Hydroformylation of 1,6-Dienes with Carbonylhydridotris(triphenylphosphine)rhodium

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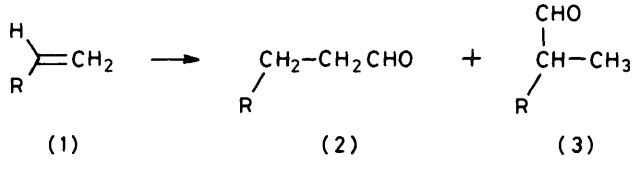
Hydroformylation of a number of 1,6-dienes has been achieved at room temperature and atmospheric pressure using [Rh(H)CO(PPh_3)$_3$] as catalyst. Octa-1,6-dienes are hydroformylated specifically at the terminal double bond and good selectivity for the n-aldehyde is observed when a 2 : 1 mixture of hydrogen and carbon monoxide are used. Both mono- and di-formyl derivatives are formed from 4,4-diacetylhepta-1,6-diene, with a strong preference for n-aldehydes. The effect of catalyst concentration on product distribution is reported. Octa-1,3,7-triene can be selectively hydroformylated by protecting the diene moiety as its cycloadduct with sulphur monoxide or dioxide, and whilst methylenecyclopentane undergoes regiospecific hydroformylation, methylenecyclobutane is isomerised to methylcyclobutene.

Hydroformylation involves the transition-metal catalysed addition of hydrogen and carbon monoxide to an alkene to give a saturated aldehyde. Terminal alkenes (1) afford a mixture of n-(2) and iso-(3) aldehydes.[1] Hydroformylation is an industrially important process particularly for the production of C_3—C_5 aldehydes which are precursors of useful alcohols, acids, diols, and amines.[2]

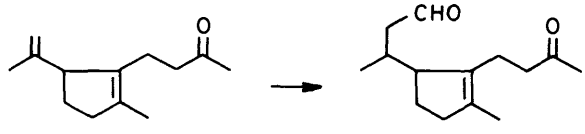
A number of transition metals catalyse the hydroformylation reaction but cobalt and rhodium are the most active. Rhodium catalysts are of special interest in synthetic organic chemistry because they are 10^3—10^4 times more active than cobalt catalysts and hydroformylations can be carried out at room temperature and atmospheric pressure.[3] The mild conditions associated with hydroformylations catalysed by [Rh(H)CO(PPh_3)$_3$] do not usually lead to double bond isomerisation or alkene hydrogenation. Alkene isomerisation and hydrogenation can however be a problem under the more vigorous conditions associated with cobalt catalysts.[1] Analogies and dissimilarities between rhodium and cobalt catalysts have been summarised by Pino.[4] The reactivity of alkenes in hydroformylation reactions follows the general pattern: $RCH{=}CH_2 > RCH{=}CHR^1 > RR^1C{=}CH_2 > RR^1C{=}CHR^2$.[1,5,6] Thus, more hindered poorly co-ordinating olefins are less reactive and so regioselective hydroformylation can be achieved, *e.g.* (4) ⟶ (5).[7]

The regioselectivity of the hydroformylation (1 ⟶ 2,3) is sensitive to a number of factors including the ratio of hydrogen to carbon monoxide used in the reaction. Using a 1 : 1 molar ratio of hydrogen to carbon monoxide the n-aldehyde (2) predominates for both rhodium and cobalt catalysts [(2) : (3) *ca.* 3 : 1]. An increase in the ratio of hydrogen to carbon monoxide to 2 : 1 greatly increases this regioselectivity in favour of the n-aldehyde (2), but can also promote undesirable hydrogenation and isomerisation reactions.[6] Polar donor solvents increase the selectivity and rate of the rhodium catalysed reactions [8] and variation of the phosphine ligand in [Rh(H)CO(PR_3)$_3$] also influences the ratio of (2) to (3).[9] Attempts have been made to correlate the effects of phosphine variation with ESCA measurements and the i.r. stretching frequency of the carbonyl ligand.[10] However, the effect of variation of phosphine ligand on the n- to iso-aldehyde ratio is complex, being related to both the steric effect of the phosphine (cone angle) and its basicity.[11] The stereochemistry of the rhodium catalysed hydroformylation has been studied and shown to involve *cis*-addition.[12]

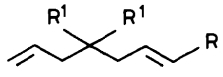
Thus, the essential stereochemical and regiochemical features of the reaction are known but despite the obvious synthetic utility of the [Rh(H)CO(PR_3)$_3$] catalysed hydroformylation reaction surprising little use has been made of the reaction in synthetic organic chemistry.[3,13]



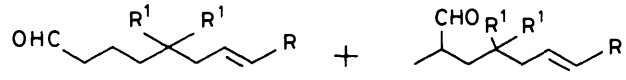
(1) (2) (3)



(4) (5)



(6) a ; R = Me, R^1 = H
b ; R = CH_2CO_2Et, R^1 = H
c ; R = Me, R^1 = Ac



(7) a ; R = Me, R^1 = H (8)
b ; R = CH_2CO_2Et, R^1 = H
c ; R = Me, R^1 = Ac

We have studied the selective hydroformylation of a number of 1,6-dienes using [Rh(H)CO(PPh_3)$_3$] as catalyst and various hydrogen–carbon monoxide mixtures at room temperature and atmospheric pressure. The hydroformylation of octa-1,6-diene (6a) using a 1 : 1 mixture of hydrogen and carbon monoxide gave a 1.8 : 1 mixture of (7a) and (8a). The ratio of (7a) to (8a) was measured by two independent methods; (*a*) g.l.c. peak areas using a 2 m, 20M Carbowax column and (b) ^{1}H n.m.r. spectroscopy. The aldehyde proton of (7a) gives rise to a triplet in the n.m.r. spectrum which is well separated from the doublet aldehyde signal of (8a). The internal double bond was still intact as shown by an n.m.r. multiplet at δ 5.2 and a band at 965 cm^{-1} in the i.r. spectrum of the mixture. When the reaction was repeated (12 h; room temperature) using a 2 : 1 ratio of hydrogen–carbon monoxide the product mixture (47%) again consisted of (7a) and (8a) in the ratio of 12 : 1.

