

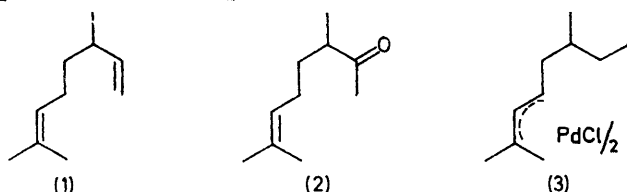
Complexing of Terpenes with Transition Metals. Part V.¹ Reactions of 3,7-Dimethylocta-1,6-diene and of 7-Methoxy-3,7-dimethyloct-1-ene with Rhodium(III) and Thallium(III)

By Francis J. McQuillin* and David George Parker, Department of Organic Chemistry, The University of Newcastle upon Tyne, Newcastle upon Tyne NE1 7RU

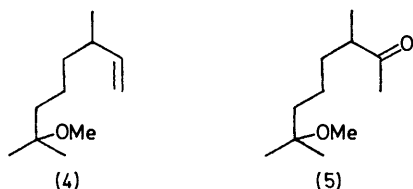
3,7-Dimethylocta-1,6-diene and 7-methoxy-3,7-dimethyloct-1-ene are catalytically oxidised at the vinyl group by $\text{RhCl}_3\text{-FeCl}_3$ in oxygen to the derived methyl ketones in good yield. An accompanying alkene isomerisation reaction ($-\text{CMe}\cdot\text{CH}:\text{CH}_2 \longrightarrow -\text{CMe}:\text{CH}\cdot\text{CH}_3$) has been studied. The above octadiene and methoxyoctene are hydroformylated ($-\text{CMe}\cdot\text{CH}:\text{CH}_2 \longrightarrow -\text{CMe}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CHO}$) in good yield by $[\text{RhH}(\text{CO})(\text{PPh}_3)_3]$, with some accompanying alkene isomerisation.

With $\text{Tl}(\text{NO}_3)_3$, 3,7-dimethylocta-1,6-diene reacts at the 6,7-double bond to give a ketone with migration of a methyl group, and at the 1,2-double bond with cyclisation to give cyclopentane derivatives.

We have previously¹ examined the reactions of (+)-3,7-dimethylocta-1,6-diene (1) with Pd^{II} and Hg^{II} salts. This survey has now been extended to include the reactions of this diene with Rh^{III} and Tl^{III} . Thallium(III) was examined since in its reactions with alkenes² it closely resembles Hg^{II} . Reaction with Rh^{III} was of interest because Rh^{III} is reported³ to oxidise ethene, and in the presence of Fe^{III} the process becomes catalytic, *i.e.* analogous to the Wacker oxidation. Although with PdCl_2 , CuCl_2 , and oxygen 3,7-dimethylocta-1,6-diene is oxidised in reasonable yield to the ketone (2), a side reaction withdraws palladium from the system as the stable π -allyl palladium derivative¹ (3). Rhodium(III)-catalysed oxidation of (1) was therefore of interest as a possible alternative procedure.



3,7-Dimethylocta-1,6-diene (14.5 mmol) with rhodium trichloride trihydrate (1.2 mmol) and iron(III) chloride (2.5 mmol) in aqueous dimethylformamide or dimethylacetamide in oxygen at 80 °C in fact yielded the ketone (2) in 80% yield. By this procedure similarly high yields of the alkan-2-one were also obtained from oct-1-ene and dec-1-ene, and 7-methoxy-3,7-dimethyloct-1-ene (4), which is directly available¹ from (1), gave the ketone

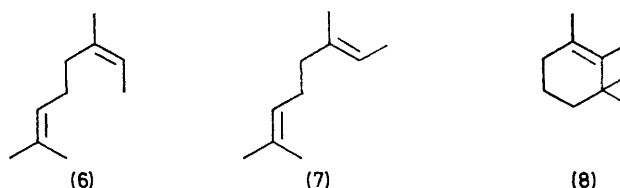


(5). Thus oxidation by Rh^{III} in the presence of Fe^{III} appears to offer a useful alternative to the Wacker oxidation.

¹ Part IV, F. J. McQuillin and D. G. Parker, *J.C.S. Perkin I*, 1974, 809.

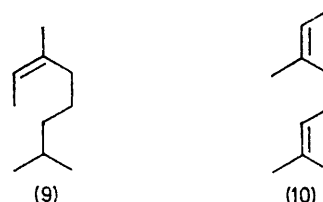
² A. McKillop, J. D. Hunt, E. C. Taylor, F. Kienzle, and E. Bingham, *J. Amer. Chem. Soc.*, 1973, **95**, 3635; A. McKillop and E. C. Taylor, *Chem. in Britain*, 1973, **9**, 4.

