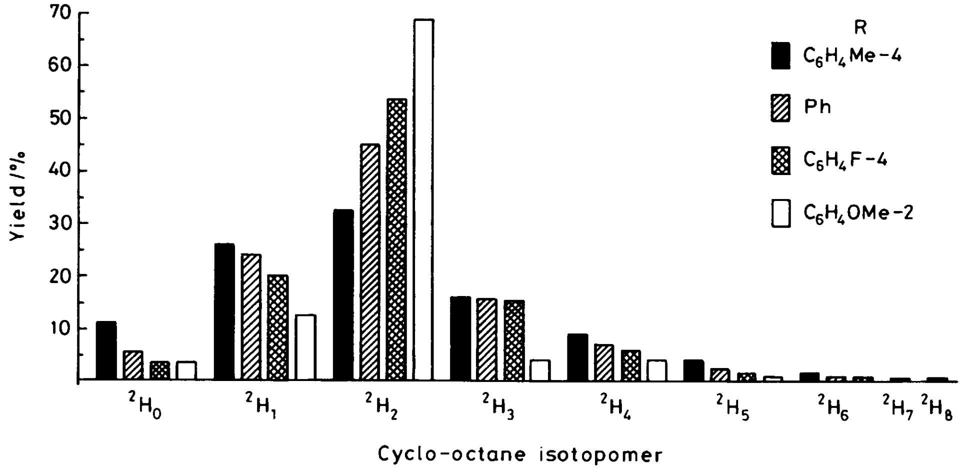


Figure 1. Yields of cyclo-octane isotopomers from $[RhCl(PR_3)_3]$-catalysed reactions

similar. They do, however, exert a marked influence on the distribution of cyclo-octane isotopomers formed in the deuteriation reactions (see Figure 1).

It can be seen that electron-donating aryl groups, with the exception of the C_6H_4OMe-2 substituent, increase the degree of polydeuteriation, whilst the converse is true for the electron-withdrawing substituent C_6H_4F-4. It is proposed that the increase in electron density on the central rhodium atom destabilizes the intermediate rhodium–cyclo-octyl complexes and renders them more liable to decompose by β-hydride abstraction [equation (1)]. The formation of $[RhH(D)L_n]$,

$$[L_nDRh\text{–}C_8H_{14}D] \rightleftharpoons [L_nRhH(D)(C_8H_{13}D)] \rightleftharpoons [L_nRhH(D)] + C_8H_{13}D \quad (1)$$

or free HD from its subsequent decomposition, accounts for the formation of $[^2H_1]$cyclo-octane [equation (2)], and the formation of $[^2H_1]$cyclo-octene (which can be detected in the reaction mixture if the reaction is stopped before completion) leads to $[^2H_3]$cyclo-octane [equation (3)].

$$[L_nRhH(D)] + C_8H_{14} \longrightarrow [L_nRh] + C_8H_{15}D \quad (2)$$

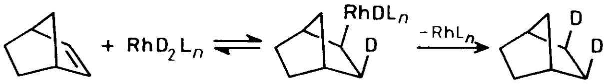
$$[L_nRhD_2] + C_8H_{13}D \longrightarrow [L_nRh] + C_8H_{13}D_3 \quad (3)$$

Repetition of the β-hydride abstraction reaction leads eventually to $[^2H_0]$-and $[^2H_x]$-cyclo-octanes depending on the gas involved and the degree of deuteriation present in the alkene substrate.

Examination of Figure 1 shows that more than four atoms of deuterium can be incorporated in the cyclo-octanes produced. This means that double-bond migration occurs; in less symmetric alkenes this process would be called isomerization. These isotopomers also arise as a consequence of the β-hydride or β-deuteride abstraction reactions. Indeed, isotope exchange is an inevitable consequence of deuterioisomerization.[7]

