927. *The Hydroformylation of 4-Methylpent-1-ene.*

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A study of the hydroformylation of 4-methylpent-1-ene has shown that olefin isomerisation involves stepwise migration of the double-bond along the carbon chain. Under typical " Oxo " reaction conditions, the rate of isomerisation is very high, increasing with temperature and catalyst concentration. The aldehydes formed in the hydroformylation of 4-methylpent-1-ene have been identified and quantitatively determined at intermediate levels of conversion. There appears to be no rearrangement of any complex involved in the reactions. It is proposed that the isomerisation involves a π-bonded complex which does not take part in hydroformylation.

THOUGH it is known that the double bond of an olefin may migrate during the " Oxo " synthesis, very little quantitative work on this aspect has been published. Pino, Pucci, and Piacenti[1] found very little such migration in the hydroformylation of (+)-(*S*)-3-methylpent-1-ene under conventional " Oxo " conditions. In a study of the isomerisation catalysed by iron pentacarbonyl, Manuel[2] concluded that rearrangement occurs within the complex species involved without the formation of intermediate olefins. To provide quantitative data on the fate of an olefin during the " Oxo " reaction, the composition of the reaction mixture as a function of time has been studied during the cobalt-catalysed hydroformylation of 4-methylpent-1-ene.

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[1] Pino, Pucci, and Piacenti, *Chem. and Ind.*, 1963, 294.

[2] Manuel, *J. Org. Chem.*, 1962, **27**, 3941.

RESULTS

Hydroformylations were carried out in a stainless-steel autoclave equipped with devices for sampling the vapour and the liquid phase of a reacting system without interrupting the reaction. Runs were done with an equimolar mixture of hydrogen and carbon monoxide at 240 atm. total pressure, at 116°, 134°, 153°, and 175°, and liquid-phase samples were taken at 15-min. intervals for 90 min. The hydrocarbon fraction of each sample was then separated by use of a standard fluorescent indicator and silica gel[3] and analysed quantitatively by gas–liquid chromatography (g.l.c.). The C_7 aldehydes formed were identified by a combination of g.l.c. and infrared spectroscopic analysis of the paraffins produced from them by a modified Wolff–Kishner reduction. The proportion of aldehyde isomers (I—V) in the total aldehyde yield was determined quantitatively by gas chromatography. The results are tabulated. The olefin distribution (VI—X) as a function of reaction time is illustrated in Figs. 1—5.

Thermodynamic calculations predict, and measurements show,[2] that the 2-methylpent-2-ene is the predominant isomer in an equilibrium mixture.

(I)	$\mathrm{Me{\cdot}CHMe{\cdot}CH_2{\cdot}CHMe{\cdot}CHO}$	$\mathrm{Me{\cdot}CHMe{\cdot}CH_2{\cdot}CH{:}CH_2}$	(VI)
(II)	$\mathrm{Me{\cdot}CHMe{\cdot}CHEt{\cdot}CHO}$	$\mathrm{Me{\cdot}CHMe{\cdot}CH{:}CHMe}$	(VII) *cis*, (VIII) *trans*
(III)	$\mathrm{Me{\cdot}CH_2{\cdot}CH_2{\cdot}CHMe{\cdot}CH_2{\cdot}CHO}$	$\mathrm{Me{\cdot}CH_2{\cdot}CH{:}CMe_2}$	(IX)
(IV)	$\mathrm{Me{\cdot}CH_2Me{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CHO}$	$\mathrm{Me{\cdot}CH_2{\cdot}CH_2{\cdot}CMe{:}CH_2}$	(X)
(V)	$\mathrm{Me{\cdot}CH_2{\cdot}CH_2{\cdot}CMe_2{\cdot}CHO}$	$\mathrm{Me{\cdot}CH_2{\cdot}CH_2{\cdot}CHMe_2}$	(XI)

In runs 1—4, aldehydes (I—IV) were produced in the hydroformylation of 4-methylpent-1-ene. In run 5, at 175°, a trace of the other possible aldehyde (V) appeared towards the end of the reaction. This aldehyde is not included in the Table.

Hydroformylation of 4-methylpent-1-ene.