Table 1. Hydroformylation of 2,5-dihydrothiophene derivatives

Substrate	Molar ratio H_2 : CO	Product ratio 11 : 12
(10a)	1 : 1	4 : 1
(10a)	1 : 2	1.5 : 1
(10a)	2 : 1	25 : 1
(10b)	1 : 1	4 : 1
(10c)	1 : 1	3 : 1

The hydroformylation of (6b) was slower (4 days; room temperature) but showed greater selectivity for the n-aldehyde (7b). Thus a 1 : 1 mixture of hydrogen and carbon monoxide gave (7b) and (8b) in the ratio of 3.7 : 1 whilst a 2 : 1 mixture of hydrogen and carbon monoxide gave some unchanged (6b) together with (7b) (60%) and only trace amounts of (8b). It should be noted that use of impure or aged [Rh(H)CO-$(PPh_3)_3$] results in less selective hydroformylation. In contrast, the hydroformylation of (6c) was slower (4 days) than (6a) but less selective. Using a 2 : 1 ratio of hydrogen–carbon monoxide, (6c) gave a 2.5 : 1 mixture (62%) of (7c) and (8c).

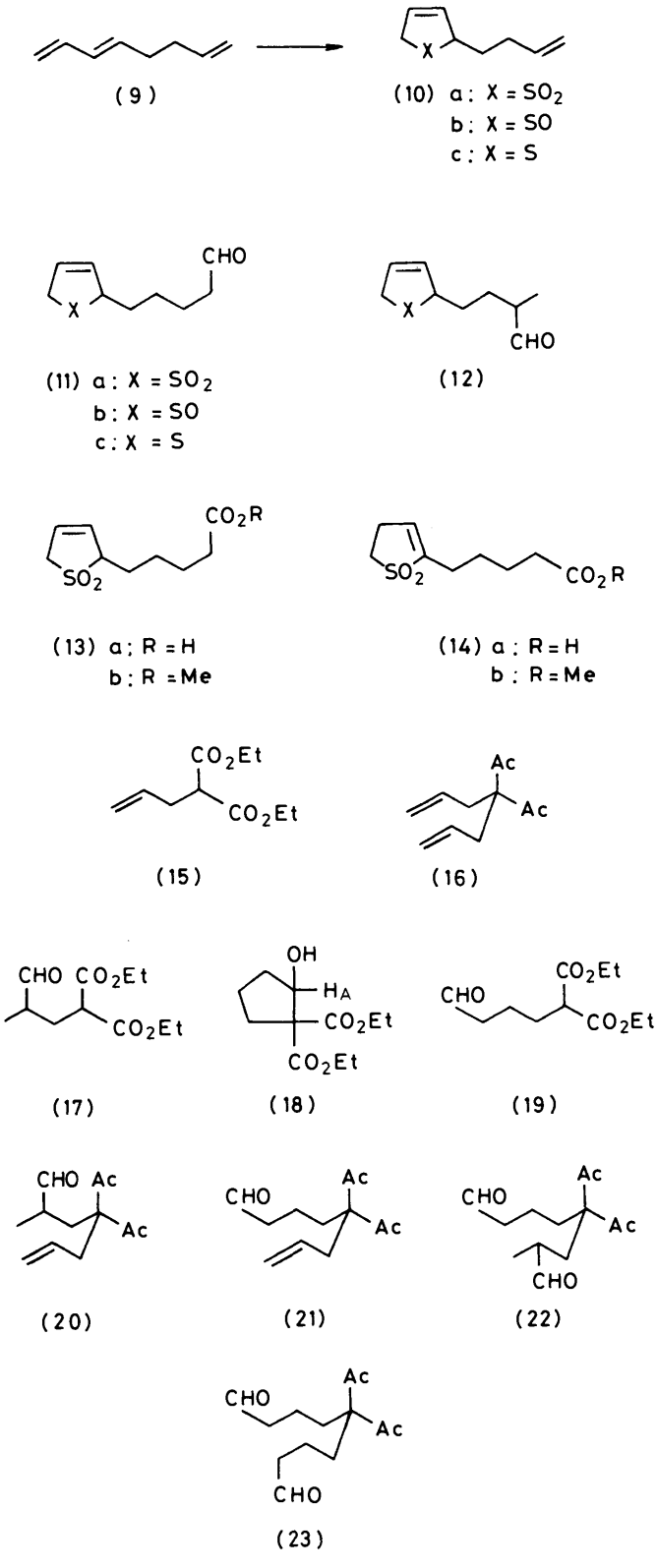
Several reports of the hydroformylation of conjugated dienes have appeared.[11] These substrates usually undergo initial hydrogenation to the monoene followed by hydroformylation to a monoaldehyde in the usual way. Bishydroformylation of conjugated dienes to dialdehydes can be achieved by rhodium catalysts in the presence of an excess of phosphine ligand. One approach to the selective monohydroformylation of an alkene in the presence of a conjugated diene moiety would be to mask the conjugated diene by cycloadduct formation, followed by hydroformylation and retrocycloaddition. This approach has been explored with the triene (9).

The triene (9) reacted with liquid sulphur dioxide in the presence of 1% (with respect to triene) of hydroquinone, to retard polysulphone formation,[14] to give the sulphone (10a) as a mobile oil in 60% conversion after 3 days. Unchanged triene was recovered by simple distillation and could be reused. The analogous sulphoxide (10b) (46%) was obtained by heating equimolar quantities of (9) and thiiran 1-oxide in boiling toluene for 2 h. Reduction of (10b) with lithium aluminium hydride in THF at room temperature gave the sulphide (10c). The rates of hydroformylation of (10a—c) were comparable and normally required 4—5 days at ambient temperature for completion. Thus (10c) showed little evidence of catalyst poisoning by the sulphide moiety. The results of the hydroformylations are summarised in Table 1.

Correct microanalyses could not be obtained for the aldehydes (11) and (12) although they gave the expected spectroscopic data. The aldehyde (11a) was thus further characterised by oxidation to the corresponding acid followed by esterification to give the methyl ester. Oxidation with Jones' reagent (CrO_3–H_2SO_4) gave the expected acid (13a) (63%) whilst oxidation with alkaline silver oxide afforded the isomerised acid (14a); (83%) and subsequently the ester (14b). Attempted oxidation of (11a) with neutral silver oxide[15] in tetrahydrofuran–water (9 : 1) at ambient temperature gave only unchanged (11a). Base catalysed isomerisation of 2,5-dihydrothiophene 1,1-dioxides to the more stable 2,3-dihydrothiophene 1,1-dioxides has been previously reported.[16]

A more detailed study of the hydroformylation of (15) and (16) was undertaken.

