Homogeneous Catalysis of Olefin Isomerisation. Part VI.[1] Pent-1-ene Isomerisation catalysed by Solutions of Dodecacarbonyltri-iron(0) and of Bis(benzonitrile)dichloropalladium(II) in Benzene

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Isomerisation of pent-1-ene to *cis*- and *trans*-pent-2-ene is catalysed at 50 °C and above by solutions in benzene of $Fe_3(CO)_{12}$ and of $PdCl_2(C_6H_5CN)_2$. In both cases, preferential formation of *trans*-pent-2-ene occurs. Isomerisation of $[1,2\text{-}^2H_2]$pent-1-ene reveals that each reaction proceeds by the intramolecular transfer of hydrogen and deuterium atoms. The reaction mechanisms involve π-allylic intermediates; for the palladium-catalysed reaction bis-π-allyl complexes may also participate.

Previous papers in this series have described the isomerisation of pent-1-ene catalysed in solution by complexes of nickel,[2] ruthenium,[1,3,4] rhodium,[4] osmium,[2] iridium,[5] and platinum,[5] each having phosphorus-containing ligands. Use of deuterium-labelled alkene has shown that these reactions occur *via* the formation of alkyl intermediates [equation (1)], the fine details of mechanism varying from one reaction to another. In no case has reaction by the alternative mechanism been observed, *i.e.* by the formation of π-allylic intermediates [equation (2)]. This experience is typical of that recorded in the literature; of all the homogeneous olefin isomerisations catalysed by Group VIII metal complexes so far reported, all but a very few occur *via* the formation of alkyl intermediates.

$$\text{pent-1-ene} + \text{H-M} \rightleftharpoons \text{(pentyl)-M} \rightleftharpoons \text{pent-2-ene} + \text{H-M} \qquad (1)$$

$$\text{pent-1-ene} + \text{M} \rightleftharpoons \text{(1-ethyl-}\pi\text{-allyl)-M-H} \rightleftharpoons \text{pent-2-ene} + \text{M} \qquad (2)$$

This situation is not surprising in view of the facility with which hydrido-complexes may be formed and their extensive chemical properties.[6] Isomerisation *via* alkyl intermediates can be expected to occur whenever reactive hydrido-complexes are formed in solution. It is not necessary for the original solid complex itself to be a hydride. Complexes without hydrogen ligands may be converted to hydrido-complexes by reaction with a wide variety of reagents (*e.g.* amine bases, alcohols, protonic acids) which may be present as the solvent, or a component of the solvent, or as a so-called co-catalyst.[4,7] If such reagents are absent, a hydrido-complex may form spontaneously by intramolecular reaction of, say, a triphenylphosphine ligand with the transition metal.[8,9]

Consequently, to observe isomerisation *via* π-allylic intermediates [equation (2)] it is necessary to choose for study systems in which these possibilities of hydrido-complex formation do not readily arise. The solvent must be inert, co-catalysts avoided, and complexes chosen which do not contain substituted phosphines as ligands. Two systems that apparently meet these requirements are $Fe_3(CO)_{12}$ in benzene, and $PdCl_2(C_6H_5CN)_2$ in benzene. Deuteriopent-1-ene isomerisation catalysed by each system is reported here.

The isomerisation of hexenes,[10] oct-1-ene,[11] and undec-1-ene [12] catalysed by $Fe_3(CO)_{12}$ has been known for some time. Although equations (1) and (2) were appreciated to be alternative mechanisms by which isomerisation might occur, the former was favoured on the grounds that iron carbonyl hydrides are easily formed,[6] are reactive even in minute concentrations,[6] and such hydrides are known to catalyse olefin isomerisation *via* the formation of alkyl intermediates.[13] How-

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ever, these conclusions have not hitherto been subjected to the test of a deuterium tracer study.

Our choice of the second reaction was influenced by the report of Harrod and Chalk [14] that [1,2-$^2H_2$]pent-1-ene isomerisation catalysed by $PdCl_2(C_6H_5CN)_2$ in benzene proceeds *via* the formation of π-allylic intermediates. Analysis of products was by n.m.r. and i.r. spectroscopy; measurements of deuterium distributions by mass spectrometry were not made. The present work seeks to confirm and extend our knowledge of this reaction.