Run no.	Temp., Co %	Time (min.)	G.l.c. of hydrocarbon fraction (% w/w)						G.l.c. of aldehyde fraction (% w/w)			
			VI	VII	VIII	IX	X	XI	I	II	III	IV
1	116°	15	77·7	3·0	19·3	—	—	T	25·0	—	—	75·0
	0·02%	30	57·9	5·2	36·4	—	—	0·5	25·0	—	—	75·0
		45	24·8	9·1	64·3	0·6	—	1·0	29·0	0·5	—	70·5
		60	3·1	10·0	66·6	16·0	0·8	3·4	35·5	2·1	—	62·5
		75	0·8	3·9	23·7	61·8	3·1	6·7	38·5	2·9	T	58·5
		90	0·3	1·4	7·5	78·3	6·4	6·1	40·0	3·7	0·5	56·0
2	134°	15	68·4	4·1	26·9	—	—	0·6	22·0	T	—	78·0
	0·02%	30	14·1	12·0	69·3	3·3	T	1·2	25·0	0·5	—	74·5
		45	2·6	9·0	48·1	35·2	2·3	2·9	33·5	2·4	T	64·0
		60	1·1	4·0	23·8	51·5	4·0	5·6	36·0	3·2	0·9	60·0
		75	0·7	2·5	15·1	65·5	7·2	9·1	38·5	3·7	1·3	56·5
		90	0·4	1·6	8·3	74·4	7·7	7·6	37·0	3·7	3·4	56·0
3	153°	15	6·7	10·0	48·2	32·0	1·3	1·8	29·0	1·90	T	69·0
	0·02%	30	1·4	7·0	28·5	53·3	4·4	5·5	33·0	3·0	1·4	62·5
		45	1·0	3·2	15·1	70·2	6·8	3·7	36·0	3·5	1·4	59·5
		60	0·9	2·5	12·6	71·3	7·6	5·0	36·0	3·6	3·2	57·0
		75	0·7	2·0	10·6	71·0	8·5	7·1	36·5	3·7	4·6	55·0
		90	1·0	2·0	9·9	71·9	8·9	6·5	36·5	3·9	5·9	54·0
4	153°	15	80·8	3·1	16·1	—	—	—	19·0	—	—	81·0
	0·01%	28	36·5	10·2	50·6	1·9	—	0·8	19·0	T	—	81·0
		42	6·2	12·4	54·5	22·9	2·2	1·9	25·5	1·7	0·4	72·5
		64	2·4	6·5	32·8	48·8	5·9	3·6	28·0	2·5	2·5	66·0
		90	2·6	2·9	14·2	64·1	9·5	6·7	32·5	3·3	4·5	59·0
5	175°	15	4·5	8·3	38·6	40·2	4·4	4·0	26·5	1·9	4·9	67·0
	0·02%	30	1·9	4·2	20·7	58·4	8·2	6·5	26·5	2·6	9·3	62·0
		45	1·2	2·9	14·4	54·4	8·5	18·6	25·5	2·8	12·5	59·5
		60	1·1	2·2	11·3	61·0	9·9	14·4	27·0	2·8	16·0	54·5
		75	1·2	2·0	10·7	54·8	9·6	21·6	26·0	2·5	17·0	54·0
		90	0·8	1·5	8·2	58·5	10·3	20·7	24·5	3·1	20·0	52·5

T = Trace.

