

Homogeneous Catalysis of Olefin Isomerisation. Part II.¹ (a) Isomerisation of Pent-1-ene Catalysed by Hydridochlorotris(triphenylphosphine)-ruthenium(II) in Benzene; and (b) a Novel Procedure for Evaluating Velocity Constants for a Network of Three First-order Reversible Reactions

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The isomerisation of pent-1-ene to *cis*-pent-2-ene (60%) and *trans*-pent-2-ene (40%) is catalysed at 50° by solutions of RuHCl(PPh₃)₃ in benzene. Reaction is of the first order with respect both to complex and to pent-1-ene when the concentrations of each are low. Departures from first-order behaviour occur because the catalytically active species are formed by dissociation of the complex, and because of changes in the nature of the solvent at the higher pentene concentrations. Interference of the reaction by-products is slight. The six velocity constants for the interconversion of the three pentene isomers have been determined by a new procedure involving the use of Laplace–Carson transforms.

Isomerisation of deuterium-labelled pent-1-ene has revealed (i) that equilibrium is established between uncoordinated and co-ordinated pent-1-ene, (ii) that redistribution of deuterium in pent-1-ene accompanies its isomerisation, (iii) that normally isomerisation involves the movement of the double bond to the adjacent position only, (iv) that *cis*- and *trans*-pent-2-ene are each formed by a mechanism involving a pentyl intermediate, (v) that a mechanism involving a π -allylic intermediate also contributes to the formation of the *trans*-isomer, and (vi) that some processes require the formation of transient species having two hydrogen atoms as ligands of ruthenium and in which two phosphine ligands have been lost by dissociation.

In this and succeeding Parts of this series we report an investigation of pent-1-ene isomerisation catalysed by at least one complex of each metal of Group VIII. Several ruthenium complexes catalyse olefin isomerisation. In 1968, pent-1-ene isomerisation catalysed by RuCl₂(PPh₃)₃ in benzene–HCl solution, and by RuHCl(PPh₃)₃ in benzene, was reported from this laboratory.² In the same year isomerisation of hex-1-ene to hex-2-ene catalysed by solutions of RuHCl(PPh₃)₃ and of RuH(OCOCF₃)(PPh₃)₃ was reported by Wilkinson and his co-workers.³ Several mono- and poly-nuclear ruthenium complexes in appropriate solvents catalyse oct-1-ene isomerisation,⁴ although in some instances the presence of molecular hydrogen is required.⁵ James has recently reviewed these and related ruthenium-catalysed reactions.⁶ The present work appears to be the first detailed study of double-bond migration catalysed by a ruthenium complex.

EXPERIMENTAL

The preparation of RuHCl(PPh₃)₃ and the purification of benzene, are described in Part I. The reaction vessel used has been described (see vessel 3, in Figure 1 of reference 2). Pent-1-ene (Newton–Maine Ltd.) was freed of peroxide impurities immediately before use by passage through a column of activated alumina. The usual ferrous thiocyanate reagent was used to test for the presence of peroxide in pent-1-ene. To determine whether pentene underwent polymerisation, each reaction contained a known concentration of 2-methylbutane which served as a marker. No loss of pentene by polymerisation was ever observed.

The isotopically labelled pent-2-ene was prepared by the

reaction of pent-1-yne with deuterium catalysed by palladium supported at a concentration of 5% (w/w) on barium sulphate. The supported catalyst (0.32 g) was poisoned for pentene hydrogenation by synthetic quinoline (0.06 g) as suggested by Augustine.⁷ The product was purified by preparative g.l.c. Mass spectrometric and n.m.r. analyses are given in Table 1. The product was sufficiently well labelled for present purposes; a superior method of preparation, giving >95% C₅H₈D₂, is described in a later Part.

Products of reaction were identified quantitatively by g.l.c. and, when necessary, the individual products were condensed after elution and analysed for deuterium content and location by mass and n.m.r. spectrometry respectively. Distributions of deuterium in pentenes were obtained using an A.E.I. MS3, the ionising voltage being 12 eV. Other analyses were performed as described in Part I.

RESULTS

Solutions of hydridochlorotris(triphenylphosphine)-ruthenium(II) in benzene at 50° catalysed the isomerisation of pent-1-ene to *trans*- and *cis*-pent-2-ene (Figure 1), and of 2-methylbut-1-ene to 2-methylbut-2-ene. 3-Methylbut-1-ene was not formed as an initial product of the latter reaction. The rate of removal of each reactant at a given instant during reaction was strictly proportional to $([P_t] - [P_\infty])$ where $[P_t]$ and $[P_\infty]$ are, respectively, the concentrations of reactant olefin after time t and at a time when isomeric equilibrium had been achieved. $[P_\infty]$ was determined experimentally as 2.5% for pent-1-ene and 7.0% for 2-methylbut-1-ene at 50°. This first-order decay of reactant concentration with time shows that co-ordination of pent-2-ene to the catalytically active complex was negligible until the near-removal of the reactant. The rate of pent-1-ene isomerisation was more rapid than that of 2-methylbut-1-ene

¹ Part I, B. Hudson, D. E. Webster, and P. B. Wells, *J.C.S. Dalton*, 1972, 1204.