The alkenes (15) and (16) were hydroformylated in benzene at ambient temperature using [Rh(H)CO$(PPh_3)_3$] as catalyst and a 2 : 1 molar mixture of hydrogen and carbon monoxide with vigorous stirring for 10 h (Table 2). The same batch of catalyst was used in all experiments. After 10 h the reaction



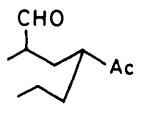
mixture was analysed by g.l.c. using hexamethylbenzene as internal standard.

Hydroformylation of (15) under these conditions gave two major products in the ratio 28 : 66 (87% conversion), together with some unchanged (15) (6%) (Table 2). The products were separated by preparative t.l.c. (silica, ether–benzene, 1 : 4). The isoaldehyde structure (17) was assigned to the minor

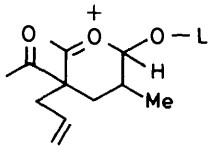
Table 2. Hydroformylation (benzene, ambient temperature, 10 h) of (15) and (16)

Substrate	[Rh(H)CO-(PPh$_3$)$_3$] (mole %)	Product distribution (%)	Yield (%) [a]
15	0.9	15 (6), 17 (28), 18 (66)	87
16	1.0	16 (19),[b] 20 (5),[b] 21 (45),[b] 22 + 23 (31) [c]	84

[a] Total yield of aldehydes calculated from g.l.c. (1.5M 5% SGR column) using hexamethylbenzene as internal standard. [b] Mainly (*ca.* 85%) hydrogenated. [c] Isomeric dialdehydes were not resolved by g.l.c. but subsequent work showed (23) comprised ≥95% of the product.



(24)



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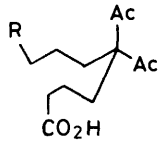
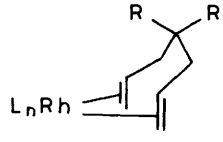


(26) a : R = CHO
b : R = CO_2H



(27)

product on the basis of its n.m.r. spectrum. The major component (18) proved to be the aldol product derived from the n-aldehyde (19). The n.m.r. spectrum of (18) showed an exchangeable proton at δ 3.29 (OH) and a triplet for the methine proton H_A at δ 4.6 (*J* 5 Hz). Examination of the n.m.r. spectrum of the crude hydroformylation mixture showed the expected signals for n-aldehyde (19) (*e.g.* δ 9.76, t, 1 H, C*H*O) and no signals for (18). Thus the aldolisation (19) ⟶ (18) occurs during p.t.l.c. on silica.

The hydroformylation of (16) was accompanied by hydrogenation of both the mono-aldehyde fraction and the diene (16) (Table 2). Problems were also encountered during the preparative t.l.c. of the product mixture from (16). The iso-monoaldehyde fraction (20) and its dihydro-derivative underwent deacylation on silica giving the corresponding mixture of monodeacylated (20) and its dihydro derivative (24). G.l.c. and n.m.r. spectra showed the presence of a 1 : 1 diastereoisomeric mixture in both cases. Deacylation of the n-aldehydes (21) and (23) did not occur on silica suggesting that the 1,5-dicarbonyl compounds are especially labile, possibly due to formation of an intermediate such as (25; L = Lewis acid).

The dialdehyde fraction from (16) was found, on preparative t.l.c., to consist mainly of the n,n-isomer (23) with ≤5% of n, i-isomer (23) or i, i-isomer (the small amounts of this isomer discouraged isolation and identification). Autoxidation of the dialdehyde (22) to the mono- and di-carboxylic acids (26a) and (26b) occurred on t.l.c. plates unless the plates were dried and extracted rapidly.

Hydroformylation of 4,4-diacetylhepta-1,6-diene (16) occurred more slowly than hydroformylation of (15). This may reflect the relative stabilities of the bis-π-olefin complex (27) compared to the mono-π-olefin complex from (*15*). Rhodium complexes of 1,6-dienes are well known [17] and 4,4-disubstitution could stabilise the rhodium complex by weak co-ordination of R (R = CO) to rhodium and/or by operation of a Thorpe–Ingold effect,[18] favouring bis-co-ordination and hence retarding hydroformylation.

The extent of conversion of (15) and (16) into products as a function of catalyst concentration was investigated and the results are shown in Figure 1. In reactions using ≥0.75 mole% [Rh(H)CO(PPh$_3$)$_3$] more than 90% conversion of substrate into products was observed and substrate hydrogenation was <10%. Analysis of the variation of product distribution with time using *ca.* 1.7 mol % [Rh(H)CO(PPh$_3$)$_3$] (Figures 2 and 3)

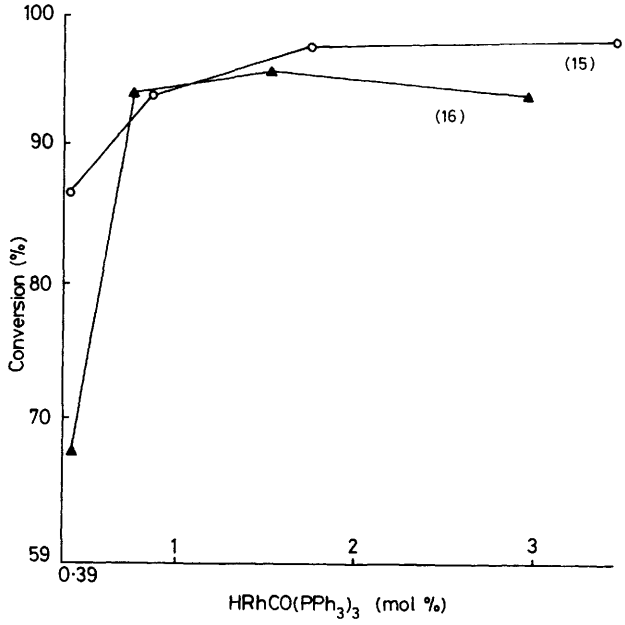


Figure 1.