Rhodium(III)-induced oxidation of (1) is not, however, entirely free of side reactions. We were not surprised to find that unoxidised diene, recovered from this reaction, had been in part isomerised to a mixture of (*E*)-3,7-dimethylocta-2,6-diene (6), and the *Z*-isomer (7). The structures of (6) and (7) were indicated by



their n.m.r. spectra, *viz.* for (6), τ 8.35 (12 H), 7.97 (4 H, d, J 3 Hz), and 4.87 (2 H, m); and for (7), τ 8.37 (12 H), 8.0br (4 H), and 4.84 (2 H, m); and confirmed by comparison (n.m.r., i.r., g.l.c., and mass spectra) with authentic samples prepared by Birch reduction of nerol and geraniol, respectively.

The allylic proton signal for (6) appears as a clear doublet at τ 7.97 and for (7) as a broad unresolved signal at τ 8.0. The *Z*-isomer (7) has greater rotational freedom



about the 4,5-bond, whereas for (6) the rotamer (9) presents considerable, and (10) appreciable steric hindrance to rotation.

Alkene isomerisation by Rh^{I} derivatives is well established,⁴ and oxidation of (1) to (2) by Rh^{III} will generate Rh^{I} species in solution.³ However, since isomerisation of (1) potentially offers a simple route to (6) or (7) this reaction was examined further.

3,7-Dimethylocta-1,6-diene (1.5 mol) with $\text{RhCl}_3\cdot 3\text{H}_2\text{O}$ (0.07 mol) in acetone at ambient temperature underwent

³ B. R. James and G. L. Rempel, *Canad. J. Chem.*, 1968, **46**, 571; 1972, **50**, 1698.

⁴ (a) R. Cramer, *J. Amer. Chem. Soc.*, 1966, **88**, 2272; (b) J. F. Harrod and A. J. Chalk, *ibid.*, 1964, **86**, 1776.

progressive isomerisation as indicated by g.l.c. analysis (see Table).

Isomerisation of 3,7-dimethylocta-1,6-diene by
RhCl₃·3H₂O in acetone

Component	Constituents of mixture (%) after		
	25 h	100 h	300 h
(A) (1)	48	23	2
(B) (6)	18.5	18	13
(C) (7)	26	45	57
(D) (8)	2.5	9	26

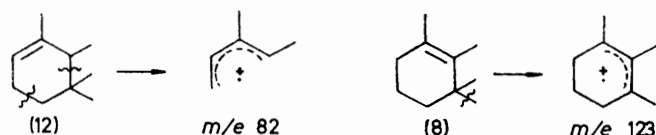
A pure sample of the *E*-isomer of 3,7-dimethylocta-2,6-diene (6), with RhCl₃·3H₂O in acetone, isomerised to the *Z*-isomer (7) which, as noted above, has greater rotational freedom than (6).

The results in the Table indicate, however, that prolonged reaction results in formation of a third, terminal product. This was recognised as 1,2,3,3-tetramethylcyclohexene (8) from spectral data, and the structure was confirmed by preparation of (8) from 1,2,6,6-tetramethylcyclohexa-1,3-diene (11). Prepared by isomerisation of 3,7-dimethylocta-1,6-diene (1), or, independently from (*Z*)-3,7-dimethylocta-2,6-diene (7), the product (8) was characterised by *m/e* 138 with an ion *m/e* 123 as the base peak, and by n.m.r. signals at τ 9.0 (6 H, s), 8.4. (6 H, s), and 8.05br (2 H). Hydrogenation gave a hydrocarbon, *m/e* 140, which proved identical (g.l.c. and n.m.r. comparison) with a sample of 1,1,2,3-tetramethylcyclohexane. Further, half hydrogenation of 1,2,6,6-tetramethylcyclohexa-1,3-diene gave a mixture of two products, separable by preparative g.l.c. into a major component, *m/e* 138, identical (g.l.c. and n.m.r. comparison) with the final product (8) of isomerisation of 3,7-dimethylocta-1,6-diene. The second tetramethylcyclohexene is clearly the isomer (12), *m/e* 138, τ 9.10