² B. Hudson, P. C. Taylor, D. E. Webster, and P. B. Wells, *Discuss. Faraday Soc.*, 1968, No. 46, 37.

³ P. S. Hallman, B. R. McGarvey, and G. Wilkinson, *J. Chem. Soc. (A)*, 1968, 3143; D. Rose, J. D. Gilbert, R. P. Richardson, and G. Wilkinson, *ibid.*, 1969, 2610.

⁴ P. Abley and F. J. McQuillin, *Discuss. Faraday Soc.*, 1968, No. 46, 31.

⁵ J. Norton, D. Valentine, and J. P. Collman, *J. Amer. Chem. Soc.*, 1969, **91**, 7537.

⁶ B. R. James, *Inorg. Chim. Acta Rev.*, 1970, **4**, 73.

⁷ R. L. Augustine, 'Catalytic Hydrogenation,' Arnold, London, 1965, 152.

by an order of magnitude; typical half-lifetimes for reactions at 50° involving 1.0 mmol l⁻¹ of complex were *ca.* 1 h for pent-1-ene isomerisation and *ca.* 20 h for 2-methylbut-1-ene isomerisation. *cis*-Pent-2-ene was formed more rapidly than *trans*-pent-2-ene from pent-1-ene, and subsequent *cis*-*trans* isomerisation was slow.

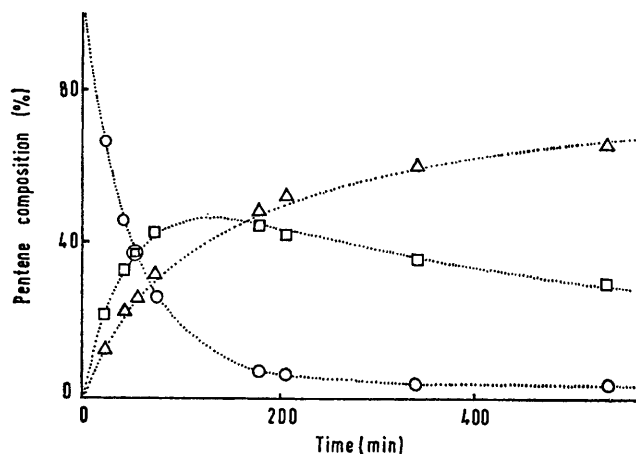


FIGURE 1 Pent-1-ene isomerisation at 50°. The points show the observed variation of pentene composition with time. The curves represent the variation of pentene composition computed from the rate constants stated in the text. [Pentene] = 0.61M; [RuHCl(PPh₃)₃] = 1.7 mM. ○ = Pent-1-ene; □ = *cis*-pent-2-ene; △ = *trans*-pent-2-ene

Orders of reaction by the initial rate method were determined for the isomerisation of 2-methylbut-1-ene (Figure 2).

by studying the reaction of deuterium-labelled pent-1-ene. The distribution of deuterium in reactant and products as

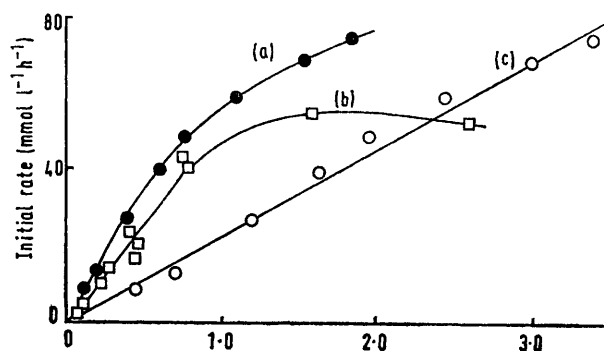


FIGURE 2 2-Methylbut-1-ene isomerisation at 50°. Dependence of initial rate of isomerisation upon the concentration of complex (curve a), [olefin] = 1.1M throughout; upon the initial concentration of 2-methylbut-1-ene (curve b), [complex] = 0.5 mM throughout; and upon the function $\{(1 - 4[\text{complex}]/K)^{1/2} - 1\}$ (line c)

isomerisation proceeded is given in Table 1, as are the locations of deuterium in the products, as determined from the ¹H n.m.r. spectrum by a subtractive procedure. As reaction proceeded, redistribution of deuterium occurred in pent-1-ene and the deuterium number fell. The *cis*- and *trans*-pent-2-ene were each formed with a deuterium content that exceeded slightly that of the original reactant, and the distributions of deuterium in these isomers were not quite identical. Isotope redistribution continued long after

TABLE 1

Distribution and location of deuterium in pentenes

[Pent-1-ene] = 0.77M initially. Volume of solution = 15ml
[RuHCl(PPh₃)₃] = 9.9 × 10⁻⁴M. Temperature = 50°