For β-hydride abstraction to occur a vacant co-ordination site on rhodium is essential. This is normally available since the five-co-ordinate alkyl complex is formed from the six-co-ordinate dideuteriorhodium(III) alkene complex in the catalytic cycle. The behaviour of the tri(2-methoxyphenyl)phosphine complex can now be rationalized. Although it contains an electron-donating aryl group, other similar, nominally five-co-ordinate, $[RhX_3L_2]$ complexes have been shown to contain a bound C_6H_4OMe group and are thus co-ordinatively saturated.[12–14] The blocking of the sixth co-ordination site by the methoxy group inhibits the β-hydride abstraction decomposition and thus a low degree of scrambled addition and polydeuteriation occurs. The co-ordinative saturation of $[RhD_2Cl\{P(C_6H_4OMe\text{-}2)_3\}_2]$ also explains why the deuteriation ceases before all the cyclo-octene and deuterium have been consumed. At low concentrations, cyclo-octene cannot compete effectively with the methoxy group for the sixth co-ordination site and thus cannot enter the catalytic cycle.

Further requirements for the successful completion of the β-hydride abstraction reaction include rotation about the rhodium–carbon bond of the alkyl complex, to bring another CH_2 group into conjunction with the vacant sixth co-ordination site. When this cannot occur then polydeuteriation is unlikely. Thus, bicyclo[2.2.1]hept-2-ene (norbornene) forms only a $^2H_2$ product (Table) [equation (4)]. It cannot isomerize in the β-hydride abstraction reaction since this would contravene Bredt's rule. Nor can rotation occur about the carbon–carbon single bond, which brings the hydrogen atom of the CHD group of the deuterioalkyl complex into conjunction with the vacant sixth co-ordination site, because of the rigidity imposed by the fused ring system.