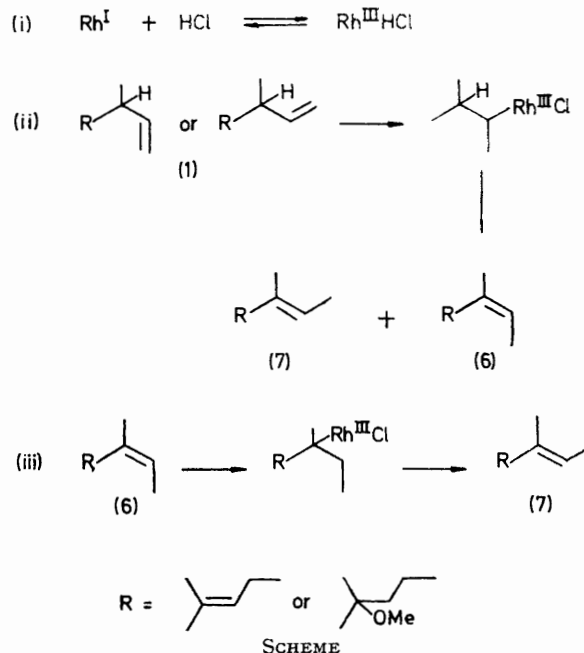
(9 H, m), 8.75 (2 H, m), 8.35 (3 H, s), 8.06 (3 H, m), and 4.73 (1 H, m).

The isomeric tetramethylcyclohexenes (8) and (12) exhibit a difference in mass spectral fragmentation consistent with the assigned structures. Isomer (8) showed a base peak *m/e* 123 due to loss of a methyl-group from the position allylic to the alkene bond, whereas the isomer (11) gave a base peak at *m/e* 82, *i.e.* corresponding to the fragmentations shown.



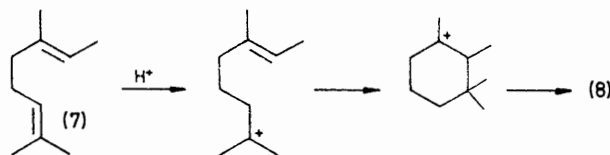
The isomerisation brought about by RhCl₃·3H₂O in acetone was accompanied by no evident colour change, the development of a little acidity, and the formation of a small amount of mesityl oxide. By column chro-

matography of the product it was also possible to isolate small amounts of a carbonyl-containing product, *m/e* 154 (C₁₀H₁₈O), ν_{CO} 1710 cm⁻¹, with g.l.c. behaviour very like that of 3,7-dimethyloct-6-en-2-one (2), and material, *m/e* 174/176 (C₁₀H₁₉Cl). This evidence of oxidation of 3,7-dimethylocta-1,6-diene (1) indicates the presence of a source of Rh^I and of hydrogen chloride, which previous research has indicated⁴ provides a route for alkene isomerisation by successive addition and elimination of a rhodium hydride (see Scheme).



Addition of a little dry potassium carbonate to the RhCl₃·3H₂O-acetone solution was found to inhibit isomerisation, *i.e.* acidity is necessary, but we have been unable to effect similar isomerisation of 3,7-dimethylocta-1,6-diene by mild acid treatment alone, and we note that acid-catalysed addition involves the 6,7- rather than the 1,2-double bond.¹

Cyclisation of (*Z*)-3,7-dimethylocta-2,6-diene (7) to 1,2,3,3-tetramethylcyclohexene, brought about by means

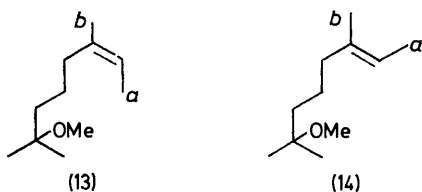


of RhCl₃·3H₂O in acetone, has the appearance of an acid-catalysed reaction as illustrated. However, the observed⁵ acid-induced cyclisation of (7) employed much more severe conditions.

7-Methoxy-3,7-dimethyloct-1-ene (4) with RhCl₃·3H₂O in acetone was found to be isomerised to a pair of products, (13) and (14), distinguished by the rather higher

⁵ G. C. Oppenlander and A. R. Day, *J. Org. Chem.*, 1956, **21**, 961.

field n.m.r. signal for protons *a* and *b* in (14) (τ 8.43) than in (13) (τ 8.37). However, these products were accompanied by compounds (1), (6), and (7) in small



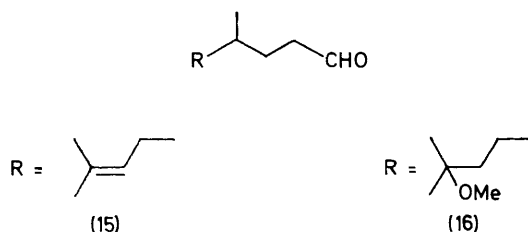
amounts indicative of acid-induced elimination of methanol.