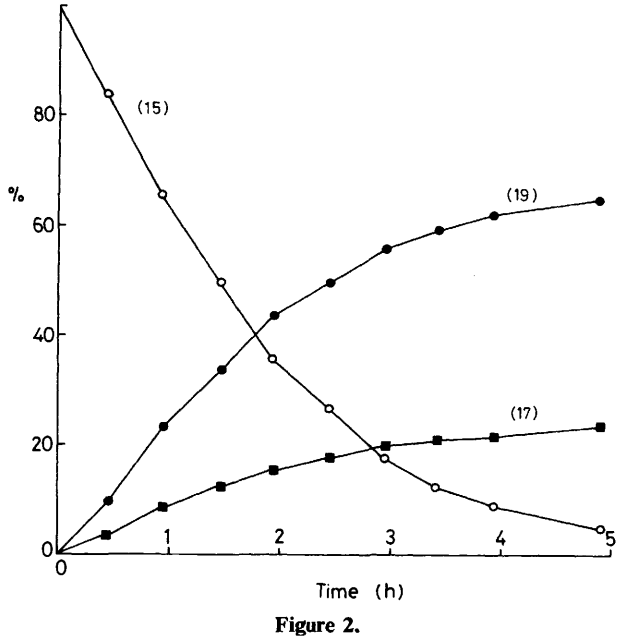


Figure 2.

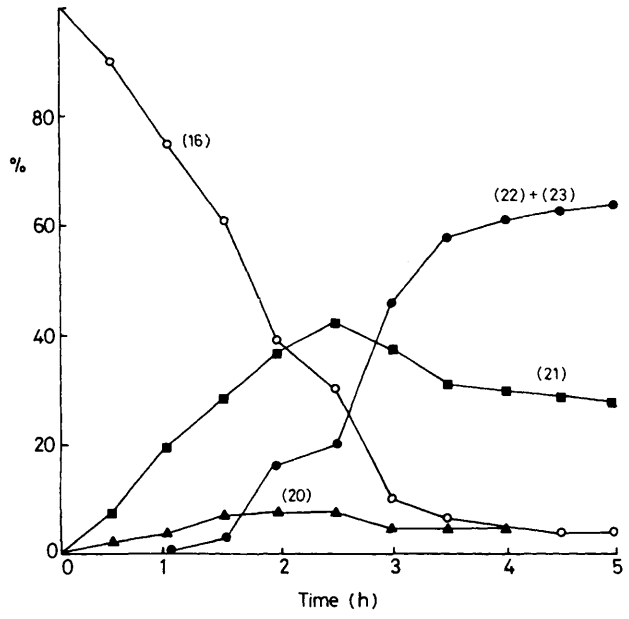


Figure 3.

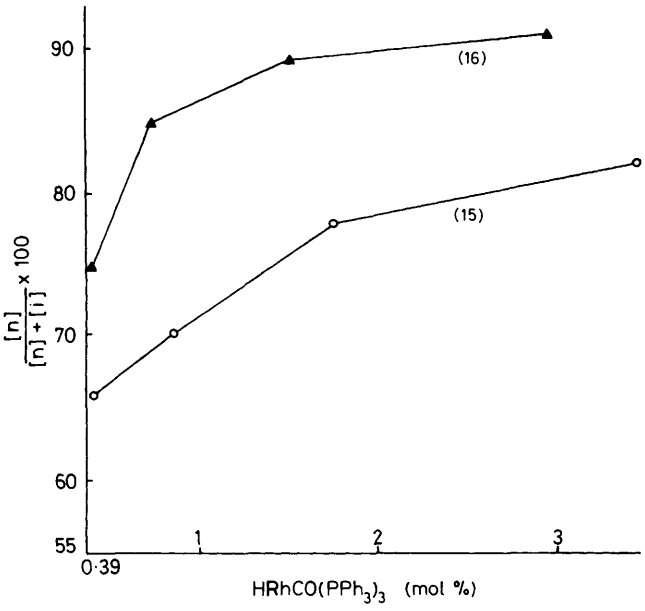
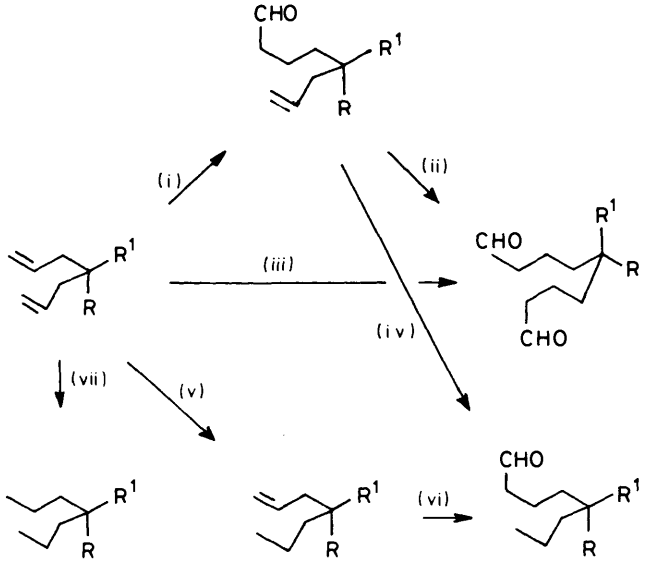
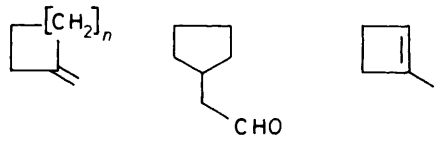


Figure 4.



Scheme 1.



(28) a; $n = 2$ (29) (30)
b; $n = 1$

provides clear evidence for dialdehyde formation *via* monoene monoaldehyde. Thus dialdehyde formation lags behind monoaldehyde formation (Figure 3) and monoaldehyde formation (saturated and unsaturated) reaches a maximum, then declines, and finally stabilises.

The failure of the monoaldehyde concentration to continue its initial decline is due to the fact that the monoaldehyde concentration is a composite of both saturated (incapable of further hydroformylation) and unsaturated aldehydes. Thus of the numerous possible paths from 1,6-diene to products (Scheme 1) the operation of paths (i), (iv) and (v), (vi) can result in saturated monoaldehyde, whereas (i), (ii) (and not (iii)) leads to dialdehyde.