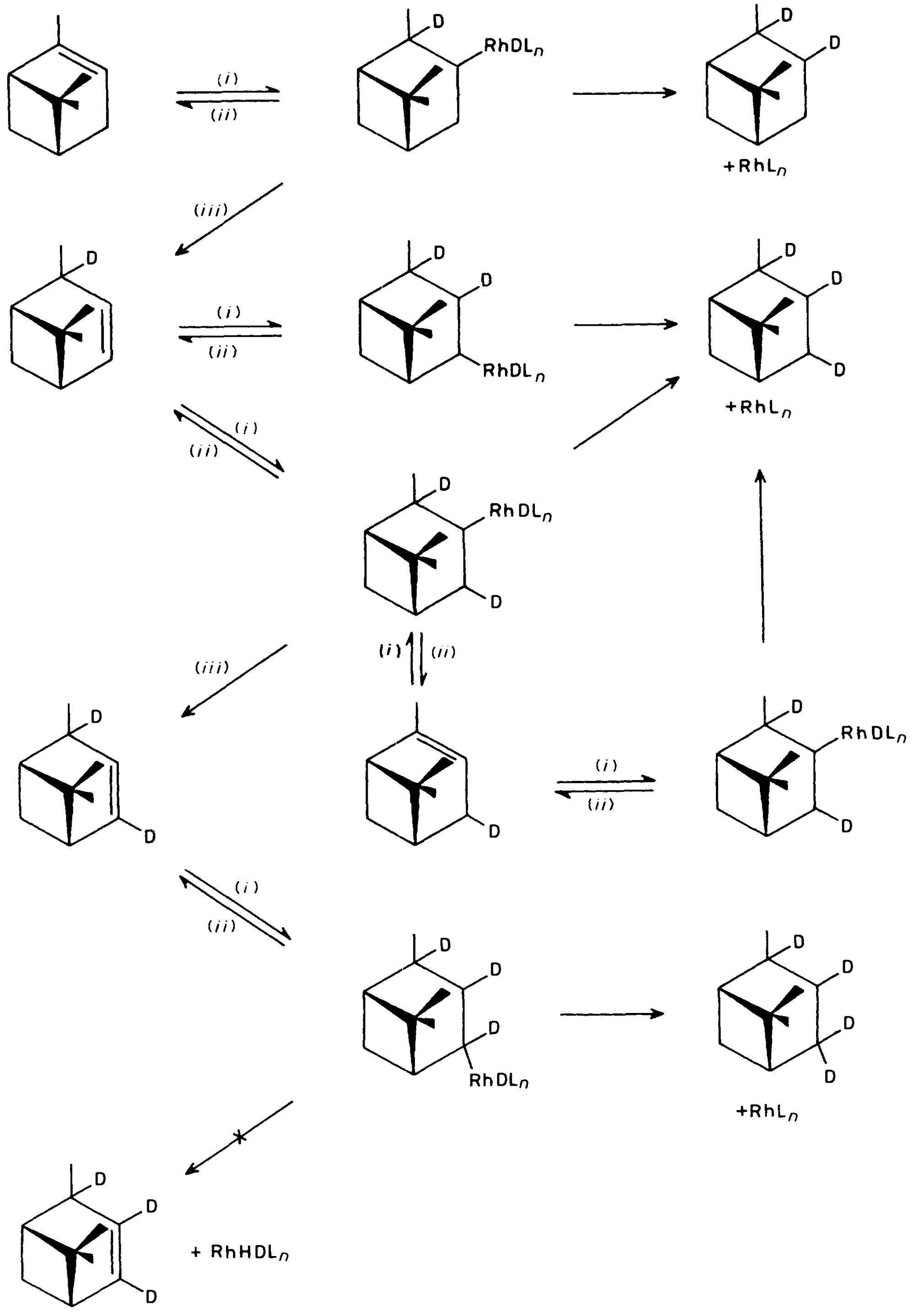


(4)

However, deuterioisomerization can and does occur in the deuteriation of (+)-2,6,6-trimethylbicyclo[3.1.1]hept-2-ene (α-pinene), since limited rotation of and β-hydride abstraction from the alkyl are both possible. A maximum of four atoms of deuterium can be incorporated in the product (Scheme). That this is a genuine maximum and not due to the undetectability of small quantities of polydeuteriated products can be seen in the absence of any $[^2H_5]$pinane despite the large quantity of $[^2H_4]$pinane produced when the deuteriation is catalysed by $[RhI(PPh_3)_3]$.

The halogeno ligand also influences the product distribution in the deuteriation of cyclo-octene using $[RhX(PPh_3)_3]$ catalysts (Figure 2). The larger halogeno ligands result in a more rapid reduction and a greater degree of polydeuteriation. Both electronic and steric factors favour this trend, although the similarities in the product distributions from $[RhCl(PPh_3)_3]$- and $[Rh(SnCl_3)(PPh_3)_3]$-catalysed reactions suggest that the former is more important.

However, in the deuteriations of terminal, acyclic alkenes (Table), less scrambled addition occurs when the iodo complex



Scheme. Formation of polydeuteriated products from α-pinene. (*i*) $+\mathrm{RhD_2L}_n$; (*ii*) $-\mathrm{RhD_2L}_n$; (*iii*) $-\mathrm{RhH(D)L}_n$

is used to catalyse the reactions. This effect has steric origins. Whereas an unsubstituted cycloalkene must form a secondary rhodium(III) alkyl complex, a terminal alkene can form either a primary 1-alkyl complex or a secondary 2-alkyl complex. The latter is inherently less stable and can undergo deuterioisomerization, however it is less likely to be formed on steric grounds when the iodo complex is the catalyst. The 1-alkyl intermediate, however, can only undergo β-hydride or β-deuteride abstraction thus limiting the scope for extensive polydeuteriation. However, in the deuteriation of internal alkenes, when secondary alkyl formation is inevitable, the chloro complex is again the preferred catalyst for clean deuteriation. It would appear that neither the chloro nor the iodo complex readily forms the unstable tertiary alkyl intermediates since the yield of 2-methyl[$^2H_2$]butane from 2-methylbut-2-ene is high in both cases and is only slightly decreased on going from the chloro to iodo catalyst. The steric crowding occurring in a tertiary alkyl intermediate is the