Extent of isomerisation (%)	Distribution (%)							Deuterium no. of sample	Mean deuterium number at each carbon atom ^c				
	C ₅ H ₁₀	C ₅ H ₉ D	C ₅ H ₈ D ₂	C ₅ H ₇ D ₃	C ₅ H ₆ D ₄	C ₅ H ₅ D ₅	C ₅ H ₄ D ₆ ^a		C-1	C-2	C-3	C-4	C-5
Pent-1-ene	0	1.4	16.6	66.6	15.0	0.4	0.0	1.96	1.06	0.87	0.00	0.01	0.02
	9	2.9	23.0	55.3	17.3	1.4	0.1	1.92					
	25	5.0	28.1	45.6	18.3	2.7	0.0	1.86	0.99	0.61	0.21	0.00	0.05
	38	5.8	30.3	42.0	18.5	3.2	0.2	1.84	0.97	0.50	0.32	0.06	0.00
	48	6.8	31.2	38.8	18.7	4.0	0.4	1.83	1.00	0.48	0.34	0.00	0.01
	67	9.8	31.4	36.0	17.9	4.4	0.5	1.77	0.87	0.42	0.48	0.00	0.00
100 ^b	11.4	27.7	30.5	18.3	8.3	2.7	1.96						
<i>cis</i> -Pent-2-ene	9	2.0	16.9	49.5	26.5	5.1	0.1	2.16	C-1	C-2 + C-3		C-4	C-5
	25	2.5	19.0	45.9	26.2	6.0	0.3	2.15	1.29	0.80		0.04	0.02
	38	2.9	20.5	45.3	25.2	5.8	0.3	2.11	1.23	0.76		0.11	0.01
	48	3.7	23.3	42.7	23.6	6.3	0.4	2.07					
	67	6.9	23.8	40.2	23.1	5.6	0.5	1.98	1.13	0.62		0.17	0.06
100 ^b	10.0	27.3	32.3	19.8	7.8	2.2	1.97	0.64	0.70		0.33	0.30	
<i>trans</i> -Pent-2-ene	25	4.0	22.2	46.2	22.1	4.9	0.5	2.03					
	38	3.9	23.0	45.0	21.7	5.0	0.4	2.00	0.99	0.86		0.15	0.00
	48	3.9	25.0	44.1	21.4	5.1	0.4	2.00					
	100 ^b	9.3	27.9	34.3	19.6	6.8	1.6	1.93	0.76	0.43		0.29	0.45

^a More highly deuteriated pentenes not observed. ^b After 48 h. ^c Values uncertain to ±0.05.

The reaction was of the first order with respect to complex concentration over the range 0.0 to 0.6 mmol l⁻¹, whereafter the order decreased. The order in olefin was unity over the range 0.0 to 0.7 mol l⁻¹ but thereafter the rate became almost independent of olefin concentration.

The detailed mechanism of isomerisation was examined

isomeric equilibrium had been achieved; after a reaction time equal to fifty times the half-lifetime of the isomerisation (hereafter called 'the long reaction') the deuterium distributions in the three isomers were similar, but they still did not correspond to a random distribution. Table 1 shows that pent-1-ene undergoes a marginal loss of deuterium at C-1,

a substantial loss at C-2, a substantial gain at C-3, and no change at C-4 and C-5 within the period of this experiment. Isomerisation of pent-1-ene to *cis*-pent-2-ene resulted in the acquisition of deuterium at C-1. No other nett movement of deuterium had occurred in this process at 25% isomerisation. After 38% reaction deuterium was observed at C-4 in the pent-2-ene. The deuterium content at C-1 in the *trans*-pent-2-ene was lower than that at the same position in *cis*-pent-2-ene. Analysis of products of the long reaction showed that deuterium was eventually incorporated into pent-2-ene at all positions, but the disparity between the deuterium contents of the two methyl groups shows that, even after this long period of reaction, isotopic equilibrium was not achieved.

In Part I, we reported that, for reactions of ethylene with benzene solutions of this complex, exchange may take place between the hydrogen atoms in the *ortho*-positions of the phenyl groups of the triphenylphosphine ligands and deuterium atoms of a deuteriated olefin. Mass spectrometric analysis of complex retrieved from solutions used in the present work showed that such exchange had occurred (Table 2). The deuterium number of the phosphine rose as a result of this exchange from zero to a value of *ca.* 1.7 and later declined to 1.2. The decline occurred because, as

benzene ($[\text{RuHCl}(\text{PPh}_3)_3] = 0.05 \text{ mmol l}^{-1}$, initial [2-methylbut-1-ene] = 0.56 mmol l^{-1} , temperature = 50° in each case). Furthermore, the colours of reaction mixtures containing high concentrations of olefin/marker or n-hexane were much paler than those containing, say, 0.3 mmol l^{-1} of aliphatic hydrocarbon. Thus, it is likely that the observed change in order is attributable, at least in part, to a change in the nature of the solvent in the experiments described in Figure 2.

The non-linearity of the dependence of initial rate upon complex concentration (curve *a*, Figure 1) occurs as a result of the dissociation of the complex in solution. Equation (1) describes the concentration of catalytically active species, $[\text{C}]_\alpha$, when an active species is obtained by the dissociation of one (phosphine) ligand from the original complex. In equation (1) K is the equilibrium constant for the process, $[\text{C}]$ the original concentration

$$[\text{C}]_\alpha = \frac{K}{2} \left\{ \left(1 + \frac{4[\text{C}]}{K} \right)^{\frac{1}{2}} - 1 \right\} \quad (1)$$

of pentene, and α the degree of dissociation. A graphical test of this equation is shown in Figure 2 (line *c*); the

TABLE 2

Distribution of deuterium in triphenylphosphine obtained (see Experimental) from the reaction described in Table 1