The presence of dialdehyde as a major product (Figure 3) suggests path (i), (iv) is the more important source of saturated monaldehyde.

The effect of catalyst concentration on the n- to iso-selectivity was also studied and the results are presented graphically in Figure 4.

The results show a general increase in n-selectivity for both (15) and (16) with increasing catalyst concentration. There are two generally accepted mechanisms for the [Rh(H)CO-$(PPh_3)_3$] catalysed hydroformylation of alkenes, the associative mechanism and the dissociative mechanism.[5] In the former mechanism the complex $[Rh(H)CO(L)_2]$ is catalytically important whilst in the latter mechanism the complex [Rh(H)CO(L)] is important.[6] The associative mechanism shows greater n-selectivity and this has been explained as due to a combination of steric and electronic factors. Wilkinson has suggested that increasing the catalyst concentration favours the associative mechanism.[6]

The hydroformylation of several 1,1-disubstituted alkenes was briefly investigated. Methylenecyclopentane (28a) afforded the terminal aldehyde (29) (34%) whilst 1,1-diphenylethylene and camphene failed to undergo hydroformylation. Methylenecyclobutane (28b) underwent slow isomerisation to methylcyclobutene (30) under the hydroformylation conditions. After 10 days at ambient temperature in benzene in the presence of *ca.* 3 mole % $[Rh(H)CO(PPh_3)_3]$ the ratio of (28b) : (30) was 0.64 : 1.

Experimental

N.m.r. spectra were determined for solutions in deuteriochloroform, except where otherwise stated, with Jeol-PMX60 (60 MHz), Bruker WP90 (90 MHz), and Bruker WP250 (250 MHz) instruments. Mass spectra were obtained by direct insertion into the ion source of an AEI MS902 instrument at

70 eV. Mass spectra/g.l.c. were recorded using a Pye Unicam 104 gas chromatograph coupled to an AEI MS30 mass spectrometer. I.r. data were determined for films, except where otherwise stated, on a Perkin-Elmer 457 i.r. spectrophotometer. M.p.s were recorded with a Kofler hot-stage apparatus and are uncorrected. Analytical g.l.c. was performed on a Perkin-Elmer F11 or Pye 104 instruments. Preparative gas chromatography was performed on a Perkin-Elmer F21 or Aerograph A-700 autoprep. Premixed hydrogen–carbon monoxide (2 : 1) was obtained from British Oxygen Co. $HRhCO(PPh_3)_3$ was prepared as described in the literature.[19] All alkenes were distilled and stored over activated 4A molecular sieves. Hydroformylations using 1 : 1 H_2 : CO were carried out in a modified atmospheric hydrogenation apparatus whilst those involving a 2 : 1 H_2–CO gas mixture were carried by bubbling the gas mixture through the vigorously stirred reaction mixture.

Non-7-en-1-al (7a) *and Non-7-en-2-al* (8a).—Octa-1,6-diene (3 g, 2.72×10^{-2} mol) and $[Rh(H)CO(PPh_3)_3]$ (0.7 g, 7.7×10^{-4} mol) were dissolved in benzene (50 ml) in a round bottom flask (250 ml) connected to modified atmospheric hydrogenation apparatus. The solution was magnetically stirred and evacuated by means of a water pump and then filled with an equimolar mixture of H_2–CO. The mixture was stirred vigorously until the calculated amount of hydrogen and carbon monoxide had been absorbed (12 h). The benzene was then removed under reduced pressure and the crude product distilled (86 °C/23 mmHg) to afford a 12 : 1 mixture (g.l.c.; 2 m, 20M Carbowax column at 180 °C) of (7a) and (8a) (1.8 g, 47%) (Found: C, 77.3; H, 11.4. $C_9H_{16}O$ requires C, 77.10; H, 11.50%), $\nu_{max.}$ 1 725 and 958 cm^{-1} (*trans*-disubstituted C=C); δ 1.34—2.43 [m, 10 H, $(CH_2)_5$], 1.64 (m, 3 H, Me), 5.39 (m, 2 H, CH=CH), 9.59 (d, 1 H, iso-CHO), and 9.76 (t, 1 H, n-CHO); *m/z* (%) 140 (M^+, 3), 122(16), 98(21), 93(16), 81(31), 69(21), 68(31), 67(34), 55(100), and 41(61).

Ethyl 10-*Oxodec-3-enoate* (7b).—Ethyl nona-3,8-dienoate (5.4 g, 2.96×10^{-2} mol) and $[Rh(H)CO(PPh_3)_3]$ (0.48 g, 5.2×10^{-4} mol) were dissolved in benzene (30 ml) and the resulting mixture degassed and stirred under an atmosphere of hydrogen and carbon monoxide (2 : 1) at room temperature for 4 days. The benzene was removed under reduced pressure and the residue distilled to afford unchanged ethyl nona-3,8-dienoate (1.7 g; 60°/1 mmHg) and (7b) (92—96 °C/0.1 mmHg) (60.5%) (Found: C, 67.9; H, 9.65. $C_{12}H_{20}O_3$ requires C, 67.90; H, 9.50%); $\nu_{max.}$ 1 730 and 960 cm^{-1} (*trans*-disubstituted C=C); δ 1.23 (t, 3 H, CH_2Me), 1.10—2.6 [m, 10 H, $(CH_2)_5$], 2.98 (m, 2 H, CH_2CO_2Et), 4.10 (q, 2 H, CH_2Me), 5.52 (m, 2 H, olefinic H), and 9.71, (t, 1 H, CHO); *m/z* (%) 212 (M^+, 1), 194(4), 168(16), 138(22), 124(23), 95(62), 94(49), 88(61), 80(71), 67(72), and 55(100).

Note that the ratio of linear : branched aldehyde is dependent on the purity of the catalyst. In several experiments using different batches of catalyst and a H_2 : CO ratio of 2 : 1, the ratio of (7; R = CO_2Et) : (8; R = CO_2Et) varied from 5 : 1 to 40 : 1.

