Homogeneous Platinum(II)-catalysed Hydrogen–Deuterium Exchange at a Saturated Carbon Atom

By C. Masters

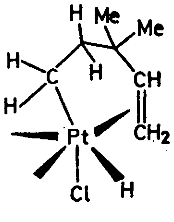
(*Koninklijke/Shell - Laboratorium, Amsterdam, Holland*)

Summary In the presence of a homogeneous platinum catalyst alkenes of the type $RC(CH_3)_2CH{=}CH_2$, ($R = C_2H_5$, C_3H_7, or C_4H_9) undergo hydrogen–deuterium exchange in the alkyl part of the molecule almost exclusively at C-5.

It has been shown that platinum(II) in an aqueous acetic acid medium can act as a homogeneous catalyst for the hydrogen–deuterium exchange in simple alkanes[1] and in the side chain of long-chain alkylbenzenes.[2] The observation[2] that with 1,1-dimethylpropylbenzene H–D exchange in the side-chain occurs almost exclusively at the γ-position prompted us to investigate the H–D exchange in alkenes of the type $RC(CH_3)_2CH{=}CH_2$ ($R = CH_3$, C_2H_5, C_3H_7, or C_4H_9).

Under conditions analogous to those of Hodges *et al.*,[1] *i.e.* 2 h at 100°, solvent: 50 mol% CH_3CO_2D in D_2O, 0·2M $HClO_4$, 0·02M K_2PtCl_4, 0·2M alkene, we obtained the results shown in the Table.

In the ^1H n.m.r. spectrum (100 MHz in $CDCl_3$) of 3,3-dimethylpent-1-ene the signals due to the alkyl protons are well separated and integration of a deuteriated sample, containing toluene as an internal standard, shows almost exclusive alkyl deuteriation at C-5. With 3,3-dimethylhex-1-ene it is impossible to distinguish between the protons on C-4 and C-5 by ^1H n.m.r. spectroscopy. However, in the ^{13}C n.m.r. spectrum of the deuteriated compound there are, after decoupling of the protons, two signals that can be assigned to the C-5 carbon: a singlet at δ (CS_2) 175·2 p.p.m. from the undeuteriated species and a 1:1:1 triplet at δ (CS_2) 175·5 p.p.m. ($J_{^{13}C-D}$ 20 Hz) from the deuteriated form, indicating that the predominant species is –CHD–. The results for 3,3-dimethylhept-1-ene are somewhat ambiguous since the ^1H n.m.r. spectrum (220 MHz) does not show distinct signals for the alkyl protons and in the ^{13}C n.m.r. spectrum the signals due to the geminal methyl carbons and C-5 are accidentally coincident. However, the



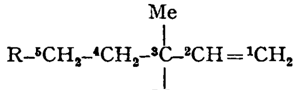
(1)

^{13}C n.m.r. spectrum of the deuteriated compound indicates deuteriation at C-5. In the absence of platinum no H–D exchange is observed in the alkyl part of the alkenes. There is, however, some exchange of the olefinic protons, which is ascribed to acid-catalysed exchange.

Table. *Exchange of hydrogen for deuterium in compound* (**2**)[a]

	D in		
R	$-CH{=}CH_2$ % ± 5	$-{}^{5}CH_2-$ % ± 5	rest of molecule %
H	15	54	<5
CH_3	23	44	<5
C_2H_5	30	[b]	[b]

[a] With 3,3-dimethylbut-1-ene 30 ± 5% exchange was found in the $-CH{=}CH_2$ unit and <5% in the rest of the molecules.
[b] ^1H n.m.r. spectrum too complex to allow accurate measurement.



$$\mathrm{R{-}^{5}CH_2{-}^{4}CH_2{-}^{3}\overset{Me}{\underset{Me}{C}}{-}^{2}CH{=}^{1}CH_2}$$

(**2**)

Treatment of 3,3-dimethylpent-1-ene with sodium chloroplatinate in aqueous acetic acid containing perchloric acid for 3 h at 100° gives bis-(3,3-dimethylpent-1-ene)dichlorodi-μ-chloro-diplatinum(II). The ^1H n.m.r. spectrum (100 MHz in $CDCl_3$) contains two singlets, at τ 8·07 and 8·38, assigned to the geminal methyl protons. The non-equivalence of the methyl groups may be due to the creation of a chiral centre at C-2 on complexation.[3] Addition of free olefin to a solution of the complex in deuteriochloroform causes coalescence of the signals assigned to the geminal methyl groups, indicating exchange between free and co-ordinated olefin. The kinetics of this exchange are now under investigation.

Thus it seems probable that the first step in the H–D exchange involves co-ordination of the alkene to the platinum, followed by hydrogen abstraction from C-5 to give an intermediate species (**1**). Analogous hydrogen abstractions by transition metals from complexed tertiary phosphine ligands are well known.[4] The preferential formation of a five-membered ring in the proposed intermediate is not unexpected since it has been shown that internal metallation of tertiary phosphine or tertiary phosphite ligands, complexed to transition metals, preferentially gives rise to complexes containing five-membered rings.[5]

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