μ -Dichlorotetraethylenedirhodium^{4a} in acetone did not isomerise the diene (1) during 6 days, but isomerisation was induced by addition of a little aqueous hydrochloric acid. This requirement for an acid co-catalyst has already been established.⁴

Chlorotris(triphenylphosphine)rhodium in refluxing chloroform⁶ brought about limited isomerisation of (1), but from similar treatment under nitrogen no isomerisation could be detected. This is in agreement with earlier observations⁷ on the effect of oxygen on this catalyst system.

Since the aim of our work was, in part, to convert 3,7-dimethylocta-1,6-diene (1) into useful derivatives, we also examined hydroformylation of the diene (1).

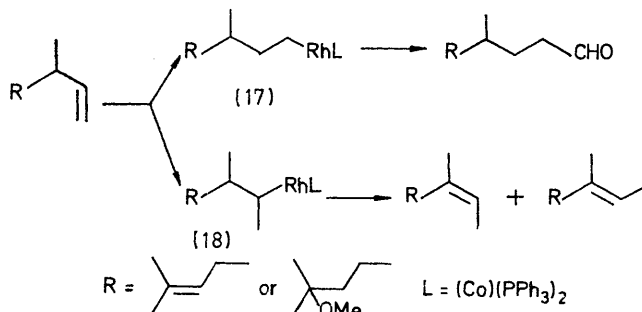
Carbonyl(hydrido)tris(triphenylphosphine)rhodium offers a convenient reagent for alkene carbonylation at atmospheric pressure.⁸ Applied to 3,7-dimethylocta-1,6-diene (1), $[\text{RhH}(\text{CO})(\text{PPh}_3)_3]$ in benzene at 70 °C with hydrogen and carbon monoxide gave the aldehyde (15) in good yield. 7-Methoxy-3,7-dimethyloct-1-ene similarly gave (16), and in neither case were we able to detect the isomeric aldehyde from carbonylation at position 2. However, the alternative mode of addition of $[\text{RhH}(\text{CO})(\text{PPh}_3)_3]$ to (1) must occur since the unchanged alkene



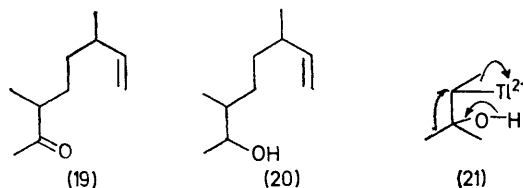
recovered from carbonylation of (1) was found to contain the isomerised olefins (6) and (7). The isomers (13) and (14) were similarly formed in the carbonylation of (4). Isomerisation of (1) by $[\text{RhH}(\text{CO})(\text{PPh}_3)_3]$ under nitrogen, *i.e.* in absence of carbon monoxide and hydrogen, was verified. Thus the alkene adduct (17) survives to undergo carbonylation whereas the adduct (18) undergoes rapid elimination.

In a previous paper¹ we compared the reactions of 3,7-

dimethylocta-1,6-diene with Pd^{II} and Hg^{II} salts. We now report preliminary results of the corresponding reactions of (1) with $\text{Tl}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$ in methanol. Reaction was rapid and the product mixture proved complex. However, g.l.c. separation gave, *inter alia*, a ketone, *m/e* 154 ($\text{C}_{10}\text{H}_{18}\text{O}$), and two isomeric products, *m/e* 200 [$\text{C}_{10}\text{H}_{18}(\text{OCH}_3)_2$]. The ketone was shown to have the structure (19) on the basis of characteristic n.m.r. signals for a vinyl residue [τ 5.18 (dd, *J* 7 and 2.5 Hz), 5.0 (dd, *J* 12 and 2.5 Hz), and 4.33 (m, *J* 12, 7, and 2.5 Hz)], a 3 H singlet (τ 7.95), and two 3 H doublets [τ 8.95 (*J* 7 Hz) and 9.05 (*J* 7 Hz)]. Further the derived carbinol, *m/e* 156, showed the same vinyl proton signals

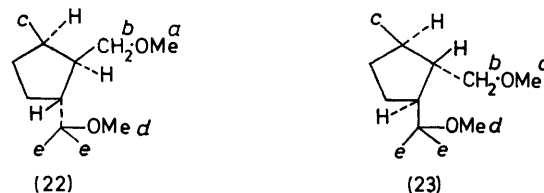


[τ 5.18, 5.0, and 4.3] but also a 3 H doublet [τ 8.78 (*J* 6 Hz)] due to $\text{CH}_3\text{-CH}(\text{OH})$, as well as a τ 6.3 signal for $\text{CH}_3\text{-CH}(\text{OH})$, *i.e.* corresponding to structure (20).