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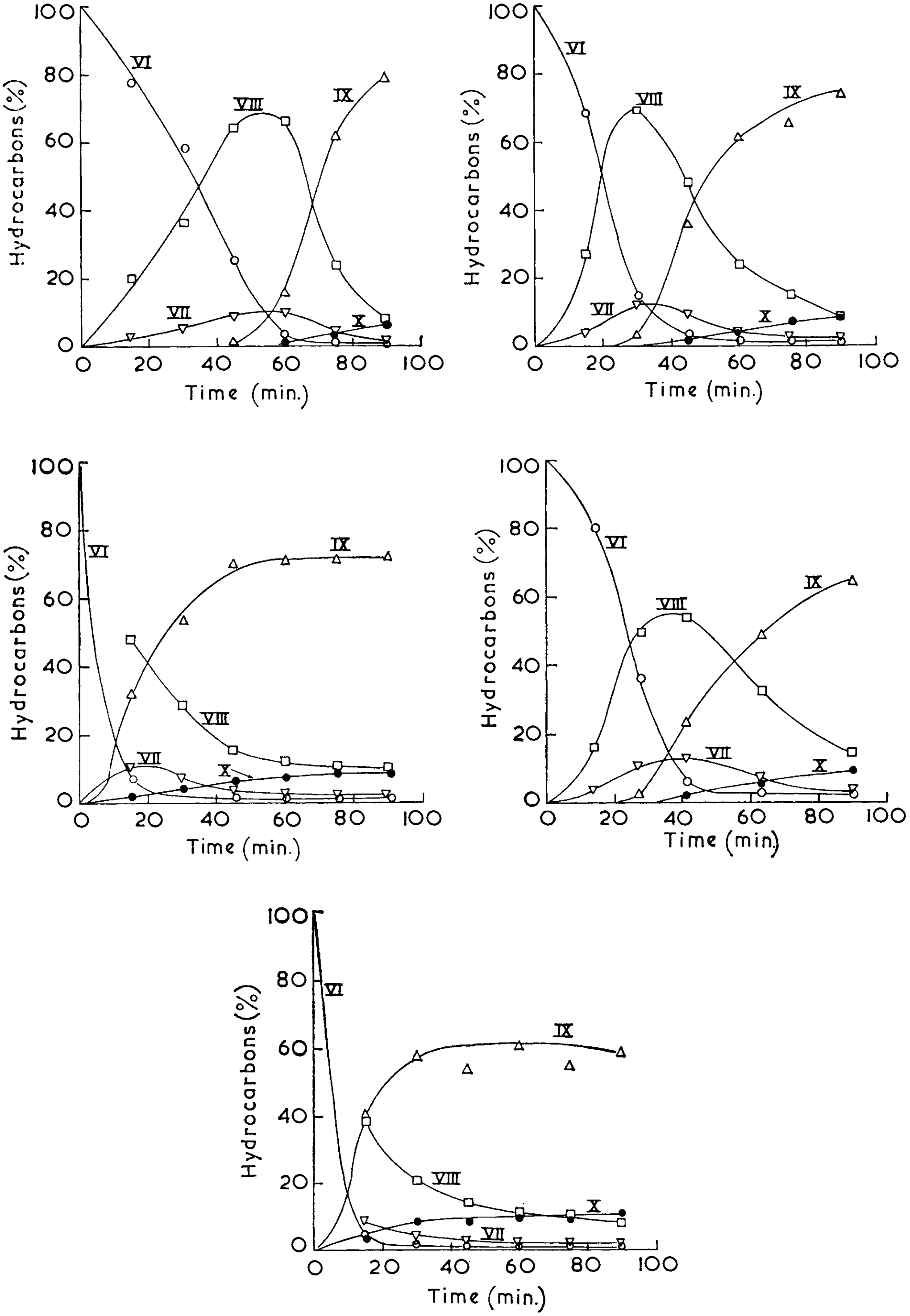
[3] Standards for Petroleum and its Products. Part I. Method I.P.156/60T. Institute of Petroleum, London, 1960, p. 283.



FIGS. 1—5. Rate of formation of isomers in runs 1—5, respectively.

DISCUSSION

Olefin Isomerisation.—It is clear that the double-bond migration along the carbon chain occurs in a stepwise manner. For example, 4-methylpent-1-ene does not isomerise to 2-methylpent-1-ene without the intermediate formation of 4-methylpent-2-ene and 2-methylpent-2-ene, successively. In fact, the concentration of *cis*- and *trans*-4-methylpent-2-ene increases to a relatively high level before the double bond moves along to the next position in the carbon chain, giving 2-methylpent-2-ene. The results are therefore not in accord with Manuel's conclusions [2] and it is considered that iron pentacarbonyl will induce analogous behaviour. The approach to an equilibrium in which 2-methylpent-2-ene is the major olefin is clearly shown.