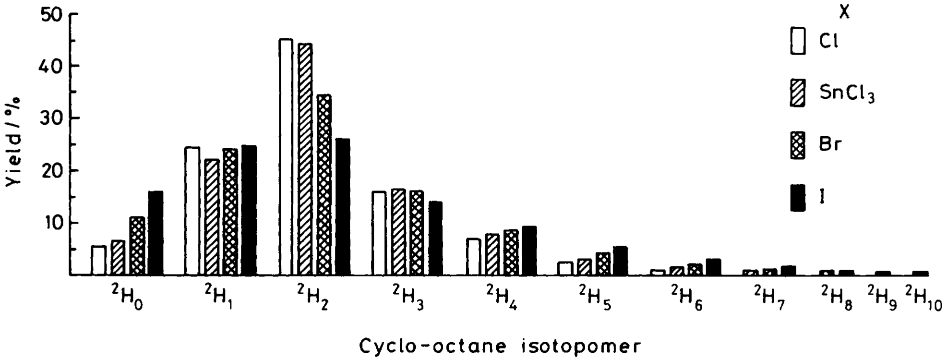


Figure 2. Yields of cyclo-octane isotopomers from $[RhX(PPh_3)_3]$-catalysed reactions

reason for omitting such a complex in the initial reaction of α-pinene in the Scheme.

It can be seen, therefore, that if sterically crowded secondary alkyl complexes are to be formed during deuteriations catalysed by Wilkinson-type catalysts then the best yields of $^2H_2$ products can be obtained from catalysts such as $[RhCl\{P(C_6H_4F\text{-}4)_3\}_3]$. Alternatively, if primary or secondary alkyl intermediates can be formed from the alkene then $[RhI(PPh_3)_3]$ is the better choice for maximum yields of the required product.

The increase in the proportion of polydeuteriated products as the reactions proceed is due to the formation of deuteriated alkenes by decomposition of the intermediate alkyl complexes. This is particularly true for acyclic alkenes since the internal alkenes resulting from isomerization are reduced more slowly than alk-1-enes and accumulate in the reaction mixture.

Experimental

Hydrated rhodium trichloride (Johnson Matthey) and tertiary phosphines (BDH or Fluorochem) were used without purification. Deuterium (BDH, 99.5%) was dried by passing it through a tower containing dry silica gel before admission to the apparatus.

Halogenotris(triphenylphosphine)rhodium(I) complexes[1] and $[\{RhCl(C_8H_{14})_2\}_2]$[15] were prepared according to directions given in the literature. It was found necessary to allow the crude material obtained from the literature preparations of $[Rh(SnCl_3)(PPh_3)_3]$[16] to react with additional PPh_3 in refluxing ethanol to obtain a pure product. The other $[RhX(PR_3)_3]$ (R = aryl) catalysts were prepared *in situ* by adding the required quantities of tertiary phosphine and $[\{RhCl(C_8H_{14})_2\}_2]$ to the catalytic solution. The dimer $[\{RhCl(PPh_3)_2\}_2]$ was prepared by allowing a solution of $[RhCl(PPh_3)_3]$ in deaerated toluene to stand under nitrogen at 40 °C for 2 h. It was filtered off under nitrogen and stored *in vacuo*.

The apparatus used to deuteriate alkenes at sub-atmospheric pressure has been described previously.[1]

The alkenes (Aldrich, Lancaster Synthesis, or Sigma) were dried and freed from hydroperoxides by distillation from sodium under nitrogen at atmospheric pressure. Where this method of purification would have brought about decomposition, they were freed from hydroperoxides by passing them down a column of activated alumina in a nitrogen atmosphere. In both cases they were admitted to the deuteriation apparatus without coming into contact with air.

The deuteriation reactions were normally carried out in dry, deaerated toluene save where this solvent would have interfered with the mass spectrometric analysis of the products. The products were separated from the catalyst by passing the solution down an activated alumina column. This procedure was adopted to avoid post-deuteriation reactions between rhodium complexes and the deuteriated hydrocarbons produced. The products had their isotopic composition determined mass spectrometrically using an AEI MS10 or MS902 instrument. The ionizing voltage was normally 70 eV (*ca.* 1.12×10^{-17} J), and only parent ions were used in computing the product yields after making due allowance, where appropriate, for other ions of the same nominal mass.

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