Formation of (19), which is evidently dependent on the presence of water, introduced in the $\text{Tl}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$, is rationalised as in formula (21) (*cf.* ref. 2).

The two products $\text{C}_{10}\text{H}_{18}(\text{OCH}_3)_2$, separated by g.l.c., are assigned the probable structures (22) and (23) on the basis of their almost identical n.m.r. spectra, their closely similar mass spectral breakdown as shown, and



τ *a* 6.7 (3 H, s), *b* 6.7 (2 H, m), *c* 9.05 (3 H, d, *J* 6 Hz)
d 6.85 (3 H, s), *e* 8.9 (6 H, s)

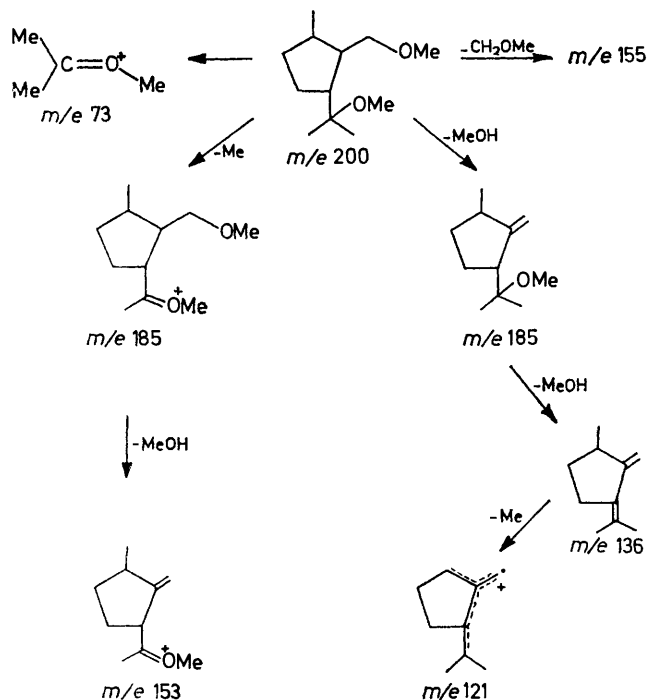
by analogy with the course of the reaction of 3,7-dimethylocta-1,6-diene with Hg^{II} .¹

⁷ R. L. Augustine and J. F. van Peppen, *Chem. Comm.*, 1970, 495, 497, 571.

⁸ D. Evans, J. A. Osborn, and G. Wilkinson, *J. Chem. Soc. (A)*, 1968, 3133.

⁶ A. J. Birch and G. S. R. Subba Rao, *Tetrahedron Letters*, 1968, 3797; E. J. Corey and J. W. Sags, *J. Org. Chem.*, 1973, 38, 3224.

Thus, as in mercuriation, Ti^{III} interacts with both alkene centres in (1) at comparable rates.



EXPERIMENTAL

(+)-3,7-Dimethylocta-1,6-diene (Bush Boake Allen Ltd.) was purified by preparative g.l.c.

Oxidation of 3,7-Dimethylocta-1,6-diene and 7-Methoxy-3,7-dimethyloct-1-ene by Rhodium(III).—(a) 3,7-Dimethylocta-1,6-diene (2 g) in either dimethylformamide or dimethylacetamide (20 ml) and water (4 ml) with rhodium trichloride trihydrate (0.26 g) and iron(III) chloride anhydrous (0.4 g) at 80 °C was stirred under oxygen and the product was monitored by g.l.c. (10 ft 10% Apiezon on Celite; 140 °C). After 24 h the product was isolated (1.5 g) and distilled to give (i) material, b.p. 30° at 4 mmHg (20%), and (ii) material, b.p. 57° at 4 mmHg (80%). The second fraction was identified as 3,7-dimethyloct-6-en-2-one (2), identical (g.l.c., n.m.r., and i.r.) with material previously prepared.¹ The first fraction contained 3,7-dimethylocta-1,6-diene (1) together with ca. 10% of the isomeric dienes discussed below.