Extent of isomerisation of pent-1-ene (%)	Distribution (%)						Deuterium no.
	$\text{PC}_{18}\text{H}_{15}$	$\text{PC}_{18}\text{H}_{14}\text{D}$	$\text{PC}_{18}\text{H}_{13}\text{D}_2$	$\text{PC}_{18}\text{H}_{12}\text{D}_3$	$\text{PC}_{18}\text{H}_{11}\text{D}_4$	$\text{PC}_{18}\text{H}_{10}\text{D}_5$ ^a	
0	100	0	0	0	0	0	0.0
9	63	26	5	2	2	2	0.6
25	48	34	13	3	1	1	0.8
38	34	32	21	10	2	1	1.2
48	24	33	27	12	3	1	1.4
67	18	31	29	16	6	1	1.7
100 ^b	29	36	23	11	1	0	1.2

^a More highly deuteriated triphenylphosphines not observed. ^b After 48 h.

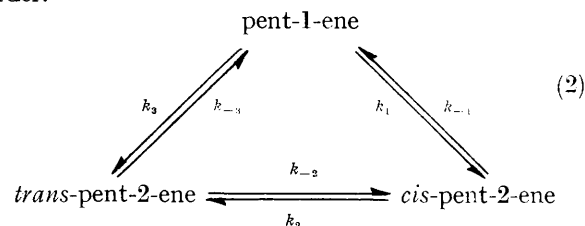
shown in Table 1, exchange in pentene extended to carbon atoms C-4 and C-5 during this period, and hence the number of protium atoms participating in the exchange reaction increased. The n.m.r. spectrum of the phosphine was not obtained but it is expected, by analogy with the previous work,¹ that exchange occurred solely in the *ortho*-positions. This is consistent with the observation that, after the long reaction, the deuterium number per site of exchange was 0.19 both for the phosphine (1.18/6) and for the pentene (1.96/10).

DISCUSSION

Kinetic Aspects of Reaction.—The change of order in pentene from first to zero may be attributable to saturation of catalytically active species by olefin at the higher olefin concentrations. Alternatively, the departure from linearity at higher concentrations may be caused by a change in the nature of the solvent as the concentration of aliphatic hydrocarbon is increased. Positive evidence in favour of the latter interpretation was obtained by substitution of part of the benzene solvent by n-hexane, an aliphatic hydrocarbon of dielectric constant similar to that of benzene. The initial isomerisation rate diminished from a value of $31 \text{ mmol l}^{-1} \text{ h}^{-1}$ in pure benzene to $15 \text{ mmol l}^{-1} \text{ h}^{-1}$ in 3M-n-hexane in

values of K required to give the best straight line is $4 \times 10^{-4} \text{ M}$, and thence $\alpha = 0.06$ when $[\text{C}] = 0.1 \text{ M}$. The n.m.r. spectrum of the complex did not exhibit absorptions attributable to dissociated species, but at such low concentration they would not have been detectable.

Figure 1 contains the information necessary for the determination of the velocity constants contained in Scheme (2) provided that each process is of the first order.



A method for the determination of velocity constants from composition-time data for such a system of coupled first-order reversible reactions has been described by Wei and Prater,⁸ and their procedure has been used in this laboratory to determine the relative velocity constants

⁸ J. Wei and C. D. Prater, *Adv. Catalysis*, 1962, **13**, 203.

for butene isomerisation catalysed by metallic iridium.⁹ One of us (B. H.) has now devised an alternative procedure for the evaluation of these constants employing Laplace-Carson transforms and a computational optimisation procedure (see Appendix). Essentially the same procedure has been reported in a preliminary communication by McLaughlin and Rozett.¹⁰ Velocity constants (units: min^{-1}) derived by this procedure for the reaction shown in Figure 1 are:

$$10^4 k_1 = 118 \pm 8; 10^4 k_2 = 23 \pm 7; 10^4 k_3 = 70 \pm 7; \\ 10^4 k_{-1} = 11 \pm 9; 10^4 k_{-2} = 5 \pm 4; 10^4 k_{-3} = 4 \pm 4.$$

In Figure 1, the points represent the experimental observations; the curves, however, have not been drawn manually, but have been obtained from the graph-plotter of the computer, and represent the expected dependence of the concentrations upon time given the above velocity constants. The agreement between observation and prediction, besides being most satisfactory, supports the assumption that the entire system can be described in terms of first-order reversible reactions.

The accurately first-order decay of pent-1-ene concentration with time enables the first-order velocity constants for the gross removal (k') and reformation (k'') of pent-1-ene to be obtained independently from the gradient of the usual semi-logarithmic function plot. These velocity constants for the reaction recorded in Figure 1 are $10^4 k' = 189 \text{ min}^{-1}$ and $10^4 k'' = 5 \text{ min}^{-1}$ which compare with computed values of $188 \times 10^{-4} \text{ min}^{-1}$ ($k' = k_1 + k_3$) and $8 \times 10^{-4} \text{ min}^{-1}$ ($k'' = 0.6 k_{-1} + 0.4 k_{-3}$). Agreement is satisfactory.

Repetition of this work showed that the experimental results were reproducible, and the velocity constants dependable.