Therefore, it is not true to say that olefin isomerisation occurs only to a limited extent in the " Oxo " reaction. On the contrary, under conditions regarded as typical of the " Oxo " reaction, double-bond migration is extremely rapid. The Figures show that its rate depends at least upon the temperature and the catalyst concentration. Even at 116°, there is a substantial amount of isomerisation. At higher temperatures, it can be so fast that the reacting species is an equilibrium mixture of olefins rather than a single olefin. For this reason, any rate measurements of hydroformylation must be interpreted with care.

Distribution of Aldehydes in the Product.—It proved possible to follow the formation of each aldehyde isomer in detail. In run 1, for example, only aldehydes (I) and (IV) appear in the product for ~30 min. of reaction time. In 45 min. a small amount of aldehyde (II) appears, but aldehyde (III) is not formed until later. At higher temperatures, the aldehydes are formed faster but in the same order. Therefore, when 4-methylpent-1-ene is the starting olefin, four aldehydes are produced in a definite sequence, and there is little doubt that this is the direct consequence of the stepwise double-bond migration along the olefin carbon chain. It is necessary for the 2-methylpent-1-ene to be formed by double-bond shift before 3-methylhexanal can be produced by hydroformylation. I conclude, therefore, that, not only is double-bond migration stepwise, but also the formation of a precursor olefin is a necessary intermediate step in the synthesis of an aldehyde.

Hughes and Kirschenbaum [4] studied the influence of temperature on the distribution of alcohol isomers in the carbonylation products of propene, but-1-ene, and hept-1-ene, showing that the n-isomer content decreases with increase in temperature. In the light of our results, their findings require qualification. With aliphatic terminal olefins other than propene, the n-aldehyde content falls during hydroformylation at high temperatures owing to the rapid double-bond migration away from the terminal position. Nevertheless, it is possible to obtain a product with a high n-isomer content at any temperature by limiting the conversion to levels where the double-bond shift is not extensive. A comparison of n/iso-aldehyde ratios over a range of temperatures is valueless unless the catalyst concentration and conversion are kept constant.

Mechanism.—There is a striking difference between the rates of hydroformylation of the terminal and the non-terminal isomers of 4-methylpent-1-ene. Aldehydes (II) and (V) are only minor products of the reaction at 175° despite the fact that one of their possible precursors (2-methylpent-2-ene) soon becomes the major olefin in the reaction mixture. Therefore, the isomer distribution in the olefin fraction will also be affected by hydroformylation to aldehyde, but this factor alone is insufficient to account for the observed changes in composition, especially at 175°. In the early stages of the reaction, or at lower temperatures, double-bond isomerisation is not extensive and the major product is aldehyde (IV). The distribution of aldehydes in the product of hydroformylation is therefore a function of (i) the relative rates of attachment of the formyl group to the different carbon atoms of the olefin skeleton, and (ii) the concentrations of the various

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[4] Hughes and Kirshenbaum, *Ind. Eng. Chem.*, 1957, **49**, 1999.

olefin precursors. The gradual increase in the relative concentration of aldehyde (I) in the product of the hydroformylation of 4-methylpent-1-ene at 116° is no doubt a consequence of the relatively high concentration of 4-methylpent-2-ene for a large part of the reaction time.

As the attachment of a formyl group to an olefin takes place preferentially at the terminal carbon atom, the hydridocarbonylcobalt catalyst is behaving in a way characteristic of hydride-ion attack.

Our results also indicate that there is no rearrangement of any complex involved in the hydroformylation sequence. For example, 3-methylhexanal does not result from a complex formed initially with 4-methylpent-1-ene. If the hydroformylation can be assumed to occur as follows:

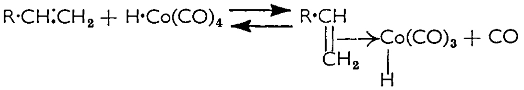
$$R\cdot CH{:}CH_2 + H\cdot Co(CO)_4 \longrightarrow R\cdot CH_2\cdot CH_2\cdot Co(CO)_4 \quad \ldots\ldots\ldots \quad (1)$$

$$R\cdot CH_2\cdot CH_2\cdot Co(CO)_4 + CO \longrightarrow R\cdot CH_2\cdot CH_2\cdot CO\cdot Co(CO)_4 \quad \ldots\ldots \quad (2)$$

$$R\cdot CH_2\cdot CH_2\cdot CO\cdot Co(CO)_4 + H_2 \longrightarrow R\cdot CH_2\cdot CH_2\cdot CHO + H\cdot Co(CO)_4 \quad \ldots\ldots \quad (3)$$

then the nature of the product is determined in the first stage of the reaction, the formation of a σ-bonded alkyl carbonyl. Insertion of carbon monoxide and removal of hydrogen occur subsequently without rearrangement of the complexes.

It is suggested that olefin isomerisation is accomplished through a π-bonded complex formed by a displacement of one of the carbonyl ligands from the hydrotetracarbonyl:



$$R\cdot CH{:}CH_2 + H\cdot Co(CO)_4 \rightleftharpoons \begin{array}{l} R\cdot CH \\ \| \longrightarrow \underset{\displaystyle H}{\underset{|}{Co}}(CO)_3 + CO \\ CH_2 \end{array} \quad \ldots\ldots \quad (4)$$

Double-bond shift could then occur by intramolecular proton exchange in a complex of the type shown. At high concentrations of carbon monoxide, the equilibrium in reaction (4) will be forced to the left, so the concentration of the complex will be decreased. This will reduce the rate of olefin isomerisation and explain the results of Pino and his co-workers.[1,5]

EXPERIMENTAL

4-*Methylpent*-1-*ene*.—Phillips Petroleum Company, " Pure Grade " (99%) material was used without further purification.

Hydroformylation.—In each run, 100 g. (150 ml.) of the olefin were charged through a capillary injection line into the 0·9-l. autoclave, which was already at the working temperature. The pressure was then raised to 200 atm. with an equimolar mixture of hydrogen and carbon monoxide, and the autoclave was then rocked. After 30 min., during which the system achieved physical equilibrium, 33 g. (50 ml.) of the olefin containing 0·422 g. of cobalt naphthenate were injected into the autoclave and the pressure rapidly adjusted to 250 atm. Reaction commenced immediately with the absorption of hydrogen and carbon monoxide (drop in pressure). When the total pressure fell to 230 atm., further quantities of 1 : 1 gas mixture were injected to readjust the pressure to 250 atm. In this way, the pressure was kept near to the working average of 240 atm. The temperature was controlled during the reaction to ±2°. Samples (5—10 g.) of the liquid phase were taken at prescribed times into a series of catchpots cooled in carbon dioxide–methanol. The whole contents of the autoclave were discharged after 90 min.

Identification of the Aldehydes.—The aldehyde isomers produced in the hydroformylation of 4-methylpent-1-ene were separated on a 200 ft. capillary (0·02″) g.l.c. column with dinonyl phthalate as the stationary phase. The identity of each aldehyde was suggested by an infrared spectroscopic examination and confirmed by reduction to the paraffin by a modified Wolff–Kishner method.

The crude product (40 g.) from run 5 was refluxed for 5 hr. with a mixture of diethylene glycol (200 ml.), potassium hydroxide (30 g.), and 80% w/w hydrazine hydrate (34 ml.). The mixture was then set aside for 16 hr. at room temperature before the mixture of water and

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[5] Pino, Piacenti, and Neggiani, *Chem. and Ind.*, 1961, 1400.

paraffin was separated by distillation up to 130°. The remaining solution was refluxed for a further 90 min., cooled, diluted with water (200 ml.), acidified with hydrochloric acid, and extracted with ether (2 × 100 ml.). The ether extracts were combined with the water–paraffin mixture, washed with aqueous sodium chloride (2 × 500 ml.), and dried (K_2CO_3). After filtration, the product was distilled through a short fractionating column, the fraction of b. p. 86—89° (6 g.) being collected. The heptanes formed in this way were readily separated from the unchanged hexenes on a 600 ft. capillary (0·01″) g.l.c. column, with squalane as the stationary phase, and were identified by comparison with known standards.

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