EXPERIMENTAL

$Fe_3(CO)_{12}$ (Alpha Inorganics) was used as received. $PdCl_2(C_6H_5CN)_2$ was prepared as described in the literature.[15] Two preparations of deuteriopent-1-ene were carried out. One, having the deuterium distribution: C_5H_{10}, 0·4%; C_5H_9D, 2·6%; $C_5H_8D_2$, 96·8%; $C_5H_7D_3$, 0·2%, and deuterium location as shown in Table 1, was prepared as described previously [2] by the reaction of deuterium with pent-1-yne catalysed by $RhCl(PPh_3)_3$. This sample was used to study the iron-catalysed reaction. A second preparation having the deuterium distribution and location shown in Table 3 was prepared as described previously [3] by the deuteriation of pent-1-yne catalysed by quinoline-poisoned palladium supported on barium sulphate. This sample was used to study the palladium-catalysed reaction.

TABLE 1

Location of deuterium in pentenes during the isomerisation of [1,2-$^2H_2$]pent-1-ene catalysed by dodecacarbonyltri-iron(0) in benzene at 50 °C

[Pent-1-ene] = 1·0M initially. [Complex] = 2·0mM. Volume of solution = 10 ml

Olefin	Extent of isomerisation (%)		Mean number of deuterium atoms present at each carbon atom [a] C-1	C-2	C-3	C-4	C-5
Pent-1-ene	0		0·97	1·00	0·00	0·00	0·00
	16		0·89	0·96	0·05	0·00	0·07
	46		0·96	0·96	0·00	0·00	0·05
cis-Pent-2-ene	46		0·52	0·55		0·61	0·49
trans-Pent-2-ene	16		0·48	0·42		0·61	0·46
	46		0·48	0·41		0·56	0·52
Pent-2-ene		*Calculated*	*0·57*	*0·48*		*0·52*	*0·40*

[a] Values correct to ±0·05. Total deuterium number of 1·97 was determined by mass spectrometry.

All other experimental and analytical procedures were performed as described earlier.[2,3]

RESULTS

The Iron-catalysed Reaction.—Deep green solutions of $Fe_3(CO)_{12}$ in benzene catalysed pent-1-ene isomerisation at 50 and 80 °C. Short induction periods were observed in reactions at 50 °C. The initial *cis* : *trans* ratio in the product was 0·35 : 1·00. The maximum rate increased with increasing complex concentration and with increasing temperature. Typical maximum rates were 0·11 mmol l^{-1} s^{-1} at 50 °C and 0·93 mmol l^{-1} s^{-1} at 80 °C when [$Fe_3(CO)_{12}$] = 3·1mM and [pent-1-ene] = 1·0M. As reactions progressed, solutions became less strongly coloured and catalytic activity diminished. The rate of decolouration increased with increasing temperature and, at 80 °C, isomerisation stopped before the pentene isomers attained thermodynamic equilibrium.

Isomerisation of [1,2-$^2H_2$]pent-1-ene was investigated at 50 °C. Full analysis was carried out at 16 and 46% removal of pent-1-ene. Both the *cis*- and the *trans*-pent-2-ene formed exhibited isotopic compositions *identical* to that of the reactant (see Experimental section). Table 1 shows that the deuterium atoms, which were located at C-1 and C-2 in the reactant, are distributed throughout the pent-2-ene. The ^1H n.m.r. spectrum of the pent-2-ene revealed that the isotopic composition of the ethyl group (*i.e.* at C-4 and C-5) was as shown in Table 2.

The Palladium-catalysed Reaction.—Solutions of $PdCl_2(C_6H_5CN)_2$ in benzene catalysed pent-1-ene isomerisation at 50 °C. Reactions exhibited a small induction period, maximum rate was achieved after 20 min and reaction was complete after 5 h (Figure 1). The induction period has been reported previously by Sparke *et al.*[16] for the isomerisation of 4-methylpent-1-ene at 50—65 °C by this complex in the absence of solvent, but not by Bond and Hellier [17] or by Harrod and Chalk [14] for pent-1-ene isomerisation catalysed by this complex in benzene at 70 or 55 °C respectively.

TABLE 2

Observed and calculated compositions of the ethyl fragment of pent-2-ene

	Iron-catalysed reaction		Palladium-catalysed reaction	
Fragment	Observed %	Calc. %	Observed %	Calc. %
$-CH_2-CH_3$	40	44	66	65
$-CHD-CH_2D$	30	34	17	19
$-CHD-CH_3$	20	16	17	11
$-CH_2-CH_2D$	10	6	Trace	5

The initial *cis* : *trans* ratio in the product was 0·6 : 1·0.