Deuterium Movement during Isomerisation.—The most important features of reaction revealed by the tracer technique are (i) the formation initially of pent-2-ene containing no deuterium at C-4 and C-5, (ii) the transfer of deuterium in pent-1-ene from C-2 to C-3, and (iii) exchange of deuterium between olefin and the triphenylphosphine ligands. The first of these observations shows, very simply, that generally the double bond moves only once, to the adjacent C(2)–C(3) position, during one period of co-ordination of the C_5 -entity at the catalytically active complex. Observation (iii) has been discussed in Part I, and will be considered here only insofar as it assists the interpretation of (ii).

The change in the mass and n.m.r. spectra of pent-1-ene as reaction progressed demonstrates that a substantial proportion of pent-1-ene undergoes co-ordination, isotope rearrangement, and dissociation from the catalyst. The transfer of deuterium from C-2 to C-3 in pent-1-ene is an important feature of reaction; simultaneously there may be a slight loss of deuterium from C-1. Transfer of deuterium between adjacent carbon atoms of a hydrocarbon definitely requires the participation of alkyl intermediates. The simplest mechanism to interpret the

shift of deuterium from C-2 to C-3 (not shown), involving the participation of the symmetrical 3-pentyl intermediate is unacceptable because the required deuterium shift would be accompanied by double-bond movement beyond C-3, which was not observed. Similarly, processes involving the re-co-ordination of pent-2-ene and its isomerisation back to pent-1-ene, which can in principle affect the desired deuterium shift, did not occur because a calculation based on the above velocity constants (see Appendix) shows that the amount of pent-1-ene reformed from *trans*- and *cis*-pent-2-ene after 67% reaction was only 0.3 and 1.3% respectively. It appears that the C-2 to C-3 deuterium shift occurs by a more complicated mechanism involving dihydrido-complexes as transient forms of the catalyst. The proposed reaction sequence is shown in Figure 3. Deuterium at C-2 is first exchanged for hydrogen by a process (steps 1 to 3) involving a 1-pentyl intermediate. Isomerisation to give co-ordinated pent-2-ene (VII) and the reformation of pent-1-ene (IX) then provide the means of obtaining an overall 2,3-shift of deuterium. Steps of the type —5 and 8 each allow formation of pent-1-ene containing no deuterium at C-1, and hence the slight loss of deuterium at C-1 is simultaneously interpreted. Exchange between deuterium of the olefin and the *ortho*-hydrogen atoms of the triphenylphosphine ligands occurred in this reaction. Since this exchange involves the formation of dihydrido-complexes, the participation of such complexes in the isomerisation is not unreasonable.

The distribution of deuterium in *cis*-pent-2-ene early in the reaction is consistent with the formation of a 2-pentyl complex [(3), step 10] and its conversion into a pent-2-ene complex [(3), step 11]. This causes no movement of deuterium to C-4 and C-5, no transfer of deuterium from or to [C(2) + C(3)], and an increase in the deuterium number at C-1. However, such pent-2-ene would be formed as both the *cis*- and *trans*-isomers, since either hydrogen atom at C-3 of the pentyl ligand in species (XI) might be abstracted in step (11), and therefore process (3) predicts that the distribution and location of deuterium should be identical in the *cis*- and *trans*-pent-2-ene so formed. The latter expectation is at variance with the results (Table 1) in that *trans*-pent-2-ene is formed with a deuterium number at C-1 that is lower than that observed in the *cis*-pent-2-ene; small differences are consequently observed in the mass spectra of the *cis*- and *trans*-pent-2-ene. This difference is resolved by supposing that an additional route [(4), below] for the formation of *trans*-pent-2-ene occurs alongside (3). Models show that the 1-ethyl- π -allyl ligand in (XII) would be least sterically hindered in the *syn*-conformation, and hence *trans*-pent-2-ene would be the preferred product. The amount of deuterium transferred to C-1 by process (4) is less than that transferred by process (3). No other process provides as satisfactory an interpretation of the observed differences

⁹ S. D. Mellor and P. B. Wells, *Trans. Faraday Soc.*, 1969, **65**, 1873.

¹⁰ E. McLaughlin and R. W. Rozett, *Chemtech.*, 1971, 120.