5,5-*Diacetylnon-7-en-1-al* (7c) *and* 4,4-*Diacetyl-2-methyloct-6-en-1-al* (8c).—4,4-Diacetylocta-1,6-diene (1.8 g, 8.1×10^{-3} mol) and $[Rh(H)CO(PPh_3)_3]$ (0.18 g, 1.96×10^{-4} mol) in benzene (50 ml) were allowed to react under an atmosphere of hydrogen and carbon monoxide (2 : 1) for 4 days at room temperature. Work-up as described above afforded unchanged starting material (0.4 g) together with a 2.5 : 1 mixture (g.l.c.; 2 m, 2.5% SGR column at 140 °C) of product aldehydes [(7c), (8c)] (1.0 g, 62.5%), b.p. 116—118 °C/0.2 mmHg (Found: C, 69.45; H, 9.05. $C_{13}H_{20}O_3$ requires C, 69.60; H, 8.90%); $\nu_{max.}$ 1 710 and 965 cm^{-1} (*trans*-disubstituted C=C); δ 1.10 (d, 3 H, Me), 1.65 (d, 3 H, C=CH*Me*), 2.09 (s, 6 H, COMe), 1.50—2.86 [m, 8 H, $(CH_2)_4$], 4.90—5.80 (m, 2 H, olefinic H), 9.46 (d, iso-CHO) and 9.72 (t, n-CHO); *m/z* (%) 224 (M^+, 2), 181(100), 125(37), 121(58), 111(33), 109(18), 93(30), and 55(55).

2-(*But-3-enyl*)-2,5-*dihydrothiophene* 1,1-*Dioxide* (10a).—A flask (250 ml) was charged with octa-1,3,7-triene (11.6 g, 0.11 mol),[20] benzene (50 ml), and hydroquinone (0.12 g) to retard polysulphone formation. Sulphur dioxide (30 ml) was condensed into the flask by means of a solid CO_2 condenser. The reaction mixture was allowed to stand for three days (being recharged with sulphur dioxide every day) at the reflux temperature of SO_2. At the end of this time the unchanged triene, benzene, and SO_2 were removed under reduced pressure to give a mobile brown oil as product (8.1 g, 44%). Attempted distillation at 0.1 mmHg led to extensive decomposition (evolution of SO_2 and polymer formation). Molecular distillation (43 °C/0.05 mmHg) gave an analytically pure sample (Found: C, 56.05; H, 7.1. $C_8H_{12}O_2S$ requires C, 55.80; H, 7.00%); $\nu_{max.}$ 1 648, 1 310 and 1 140 (SO_2), and 990 and 910 cm^{-1} (terminal allyl); δ 1.50—2.40 [m, 4 H, $(CH_2)_2$], 3.63br (s, 3 H, CH_2SO_2CH), 4.80—5.90 (m, 3 H, CH_2=CH), and 5.93 (s, 2 H, CH=CH); *m/z* (%) 127 (M^+, not observed), 108(16), 107(19), 93(16), 91(8), 79(21), 67(100), and 64(38).

2-(*But-3-enyl*)-2,5-*dihydrothiophene* 1-*Oxide* (10b).—A solution of octa-1,3,7-triene (15 g, 0.14 mol) and thiiran 1-oxide (12 g, 0.16 mol)[21] in dry toluene (75 ml) was heated under reflux for 3 h. The toluene, unchanged triene, and thiiran 1-oxide were then removed under reduced pressure to leave the crude sulphoxide (10b) (10 g, 46%). Attempted distillation (<0.1 mmHg) led to extensive decomposition. Molecular distillation (100 °C/0.2 mmHg) gave an analytically pure sample (Found: C, 61.35; H, 7.7. $C_8H_{12}OS$ requires C, 61.50; H, 7.75%); $\nu_{max.}$ 1 645, 1 035 (SO), and 990 and 910 cm^{-1} (terminal allyl); δ 1.70—2.17 [m, 4 H, $(CH_2)_2$], 3.5—3.7 (m, 3 H, CH_2SOCH), 4.8—5.9 (m, 3 H, CH_2=CH), and 5.99 (s, 2 H, CH=CH); *m/z* (%) 156 (M^+, not observed), 108(16), 107(33), 97(50), 93(42), 92(67), 91(100), 85(50), 79(59), and 67(92).

2-(*But-3-enyl*)-2,5-*dihydrothiophene* (10c).—A solution of the crude sulphoxide (10b) (3.1 g, 20 mmol) in dry tetrahydrofuran (20 ml) was added slowly, with stirring, to a slurry of lithium aluminium hydride (0.8 g, 20 mmol) in dry tetrahydrofuran (30 ml), the mixture being maintained at 25 °C. After completion of the addition the mixture was stirred for a further 4 h and the excess of lithium aluminium hydride then destroyed by the addition of water (3 ml), 15% aqueous sodium hydroxide (2 ml), and water (3 ml). The granular precipitate was removed by filtration and the filtrate dried (sodium sulphate). The solvent was removed under reduced pressure to leave the crude sulphide (10c) (1.3 g, 46.5%). Molecular distillation (33 °C/0.05 mmHg) gave an analytically pure sample (Found: C, 68.3; H, 9.25. $C_8H_{12}S$ requires C, 68.50; H, 9.20%); $\nu_{max.}$ 1 635, 990 and 910 cm^{-1} (terminal allyl); δ 1.50—2.40 [m, 4 H, $(CH_2)_2$], 3.75 (m, 3 H, CH_2SOCH), 4.90—6.0 (m, 3 H, CH_2=CH), and 5.83 (s, 2 H, CH=CH); *m/z* (%) 140 (M^+, 7), 127(2), 111(3), 105(4), 99(13), and 85(100).

Hydroformylation of 2-(*But-3-enyl*)-2,5-*dihydrothiophene* 1,1-*Dioxide* (10a).—2-(But-3-enyl)-2,5-dihydrothiophene 1,1-dioxide (4.5 g, 26 mmol) and $[Rh(H)CO(PPh_3)_3]$ (0.45 g, 4.9×10^{-4} mol) in benzene (30 ml) were allowed to react under an atmosphere of hydrogen and carbon monoxide (2 : 1) for 4

days at room temperature. Removal of the solvent afforded the crude 2-(5-oxopentyl)-2,5-dihydrothiophene 1,1-dioxide (5.28 g, 100%). A satisfactory analysis could not be obtained despite attempted purification by molecular distillation (60 °C/0.05 mmHg), $\nu_{max.}$ 1 720, 1 300 and 1 120 cm^{-1} (SO_2); δ 1.0—2.6 [m, 8 H, $(CH_2)_4$], 3.70 (s, 3 H, CH_2SO_2CH), 6.0 (s, 2 H, CH=CH), and 9.70 (t, 1 H, n-CHO); no iso-aldehyde was present; *m/z* (%) 202 (M^+, 2), 201(2), 174(4), 159(2), 154(4), 138(8), 109(16), 94(19), 80(38), 79(54), 67(78), and 64(100).