Isomerisation of deuteriated pent-1-ene is described in Table 3; full analysis was carried out after 5 and 52% conversion. Little change in the distribution or location of deuterium in pent-1-ene occurs during reaction. Isomerisation is accompanied by little intermolecular hydrogen or deuterium transfer, but once again the ^1H n.m.r. spectra reveal that the deuterium atoms formerly present at C-1 and C-2 in the reactant become distributed throughout pent-2-ene during the course of isomerisation. The proportions of various ethyl groups present in the pent-2-ene are recorded in Table 2.

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[14] J. F. Harrod and A. J. Chalk, *J. Amer. Chem. Soc.*, 1966, **88**, 3491.

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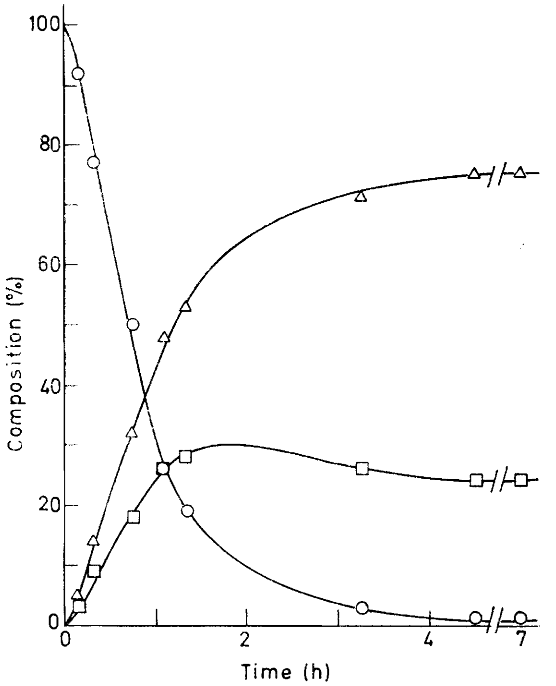

FIGURE 1 Isomerisation of pent-1-ene catalysed by $PdCl_2(C_6H_5CN)_2$ in benzene: variation of composition with time. ○, Pent-1-ene; △, *trans*-pent-2-ene; □, *cis*-pent-2-ene. [Olefin] = 1·6M. $[PdCl_2(C_6H_5CN)_2]$ = 2·8mM. Temperature = 50 °C

DISCUSSION

The Iron-catalysed Reaction.—Table 1 shows that isomerisation occurred by intramolecular transfer of hydrogen or deuterium atoms; this is interpreted by the mechanism involving π-allylic intermediates in Figure 2. The mechanism shows that, because deuterium moves by 1,3- and 2,4-shifts, deuterium is conserved as between (C-1 + C-3 + C-5) and (C-2 + C-4) and hence only six isotopically distinguishable pent-2-enes can be formed. These six distinguishable pent-2-enes possess between them the four isotopically distinguishable ethyl groups, listed in Table 2. Figure 2 shows that the most abundant is formed as a result of one hydrogen transfer, and the least abundant by not less than four such transfers. This indicates that pent-2-ene complexed to the catalyst must be displaced (probably by pent-1-ene) before undergoing further reaction. The probability of this happening can be determined quantitatively.[18] Let the probability of isomerisation of co-ordinated pent-2-ene be *a* and the probability of displacement of pent-2-ene be $(1 - a)$. Further, let *b* be the fraction of isomerisation that gives rise to a pent-1-ene complex and $(1 - b)$ be the fraction that gives another pent-2-ene complex by a further movement of the double bond. On the assumption that steady state conditions pertain, six equations relating the concentrations of the six isotopically distinguishable pent-2-enes and *a* and *b* can be derived. These can be solved for given values of *a* and *b*, and the calculated locations of deuterium compared with experiment. Table 1 shows the result of a calculation for which $a = 0{\cdot}700$ and $b = 0{\cdot}005$ which provides fair agreement with the experimental result obtained after 16% reaction. The value of *a* shows that pent-2-ene has a 30% chance of being displaced from the catalytically active complex. Further, the conversion of co-ordinated pent-2-ene to co-ordinated pent-1-ene is seen from the value of *b* to be an unfavourable process. This alone suffices to interpret why no isotopic change is observed in pent-1-ene during reaction. The relative abundances of the four isotopically distinguishable ethyl groups derived from the calculation are shown in Table 2. The calculated values agree well with experiment.