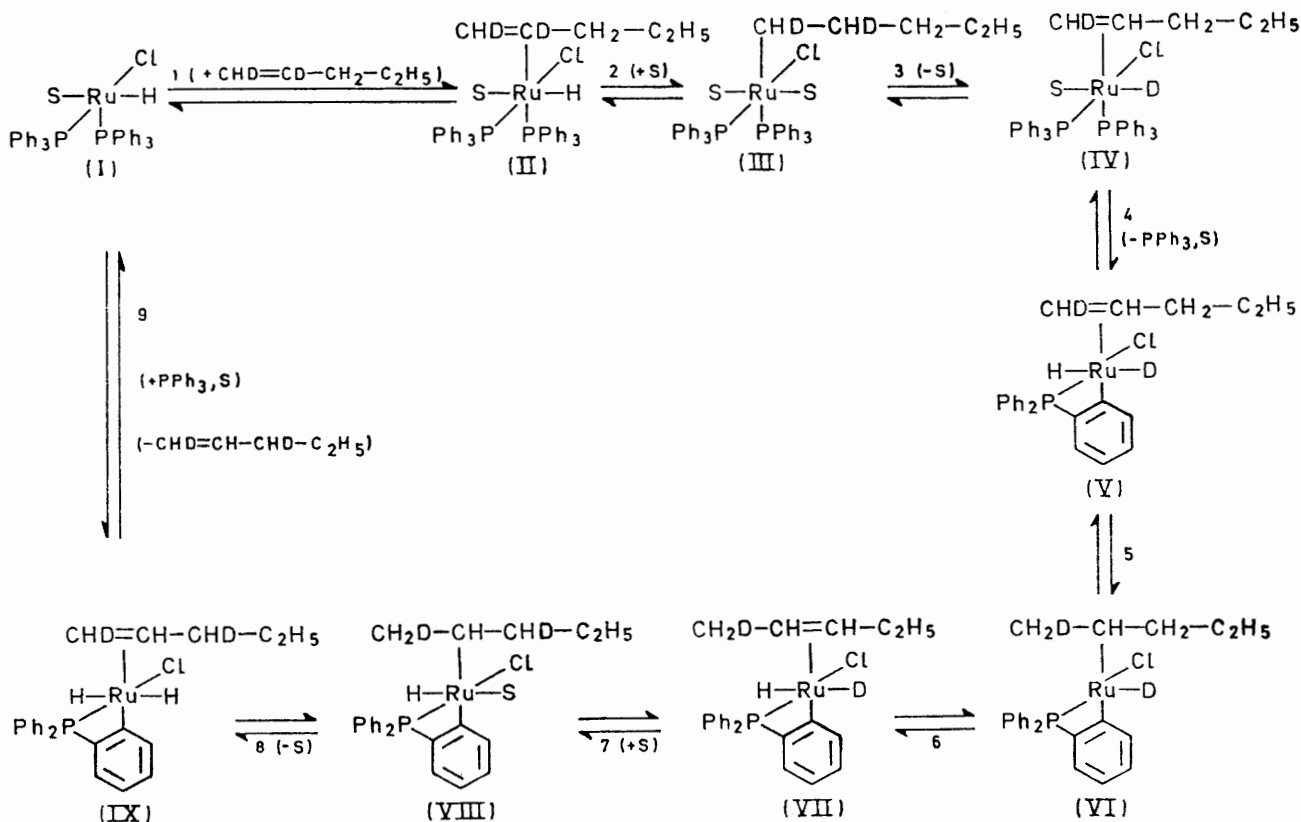
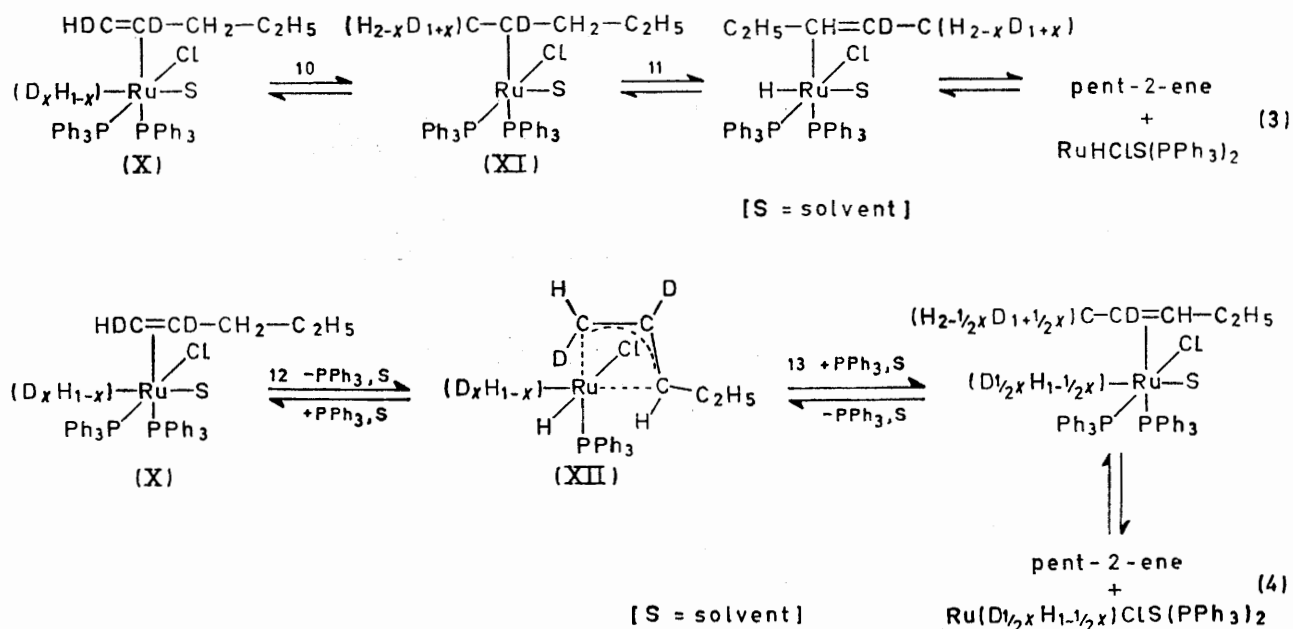


FIGURE 3 A mechanism for the 2,3-shift of deuterium in pent-1-ene



between the distributions of deuterium in *cis*- and in *trans*-pent-2-ene. Quantitative calculations¹¹ based on processes (3) and (4) show that a substantial proportion of the *trans*-pent-2-ene may be formed by (4).