(b) A similar experiment with 7-methoxy-3,7-dimethyloct-1-ene (4) gave 7-methoxy-3,7-dimethyloctan-2-one (5) (35%), b.p. 115° at 15 mmHg, identical with a sample previously prepared¹ by Pd^{II} -catalysed oxidation. The yield of product could be raised to 70% by using a longer reaction time (120 h), but 7-methoxy-3,7-dimethyloct-1-ene (4) appears to react more slowly than the diene (1).

Rhodium(III) Chloride-induced Isomerisation of 3,7-Dimethylocta-1,6-diene and of 7-Methoxy-3,7-dimethyloct-1-ene.—(a) 3,7-Dimethylocta-1,6-diene (2 g) with $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ (0.2 g) in acetone (10 ml) was stirred at ambient temperature. G.l.c. monitoring (7 ft 15% Apiezon on Celite; 100 °C) indicated the presence of 3,7-dimethylocta-1,6-diene (A), t_R 14 min, and the development of new components (B), t_R 18, (C), t_R 20, and (D), t_R 22 min (see Table). Components (B)—(D) were isolated by g.l.c. and characterised.

Component (B) was identified as (*E*)-2,6-dimethylocta-2,6-diene (6), m/e 138, n.m.r. spectrum as above, identical (g.l.c., n.m.r.) with a sample obtained by Birch reduction of nerol.

Component (C) was identified as (*Z*)-2,6-dimethylocta-2,6-diene (7), m/e 138, from the n.m.r. spectrum, and from comparison (g.l.c., n.m.r.) with a sample prepared by Birch reduction of geraniol.

Component (D) was recognised as 1,2,3,3-tetramethylcyclohexene (8) from its n.m.r. signals (above), and mass spectral data. Hydrogenation over platinum on Celite in a g.l.c. column at 50 °C gave a 1,2,3,3-tetramethylcyclohexane, m/e 140, τ 8.42 (2 H, m), 8.75 (6 H, m), and 9.15 (12 H, m), identical (g.l.c. and n.m.r.) with a sample obtained in the same way from 1,2,6,6-tetramethylcyclohexa-1,2-diene.

1,2,6,6-Tetramethylcyclohexa-1,3-diene hydrogenated over Adams platinum catalyst in ether in the presence of a little NaNO_2 afforded a product separated by g.l.c. (7 ft 15% Apiezon on Celite; 110 °C) to give a main component (80%) indistinguishable from product (D) by n.m.r. and g.l.c.

Birch reduction⁹ of nerol or geraniol (3 g) in ethanol (15 ml) and liquid ammonia (200 ml) was effected by addition of sodium until a blue colour persisted. The isomeric 3,7-dimethylocta-2,6-dienes were isolated and distilled; yield 1.5 g from nerol and 1.4 g from geraniol, b.p. 55—60° at 15 mmHg in each case.

In addition to components (A)—(D) noted above, g.l.c. revealed a small amount of a substance, t_R 5 min, which was isolated and showed m/e 98 ($\text{C}_6\text{H}_{10}\text{O}$), ν_{CO} 1 690 cm^{-1} , τ 3.9 (1 H, s), 7.9 (3 H, s), and 7.9 and 8.16 (each 3 H, s). This proved to be indistinguishable from mesityl oxide. It was confirmed that mesityl oxide may be detected (g.l.c.) in a 5% solution of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ in acetone within 30 min.

From the isomerisation reaction in acetone it was also possible by chromatography on silica gel to isolate in 2% yield material which was resolved by g.l.c. (7 ft 15% Apiezon on Celite; 120 °C) to give compounds m/e 174/176 ($\text{C}_{10}\text{H}_{18}\text{Cl}$), and m/e 154 ($\text{C}_{10}\text{H}_{18}\text{O}$), ν_{CO} 1 730 and 1 710 cm^{-1} .

(b) 3,7-Dimethylocta-1,6-diene (0.5 g) with $[(\text{C}_2\text{H}_5)_2\text{RhCl}]_2$ (0.1 g) in acetone (10 ml) showed no isomerisation after 6 days, but isomerisation was induced by addition of a little aqueous 0.1M-hydrochloric acid.

(c) 3,7-Dimethylocta-1,6-diene (2 g) with $[\text{RhCl}(\text{PPh}_3)_3]$ (0.1 g) in chloroform (15 ml) under reflux showed ca. 10% of isomerised materials, identified as (6) and (7), after 24 h. In a similar experiment carried out under nitrogen, however, no isomerisation was detected after heating under reflux for 5 days.