The mechanism (Figure 2) is consistent with the observed preferential formation of pent-2-ene in the *trans*-configuration, because it is known from studies of 1-methyl-π-allyl tricarbonyl halides of iron that the *syn*-conformer (which gives *trans*-pent-2-ene on hydrogen atom addition) is more stable than the alternative *anti*-conformer.[19]

TABLE 3

Distribution and location of deuterium in pentene during isomerisation of $[1,2\text{-}^2H_2]$pent-1-ene catalysed by bis(benzonitrile)dichloropalladium(II) in benzene at 50°

[Pent-1-ene] = 1·4M initially. [Complex] = 2·7mM. Volume of solution = 3 ml

Olefin	Extent of isomerisation (%)	Deuterium distribution (%)							Mean number of deuterium atoms present at each carbon atom [c]				
		C_5H_{10}	C_5H_9D	$C_5H_8D_2$	$C_5H_7D_3$	$C_5H_6D_4$ [a]	D.N.[b]		C-1	C-2	C-3	C-4	C-5
Pent-1-ene	0	1·4	16·6	66·6	15·0	0·4	1·96		1·07	0·88	0·02	0·01	0·00
	5	1·8	18·2	64·7	13·5	2·0	1·96		1·08	0·91	0·00	0·00	0·00
	52	1·9	19·3	64·1	13·6	1·1	1·93		1·00	0·83	0·00	0·00	0·10
cis-Pent-2-ene	5	3·0	17·4	61·5	16·3	1·7	1·96						
	52	2·5	20·8	57·3	17·7	1·7	1·95		0·60	0·76 [d]		0·34	0·25
trans-Pent-2-ene	5	3·0	19·2	59·3	15·5	3·0	1·96						
	52	2·3	21·4	56·5	17·9	1·8	1·95		0·66	0·68 [d]		0·30	0·31
Pent-2-ene								*Calc.*	*0·60*	*0·72*		*0·34*	*0·29*

[a] More highly deuteriated pentenes not observed. [b] D.N. = deuterium number of the pentene sample. [c] Values uncertain to ±0·10. [d] Majority of deuterium at C-2.

The Palladium-catalysed Reaction.—Once again, intramolecular transfer of hydrogen or deuterium atoms, and relocation of deuterium throughout pent-2-ene are the main features that accompany pent-1-ene isomerisation, and hence the mechanism is again represented by

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[18] B. Hudson, Ph.D. Thesis, University of Hull, 1971.

[19] M. L. H. Green, in ' Organometallic Compounds, ' Methuen, London, 1968, p. 57, and references contained therein.

Figure 2. A satisfactory calculation of the location of deuterium in pent-2-ene was obtained using $a = b = 0{\cdot}95$. Thus, by comparison with the iron-catalysed reaction, the probability of displacement of co-ordinated pent-2-ene by pent-1-ene was reduced, and the fraction of isomerisation that gives pent-1-ene was greatly increased. Consequently, failure of the reaction to produce free pent-1-ene containing considerable quantities of deuterium at C-3, C-4, and C-5 indicates that the rate of displacement of co-ordinated pent-1-ene was virtually zero. The calculated and observed relative abundances of the four isotopically distinguishable ethyl groups in pent-2-ene again show satisfactory agreement (Table 2).