Supposing it to be thus established that π -allylic inter-

mediates participate in isomerisation, an additional mechanism for the 1,2-deuterium shift in pent-1-ene is available. The sequence of steps 1, 2, and 3 shown in Figure 3, followed by 12 and -12 shown in (4) achieve the

¹¹ B. Hudson, Ph.D. Thesis, University of Hull, 1971.

desired isotope shift. This process, like the whole sequence in Figure 3, requires the formation of a dihydrido-complex by the dissociation of a total of two triphenylphosphine ligands.

APPENDIX

Reversible First-order Three-component System.—If a_1 , a_2 , and a_3 are the concentrations of A_1 (pent-1-ene), A_2 (*cis*-pent-2-ene), and A_3 (*trans*-pent-2-ene) in equation (2) (see Discussion) then the rate of change of concentration of each species with respect to time is given by:

$$\left. \begin{aligned} da_1/dt &= -(k_1 + k_3)a_1 + k_{-1}a_2 + k_{-3}a_3 \\ da_2/dt &= k_1a_1 - (k_2 + k_{-1})a_2 + k_{-2}a_3 \\ da_3/dt &= k_3a_1 + k_2a_2 - (k_{-2} + k_{-3})a_3 \end{aligned} \right\} (5)$$

This set of linear differential equations may be solved by an operator method. Replacing da_i/dt by $Pa_i - Pa_i^\circ$, where a_i° is the initial concentration of A_i , equation (5) becomes:

$$\left. \begin{aligned} Pa_1^\circ &= (P + k_1 + k_3)a_1 - k_{-1}a_2 - k_{-3}a_3 \\ Pa_2^\circ &= -k_1a_1 + (P + k_2 + k_{-1})a_2 - k_{-2}a_3 \\ Pa_3^\circ &= -k_3a_1 - k_2a_2 + (P + k_{-2} + k_{-3})a_3 \end{aligned} \right\} (6)$$

When a_2° and a_3° are zero, the solution of the equations comprising (6) is:

$$\left. \begin{aligned} a_1 &= a_1^\circ P \{ (P + k_{-1})(P + k_{-3} + k_{-2}) + k_2(P + k_{-3}) \} / D \\ a_2 &= a_1^\circ P \{ k_1(P + k_{-2} + k_{-3}) + k_3k_{-2} \} / D \\ a_3 &= a_1^\circ P \{ k_3(P + k_2 + k_{-1}) + k_1k_2 \} / D \end{aligned} \right\} (7)$$

where $D = (P + k_1 + k_3)[k_2k_{-2} - (P + k_2 + k_{-1})(P + k_{-2} + k_{-3})]$

Now, provided $P = [k_1 + k_2 + k_3 + k_{-1} + k_{-2} + k_{-3}]$

and Q is defined as

$$[P^2 - 4\{(k_{-1} + k_1)(k_{-2} + k_{-3}) + k_3(k_{-1} + k_{-2} + k_2) + k_2(k_2 + k_{-3})\}]^{1/2}$$

then γ_1 and γ_2 , which will be defined as $(P + Q)/2$ and $(P - Q)/2$ respectively, are the roots of the quadratic:

$$\gamma^2 - \gamma(k_1 + k_2 + k_3 + k_{-1} + k_{-2} + k_{-3}) + (k_{-1} + k_1)(k_{-2} + k_{-3}) + k_3(k_{-1} + k_{-2} + k_2) + k_2(k_1 + k_{-3}) = 0 \quad (8)$$

Thus, rearrangement of equations (7) gives:

$$\left. \begin{aligned} a_1 &= \frac{a_1^\circ [P^2 + P(k_{-1} + k_{-2} + k_{-3} + k_2) + k_{-1}(k_{-2} + k_{-3}) + k_2k_{-3}]}{(P + \gamma_1)(P + \gamma_2)} \\ a_2 &= \frac{a_1^\circ [k_1P + k_{-2}(k_1 + k_{-3}) + k_1k_{-3}]}{(P + \gamma_1)(P + \gamma_2)} \\ a_3 &= \frac{a_1^\circ [k_3P + k_2(k_1 + k_3) + k_{-1}k_3]}{(P + \gamma_1)(P + \gamma_2)} \end{aligned} \right\} (9)$$

The equations (9) are then converted, using a table of Laplace-Carson transforms, into (10), which are a set which express explicitly the dependence of the concentrations of the species A_1 , A_2 , and A_3 upon time.