Oxidation of 2-(5-*Oxopentyl*)-2,5-*dihydrothiophene* 1,1-*Dioxide*.—(a) *With Jones reagent*. Jones reagent was prepared by the addition of concentrated sulphuric acid (1.2 ml) to a solution of chromium trioxide (1.4 g) in water (2.5 ml). This was then added dropwise with vigorous stirring to a solution of 2-(5-oxopentyl)-2,5-dihydrothiophene 1,1-dioxide (2.2 g, 1.09×10^{-2} mol) in acetone (15 ml), the temperature being maintained at *ca.* 30 °C. Upon addition of the reagent a green precipitate formed (H_2CrO_3) and addition was continued until the yellow colour of the reagent persisted. The solution was filtered to remove the green precipitate and a few drops of isopropyl alcohol were added to the filtrate to destroy the excess of reagent. The acetone was then removed under reduced pressure and the crude product taken up in chloroform, washed with water, dried ($MgSO_4$), and the solvent removed to afford the crude acid (13a) (1.5 g, 63%). Treatment of the acid with ethereal diazomethane afforded the ester, methyl 5-(2,5-dihydro-2-thienyl)pentanoate 1,1-dioxide (13b). Molecular distillation (60 °C/0.2 mmHg) gave an analytically pure sample (Found: C, 52.0; H, 7.0. $C_{10}H_{16}O_4S$ requires C, 51.70; H, 6.95%); $\nu_{max.}$ 1 735, 1 310 and 1 135 cm^{-1} (SO_2); δ 0.76—2.43 [m, 8 H, $(CH_2)_4$], 3.69 (s, 3 H, CO_2Me), 3.73br (s, 3 H, CH_2SO_2CH), and 6.06br (s, 2 H, CH=CH); *m/z* (%) 232 (M^+, 1), 201(15), 168(47), 137(18), 136(24), 109(12), 108(21), 107(12), 94(100), 88(30), 81(26), 80(29), 79(67), 67(62), 64(53), 54(38), and 41(50).

(b) *With alkaline silver oxide*. The alkaline silver oxide was prepared *in situ* by the addition of 10% aqueous sodium hydroxide (34 ml) to a solution of silver nitrate (3.08 g, 2.4×10^{-2} mol) followed by the addition of dioxan (34 ml). 2-(5-Oxopentyl)-2,5-dihydrothiophene 1,1-dioxide (2.60 g, 1.29×10^{-2} mol) was then added and the reaction mixture stirred at ambient temperature overnight. The alkaline solution was acidified with hydrochloric acid (0.5M), taken to dryness on a Rotavapor and subsequently extracted with chloroform. The chloroform extracts were dried ($MgSO_4$) and removal of the chloroform afforded the crude acid (14a) (2.3 g, 83%). The acid was converted into its methyl ester (14b) by reaction with ethereal diazomethane. Sublimation followed by crystallisation from methanol afforded colourless needles of methyl 5-(2,3-dihydro-2-thienyl)pentanoate 1,1-dioxide (14b), m.p. 69 °C (Found: C, 52.1; H, 7.1. $C_{10}H_{16}O_4S$ requires C, 51.70; H, 6.95%); $\nu_{max.}$ (KBr) 1 730, 1 290 and 1 130 cm^{-1} (SO_2); δ 1.5—2.5 [m, 8 H, $(CH_2)_4$], 2.7—2.8 (m, 2 H, CH_2–CH=CR), 3.2—3.3 (m, 2 H, CH_2SO_2), 3.67 (s, 3 H, CO_2Me), and 6.5 (m, 1 H, CH=CR); *m/z* (%) 232 (M^+, 1), 201(50), 200(62), 173(16), 159(25), 94(81), and 79(100).

Hydroformylation of 2-(*But*-3-*enyl*)-2,5-*dihydrothiophene* 1-*Oxide* (10b).—2-(But-3-enyl)-2,5-dihydrothiophene 1-oxide (0.5 g, 3.2×10^{-3} mol) in benzene (10 ml) was hydroformylated using $[Rh(H)CO(PPh_3)_3]$ (0.1 g, 1×10^{-4} mol) as catalyst and required 4 days at ambient temperature for complete uptake of hydrogen and carbon monoxide (1 : 1). After removal of the benzene solvent the crude hydroformylation product was distilled (90 °C/0.1 mmHg) in a molecular still to give a colourless oil whose n.m.r. spectrum (below) showed it to comprise a 4 : 1 mixture of 2-(5-oxopentyl)-2,5-dihydrothiophene 1-oxide (11b) and 2-(3-formylbutyl)-2,5-dihydrothiophene 1-oxide (12b) (Found: C, 59.4; H, 7.85. $C_9H_{14}O_2S$ requires C, 60.15; H, 8.10%); $\nu_{max.}$ 1 720 and 1 035 cm^{-1} (SO); δ 1.14—2.65 [m, 8 H, $(CH_2)_4$], 3.55—3.82 (m, 3 H, CH_2SOCH), 5.95 (s, 2 H, CH=CH), 9.60 (d, iso-CHO), and 9.77 (t, n-CHO). The ratio of normal- to iso-aldehyde was found to be 4 : 1 by integration of their respective signals.