(d) 7-Methoxy-3,7-dimethyloct-1-ene (1 g), stirred with $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ (0.2 g) in acetone (10 ml) at ambient temperature, gave, by preparative g.l.c. (10 ft 10% Apiezon on Celite; 135 °C), unchanged 7-methoxy-3,7-dimethyloct-1-ene, material of t_R 9.5 min (50%), m/e 170 and 73 (base peak), τ 4.77 (q, J 6 Hz), 6.85 (3 H, s), 8.0 (2 H, m), 8.37 (6 H, m), 8.56 (4 H, m), and 8.87 (6 H, s), ν_{max} 1 090 cm^{-1} , i.e. (*E*)-7-methoxy-3,7-dimethyloct-2-ene (13), and material of t_R 10.5 min (34%), m/e 170 and 73 (base peak), τ 4.8 (q, J 6 Hz), 6.85 (3 H, s), 8.06 (2 H, m), 8.43br (6 H, s), 8.57 (4 H, m), and 8.90 (6 H, s), ν_{max} 1 090 cm^{-1} , i.e. (*Z*)-7-methoxy-3,7-dimethyloct-2-ene (14).

⁹ W. E. Shelberg, J. F. Pestaner, and R. Y. Yahiku, *Nature*, 1963, 200, 755.

Hydroformylation of 3,7-Dimethylocta-1,6-diene and 7-Methoxy-3,7-dimethyloct-1-ene.—(a) Carbon monoxide (1.5 ml s⁻¹) and hydrogen (1 ml s⁻¹) were pre-mixed and dried (conc. H₂SO₄) and passed through benzene (20 ml) which had been dried by distillation from sodium hydride. After warming to 70 °C carbonylhydridotris(triphenylphosphine)rhodium (0.2 g) was added, and, after 10 min, 3,7-dimethylocta-1,6-diene (2.5 g) was injected. After reaction for 4 h, the solution was concentrated *in vacuo* and treated with light petroleum, and the precipitated rhodium complex was filtered off. Evaporation of the filtrate gave a yellow oil (2.9 g), which was separated by g.l.c. (10 ft 10% Apiezon on Celite; 170 °C) into materials (i), *t*_R 2 min and (ii), *t*_R 7 min. The latter showed *m/e* 168.1505 (C₁₁H₂₀O requires *M*, 168.1514) and fragment ions *m/e* 150, 135, 125, 109, 83, 81, and 69 (base peak); τ 0.32 (1 H, *t*, *J* 1.6 Hz), 4.98 (1 H, *t*, *J* 7 Hz), 7.65 (2 H, *dt*, *J* 6 and 1.6 Hz), 8.04 (2 H, *m*), 8.34 (3 H, *s*), 8.42 (3 H, *s*), and 9.11 (3 H, *d*, *J* 5 Hz), ν_{CO} 1 725 cm⁻¹. This corresponds with 4,8-dimethylnon-7-enal (15); 2,4-dinitrophenylhydrazone, m.p. 55—57° (from ethanol) (Found: C, 58.3; H, 6.75; N, 15.9. C₁₇H₂₄N₄O₄ requires C, 58.6; H, 6.9; N, 16.1%).

The derived 4,8-dimethylnon-7-en-1-ol, obtained by reduction with lithium aluminium hydride in ether, was isolated by g.l.c. and characterised by *m/e* 170 (C₁₁H₂₀O), τ 7.67br (1 H), 8.07 (2 H, *m*), 8.35 (3 H, *s*), 8.42 (3 H, *s*), and 9.13 (3 H, *d*, *J* 5 Hz), ν_{max} 3 350 and 1 055 cm⁻¹.

Acetylation with acetic anhydride-pyridine gave 4,8-dimethylnon-7-enyl acetate as an oil which was purified by g.l.c. (Found: *m/e*, 212.1775. C₁₃H₂₄O₂ requires *M*, 212.1776), τ 5.07 (1 H, *t*, *J* 7 Hz), 6.14 (2 H, *t*, *J* 6 Hz), 8.1 (3 H, *s*), 8.1 (2 H, *m*), 8.37 (3 H, *s*), 8.47 (3 H, *s*), and 9.13 (3 H, *d*, *J* 6 Hz); ν_{max} 1 740 cm⁻¹.