Equations (10) have been used to obtain calculated concentrations of pent-1-ene, *cis*-pent-2-ene, and *trans*-pent-2-ene at time t , denoted as C_{1t} , C_{2t} , and C_{3t} respectively, using guessed sets of velocity constants, and these have been compared with the experimentally determined quanti-

ties, denoted as A_{1t} , A_{2t} , and A_{3t} . The best choice of velocity constants is that which gives the minimum value

$$\left. \begin{aligned} a_1 &= a_1^\circ \left[\frac{k_{-1}(k_{-2} + k_{-3}) + k_2k_{-3}}{\gamma_1\gamma_2} + \frac{\gamma_1^2 + \gamma_1(k_{-1} + k_{-2} + k_{-3} + k_2) + k_{-1}(k_{-2} + k_{-3}) + k_2k_{-3}}{\gamma_1(\gamma_1 - \gamma_2)} e^{-\gamma_1 t} + \frac{\gamma_2^2 - \gamma_2(k_{-1} + k_{-2} + k_{-3} + k_2) + k_{-1}(k_{-2} + k_{-3}) + k_2k_{-3}}{\gamma_2(\gamma_2 - \gamma_1)} e^{-\gamma_2 t} \right] \\ a_2 &= a_1^\circ \left[\frac{k_1(k_{-2} + k_{-3}) + k_{-2}k_3}{\gamma_1\gamma_2} + \frac{k_1(k_{-2} + k_{-3}) + k_{-2}k_3 - k_1\gamma_1}{\gamma_1(\gamma_1 - \gamma_2)} e^{-\gamma_1 t} + \frac{k_1(k_{-2} + k_{-3}) + k_{-2}k_3 - k_1\gamma_2}{\gamma_2(\gamma_2 - \gamma_1)} e^{-\gamma_2 t} \right] \\ a_3 &= a_1^\circ \left[\frac{k_3(k_2 + k_{-1}) + k_1k_2}{\gamma_1\gamma_2} + \frac{k_3(k_2 + k_{-1}) + k_1k_2 - k_3\gamma_1}{\gamma_1(\gamma_1 - \gamma_2)} e^{-\gamma_1 t} + \frac{k_3(k_2 + k_{-1}) + k_1k_2 - k_3\gamma_2}{\gamma_2(\gamma_2 - \gamma_1)} e^{-\gamma_2 t} \right] \end{aligned} \right\} (10)$$

to E [equation (11)], and this choice was obtained by computation using a Simplex method.¹² The computer program enabled the values of one or more velocity constants to be fixed whilst the remainder were adjusted to obtain a fresh value of E , denoted E' . An estimate of the accuracy

$$E = \sum_{t=0}^{\infty} \{ (A_{1t} - C_{1t})^2 + (A_{2t} - C_{2t})^2 + (A_{3t} - C_{3t})^2 \} \quad (11)$$

of each velocity constant was obtained by giving it a value different from its best value, and comparing E' so obtained with E . The uncertainties in the velocity constants quoted in the Discussion constitute the adjustment required to give the ratio E'/E the arbitrary value of 2.0. A visual check of the correctness of the calculated velocity constants was obtained by programming the computer to plot the theoretical concentration versus time curves together with the experimental points.

Determination of the Concentration of Pent-1-ene Reformed from Pent-2-ene.—If a_{12} and a_{13} are the concentrations of pent-1-ene reformed from *cis*- and *trans*-pent-2-ene respectively, then

$$da_{12}/dt = k_{-1}a_2 \text{ and } da_{13}/dt = k_{-3}a_3 \quad (12)$$

Substituting for a_2 and a_3 , using (10) we obtain equations (13), where A , B , C , D , E , F , γ_1 , and γ_2 are constants which can be evaluated using the six velocity constants obtained as described above.

$$\left. \begin{aligned} a_{12} &= k_{-1}a_1^\circ \left[At - \frac{Be^{-\gamma_1 t}}{\gamma_1} - \frac{Ce^{-\gamma_2 t}}{\gamma_2} \right] \\ a_{13} &= k_{-3}a_1^\circ \left[Dt - \frac{Ee^{-\gamma_1 t}}{\gamma_1} - \frac{Fe^{-\gamma_2 t}}{\gamma_2} \right] \end{aligned} \right\} (13)$$

After long reaction times a significant proportion of reformed pent-1-ene will be converted again into pent-2-ene; the

¹² J. A. Nelder and R. Mead, *Computer J.*, 1965, 7, 308.

amount so converted is calculated by treating a_{12} and a_{13} in a manner analogous to that used for a_2 and a_3 . The improved expressions, which involve k_1 and k_3 , are shown in (14).

$$\left. \begin{aligned} a_{12} &= k_{-1}a_1 \circ \left[\frac{At(t+2)}{2} - (\gamma_1 + k_1 + k_3) \frac{Be^{-\gamma_1 t}}{\gamma_1^2} \right. \\ &\quad \left. - (\gamma_2 + k_1 + k_3) \frac{Ce^{-\gamma_2 t}}{\gamma_2^2} \right] \\ a_{13} &= k_{-3}a_1 \circ \left[\frac{Dt(t+2)}{2} - (\gamma_1 + k_1 + k_3) \frac{Ee^{-\gamma_1 t}}{\gamma_1^2} \right. \\ &\quad \left. - (\gamma_2 + k_1 + k_3) \frac{Fe^{-\gamma_2 t}}{\gamma_2^2} \right] \end{aligned} \right\} (14)$$

Equations (14) were used to evaluate the concentrations of pent-1-ene reformed from *trans*-pent-2-ene and *cis*-pent-2-ene in the experiment shown in Figure 1. After 67% isomerisation the amount reformed from *trans*-pent-2-ene was 0.3%, and that from *cis*-pent-2-ene 1.3%.

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