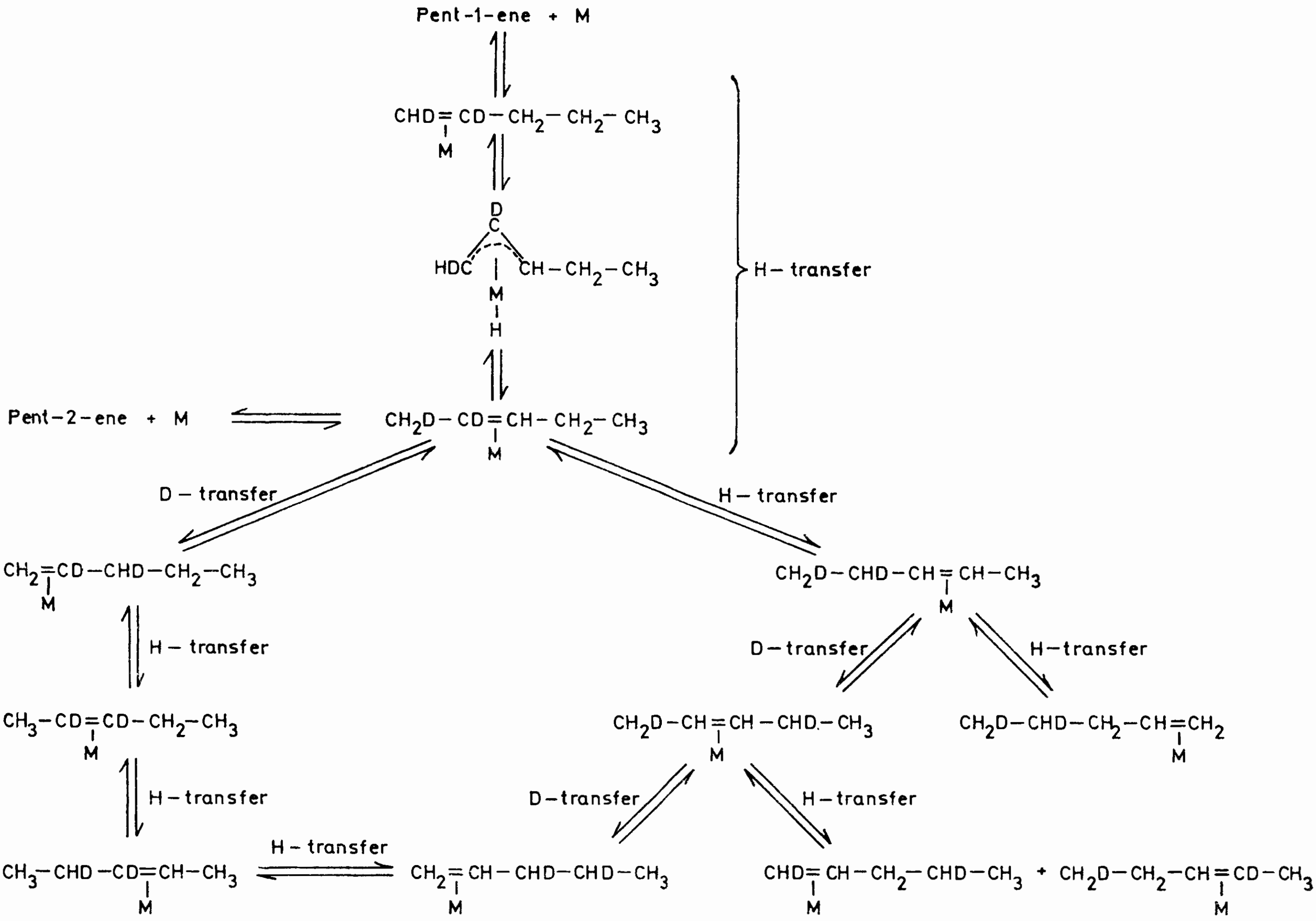
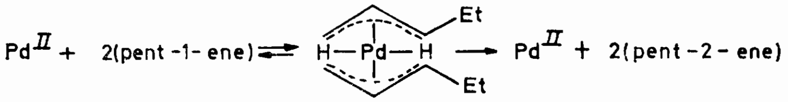


FIGURE 2 A mechanism for the isomerisation of pent-1-ene *via* π-allylic intermediates

The small amount of deuterium redistribution evident in Table 3 is not interpreted by Figure 2. That this may have occurred as a result of a small amount of isomerisation *via* the formation of alkyl intermediates is discounted on the ground that this catalyst solution was not active for the redistribution of deuterium in *trans*-[$^2H_2$]ethylene.[9] Hence, the redistribution in Table 3 seems to have occurred *via* the formation of π-allylic intermediates. Equation (3) provides a possible route: if the hydrogen ligands of the bis-π-allylic complex were equivalent, the chances of intermolecular and intramolecular transfer of hydrogen during isomerisation would be equal.



$$\mathrm{Pd^{II}} + 2(\text{pent-1-ene}) \rightleftharpoons \overset{\text{Et}}{\underset{\text{Et}}{\mathrm{H{-}Pd{-}H}}} \longrightarrow \mathrm{Pd^{II}} + 2(\text{pent-2-ene}) \quad (3)$$

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