(b) Hydroformylation of 7-methoxy-3,7-dimethyloct-1-ene (5 g) similarly gave a product separated as fractions (i), b.p. 60—70° at 2.5 mmHg (47%), and (ii) b.p. 92° at 2.5 mmHg (53%). Fraction (ii) showed *m/e* 185 (C₁₁H₂₁O₂—Me) and 73 (base peak), τ 0.2 (1 H, *t*, *J* 1.6 Hz), 6.83 (3 H, *s*), 7.54 (2 H, *dt*, *J* 7 and 1.6 Hz), 8.87 (6 H, *s*), and 9.1 (3 H, *d*, *J* 5 Hz), ν_{max} 1 725 cm⁻¹, corresponding with 8-methoxy-4,8-dimethylnonan-1-ol (16).

Reduction with lithium aluminium hydride gave 8-methoxy-4,8-dimethylnonan-1-ol, purified by g.l.c., *m/e* 203 (*M* + 1 for C₁₂H₂₆O) and 73 (base peak), τ 6.4 (2 H, *m*), 6.83 (3 H, *s*), 7.68br (1 H), 8.9 (6 H, *s*), and 9.1 (3 H, *d*, *J* 5 Hz), ν_{max} 3 400, 1 090, and 1 070 cm⁻¹.

Isomerisation with Carbonylhydridotris(triphenylphos-

phine)rhodium.—The material of *t*_R 2 min isolated in (a) above from hydroformylation of 3,7-dimethylocta-1,6-diene was found by g.l.c. to comprise (*E*)- (44%) and (*Z*)-2,6-dimethylocta-2,6-diene (56%), *i.e.* (6) and (7). The lower boiling product from hydroformylation of 7-methoxy-3,7-dimethyloct-1-ene was similarly found to contain (13) and (14) in closely similar amounts.

Isomerisation by [RhH(CO)(PPh₃)₃] could be verified. 3,7-Dimethylocta-1,6-diene (2.5 g) with [RhH(CO)(PPh₃)₃] (0.2 g) in benzene (20 ml) in nitrogen was found after 4 h to contain unisomerised diene (60%), and (*E*)- (13.8%) and (*Z*)-3,7-dimethylocta-2,6-diene (26.2%), identified by comparison (g.l.c., n.m.r.) with authentic material.

3,7-Dimethylocta-1,6-diene with Thallium(III) Nitrate in Methanol.—Thallium trinitrate trihydrate (6.4 g) in methanol (10 ml) was added to a stirred solution of 3,7-dimethylocta-1,6-diene (2.2 g) in methanol (10 ml). After 30 min the precipitated TlNO₃ was filtered off, the filtrate was acidified (2N-H₂SO₄; 50 ml), and the products were taken into ether. The organic product was resolved by programmed g.l.c. (25 ft 10% Apiezon on Celite; 50—200 °C at 6° min⁻¹) to obtain (i) unchanged diene (28%), materials of *t*_R, (ii) 8.5 min (22%), (iii) 23 min (10%), (iv) 25 min (15%), and some material (20%) of *t*_R 14—18 min.

Fraction (ii) was identified as 3,6-dimethyloct-7-en-2-one (19), *m/e* 154 (C₁₀H₁₈O) with prominent fragment ions *m/e* 43 (CH₃C=O⁺) and 72 [CH₃·CH=C(CH₃)OH]⁺, τ 4.33 (1 H, *m*, *J* 2.5, 7, and 12 Hz), 5.0 (1 H, *dd*, *J* 7 and 2.5 Hz), 7.57 (1 H, *m*), 7.9 (3 H, *s*), 8.95 (3 H, *d*, *J* 7 Hz), and 9.05 (3 H, *d*, *J* 7 Hz), ν_{max} 1 710 cm⁻¹.

Fraction (iii) showed *m/e* 200 (C₁₂H₂₄O₂) and 73 (base peak) (Me₂C=O+Me), τ 6.7 (2 H, *m*), 6.7 (3 H, *s*), 6.85 (3 H, *s*), 8.9 (6 H, *s*), and 9.05 (3 H, *d*, *J* 6 Hz), and is regarded as *t*-2-methoxymethyl-*r*-1-(1-methoxy-1-methylethyl)-*t*-3-methylcyclopentane (22).

Fraction (iv) showed *m/e* 200 (C₁₂H₂₄O₂) and an n.m.r. spectrum essentially the same as that of fraction (iii). However, being separable from (iii) by g.l.c., it is regarded as an isomer, provisionally *t*-2-methoxymethyl-*r*-1-(1-methoxy-1-methylethyl)-*c*-3-methylcyclopentane (23).

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