General Method for Hydroformylation of (15) *and* (16).—$HRhCO(PPh_3)_3$ (*ca.* 1 mol %) (Table 2) was weighed into a 3-neck round bottomed flask (100 ml) containing a magnetic stirring bar and equipped with a 250 ml pressure-equalised dropping funnel containing a solution of the alkene (1 g) in benzene (6 ml). A septum cap was fitted to one neck of the reaction flask to allow easy removal of reaction samples. The benzene solution was degassed and repressurised five times with a 2 : 1 hydrogen–carbon monoxide gas mixture and then allowed to drain into the reaction flask. A 2 : 1 hydrogen–carbon monoxide gas mixture was then passed slowly over the rapidly stirred reaction mixture. After completion of the reaction the solvent was removed, the residue dissolved in ether–benzene (17 : 83, v/v), filtered to remove catalyst, and separated by thin layer chromatography on silica. Products were extracted from the plates with methanol and aldehyde samples were sealed in ampoules and stored at 0 °C to retard autoxidation.

2,2-*Diethoxylcarbonylcyclopentanol* (18). This was obtained as a colourless oil (Found: C, 57.45; H, 7.75. $C_{11}H_{18}O_5$ requires C, 57.40; H, 7.90%); $\nu_{max.}$ 3 500 and 1 720 cm^{-1}; δ 1.26 (m, 6 H, 2 × CH_2Me), 1.63—2.07 (m, 4 H, 2 × CH_2), 2.21 and 2.37 (2 × m, 2 H, CH_2), 3.29 (brs, 1 H, OH), 4.23 (m, 4 H, 2 × CH_2Me), and 4.16 (t, 1 H, CHOH); *m/z* (%) (CI), 231 ($M + 1$, 21), 185(4), and 57(100).

2-*Methyl*-4,4-*diethoxycarbonylbutanal* (17). This was obtained as a colourless oil (Found: C, 57.9; H, 7.8. $C_{11}H_{18}O_5$ requires C, 57.40; H, 7.90%); $\nu_{max.}$ 1 720 cm^{-1}; δ 1.16 (d, 3 H, CH*Me*), 1.31 (m, 6 H, 2 × CH_2Me), 1.88 (m, 1 H), 2.42 [m, 2 H, CH(CHO)-CHH'], 3.47 [t, 1 H, $CH(CO_2Et)_2$], 4.24 (m, 4 H, 2 × CH_2Me), and 9.63 (d, 1 H, CHO).

5,5-*Diacetyloct*-7-*enal* (21). This was obtained as a colourless oil (Found: C, 68.35; H, 8.9. $C_{12}H_{18}O_3$ requires C, 68.55; H, 8.65%); $\nu_{max.}$ 1 714 and 1 689 cm^{-1}; δ 1.38 (m, 2 H, CH_2), 1.88 (m, 2 H, CH_2), 2.12 (s, 6 H, 2 × CO*Me*), 2.50 (m, 2 H, CH_2CHO), 2.68 (m, 2 H, =CHCH_2), 5.06—5.62 (m, 3 H, CH_2=CH), and 9.77 (t, 1 H, CHO).

2-*Methyl*-4-*acetylhept*-6-*enal*. This was obtained as a colourless oil comprising an 50 : 50 mixture of diastereoisomers; $\nu_{max.}$ ($CHCl_3$) 1 706 and 1 633 cm^{-1}; δ 1.11 (2 × d, 3 H, diastereomeric Me's), 1.35 (m, 0.5 H), 1.75 (m, 1 H), 2.15 (s, 3 H, COMe), 2.2 (m, 0.5 H), 2.3 (m, 3 H, CH_2CH=CH_2 and CH(Me)CHO], 2.7 (m, 1 H, CHCOMe), 5.07 (m, 2 H, CH_2=CH), 5.7 (m, 1 H, CH_2=CH), and 9.57 (m, 1 H, CHO) (Found: M^+, 168.1149. $C_{10}H_{16}O_2$ requires *M*, 168.115 03).

5,5-*Diacetylnonane*-1,9-*dial* (23). This was obtained as a colourless oil (Found: C, 64.9; H, 8.55. $C_{13}H_{20}O_4$ requires C, 65.00; H, 8.40%); $\nu_{max.}$ ($CHCl_3$) 1 700 cm^{-1}; δ 1.25 (m, 4 H, 2 × CH_2), 1.80 [m, 4 H, 2 × $CH_2C(COMe)_2$], 2.02 (s, 6 H, 2 × COMe), 2.42 (m, 4 H, 2 × CH_2CHO), and 9.67 (t, 2 H, 2 × CHO); *m/z* (%) 241 ($M + 1$, 0.3), 198(3), 180(2), 170(3), 165(2), 154(2), 152(4), 141(12), and 95(21).

Cyclopentylacetaldehyde (29).—Methylenecyclopentane (1.5 g, 1.83×10^{-2} mol) was hydroformylated in benzene (15 ml) containing $[Rh(H)CO(PPh_3)_3]$ (0.2 g, 2.18×10^{-4} mol) under an atmosphere of hydrogen–carbon monoxide (2 : 1) for 4 days at room temperature. Removal of the benzene and the distillation of the residue afforded cyclopentylacetylaldehyde (0.7 g, 34%), b.p. 47 °C/14 mmHg, as a colourless oil. The

2,4-dinitrophenylhydrazine derivative had m.p. 127 °C (lit.,[22] m.p. 128—129 °C); $\nu_{max.}$ 1 720 cm^{-1}; δ 0.83—2.20 [m, 9 H, $(CH_2)_4$ and $CHCH_2CHO$], 2.47 (m, 2 H, CH_2CHO), and 9.73 (t, 1 H, CHO).

Isomerisation of Methylenecyclobutane (28b).—A mixture of methylenecyclobutane (1 g, 1.47×10^{-2} mol) and $[Rh(H)CO(PPh_3)_3]$ (0.48, 4.36×10^{-4} mol) in benzene (20 ml) was stirred at ambient temperature under a nitrogen atmosphere. Samples were withdrawn periodically and analysed by g.l.c. on a 100 m polypropylene glycol capillary column at ambient temperature. The ratio of 1-methylcyclobutene (30) to methylenecyclobutane (28b) was 1 : 0.68 after 10 days and remained constant thereafter. The n.m.r. (C_6D_6) of the mixture showed the expected signals for both compounds, *i.e.* (28b), δ 1.80 (q, 2 H, CH_2), 2.60 [m, 4 H, $CH_2=C(CH_2)_2$], and 4.72 (m, 2 H, $CH_2=C$); (30), δ 1.55br (s, Me), 2.33 (s, 4 H, 2 × CH_2), and 5.60 (m, 1 H, $CH=CMe$).

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