Synthesis of *meso*- and (±)-3,4-Dimethylhexa-1,5-diene and Their Acetylacetonatorhodium(I) Complexes

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Controlled addition of dry hydrogen chloride to a mixture of propionaldehyde and *trans*-crotyl alcohol at −5° gives *cis*- and *trans*-prop-1-enyl *trans*-but-2-enyl ether which are separable by spinning-band fractional distillation. At 142° the *cis*-isomer is cleanly converted into *erythro*-2,3-dimethylpent-4-enal, the *trans*-isomer giving the *threo*-isomer. The aldehydes are separately transformed into *meso*- and (±)-3,4-dimethylhexa-1,5-diene respectively by reaction with methylenetriphenylphosphorane in dimethyl sulphoxide; the isomeric purity of the resulting olefins is 95% (*meso*) and 96·5% [(±)]. The dienes react with acetylacetonato(bis-ethylene)rhodium(I) to form the corresponding hexadiene complexes; evidence pertaining to their stereochemistry, relative stability, and thermal stability is presented.

WE have been interested in the effect of co-ordination to metallic centres on the facility and course of thermal rearrangements of unsaturated hydrocarbons, and previously reported [1] the stabilisation of *endo*-6-vinylbicyclo[3.1.0]hex-2-ene by formation of its acetylacetonatorhodium(I) complex. The easy Cope rearrangement of the parent diene is effectively suppressed in this complex and when the diene (in the complex) does rearrange an alternative pathway is followed. As part of this study, it was desirable to prepare organometallic complexes of acyclic 1,5-dienes of defined stereochemistry and examine their thermal properties. *meso*-(1) and (±)-3,4-Dimethylhexa-1,5-diene (2) and their acetylacetonatorhodium(I) complexes (3) and (4), respectively, were chosen as suitable subjects for study.

Doering and Roth [2] reported the synthesis of dienes (1) and (2) by treating crotylmagnesium bromide with crotyl bromide. Other C$_8$ dienes (especially 3-methylhepta-1,5-diene) predominate in the products from this reaction and the desired products (1) and (2) could only be separated by preparative g.l.c. This synthesis is limited to the production of quantities of *ca.* 100 mg of dienes (1) and (2) and we therefore sought an alternative method. The high degree of stereoselectivity observed by Schmid and his co-workers [3] in the Claisen rearrangement of the allyl vinyl ethers (5) and (6) is of especial relevance. The derived aldehydes [(7) and (8), respectively] are obviously only a Wittig reaction removed from the dienes (1) and (2), respectively. However, Schmid's method for preparing the ethers (5) and (6) required preparative g.l.c. and so we devised a new route to these compounds more suited to large scale preparations.

Synthesis of meso-*and* (±)-3,4-Dimethylhexa-1,5-diene. —Whilst alkyl vinyl ethers are readily prepared [4] by dehydrochlorination of 1-chloroethers formed *via* hemiacetals from the hydrogen chloride-promoted condensation of an aldehyde and primary alcohol, allyl vinyl ethers have not been produced by this method. They have been made either by the mercuric acetate-catalysed exchange of alkyloxy for allyloxy on treating an alkyl vinyl ether with allyl alcohol,[5] a process which often proceeds in low yield, or by the thermolysis of bis-allyl acetals.[6] Presumably the direct approach has been avoided on the grounds that hydrogen chloride might be expected to react with allyl alcohol, with the consequence of addition, substitution,[7] or geometrical isomerisation.[8] We reasoned that the acid-catalysed formation of a hemiacetal would be second order in hydrogen chloride in a non-polar medium and equilibrium would be rapidly displaced by chloride ion attack on the protonated hemi-acetal. In contrast, the reaction of hydrogen chloride with olefins is third order in non-polar media,[9] so that controlled slow addition of gaseous hydrogen chloride should favour the former pathway. This was found to be the case, and (9) was formed smoothly in the reaction without apparent intervention of olefin-consuming competitive steps. The chloro-ether was best dehydrochlorinated by limited contact with an excess of refluxing dry pyridine and in this way a mixture of (5) and (6) † was obtained (Scheme), in which (5) predominated. Other reaction conditions (*e.g.* dehydrochlorination with Oediger's base) offered no advantage in selectivity, and attempted interconversions of (5) and (6) with iodine in acetone under illumination, or with mercuric acetate seemed to produce an equimolar mixture. Separation of the two vinyl ethers could, however, be achieved by careful fractionation at reduced pressure and in this way substantial samples (≥95% stereo-

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† The assigned stereochemistry of compounds (5) and (6) is based on n.m.r. data (*cf.* Experimental section and ref. 3) and their conversion into (1) and (2) respectively. It follows that (9) must be substantially the *trans*-isomer.

[1] V. Aris, J. M. Brown, and B. T. Golding, *J.C.S. Chem. Comm.*, 1972, 1203.

[2] W. von E. Doering and W. R. Roth, *Tetrahedron*, 1962, **18**, 67.

[3] P. Vitorelli, T. Winkler, H.-J. Hansen, and H. Schmid, *Helv. Chim. Acta*, 1968, **51**, 1457.

[4] With the sole exception of the parent allyl vinyl ether: C. R. Hurd, I. G. Ginger, L. L. Gershbein, and W. A. Yarnall, *J. Amer. Chem. Soc.*, 1952, **74**, 5128; M. F. Shostakovskii, B. A. Trofimer, A. S. Atavin, and V. I. Lavrov, *Russ. Chem. Rev.*, 1968, **37**, 907; D. S. Connor, G. W. Klein, and G. N. Taylor, *Org. Synth.*, 1972, **52**, 16.

[5] L. K. Montgomery, J. W. Matt, and J. R. Webster, *J. Amer. Chem. Soc.*, 1967, **89**, 923; W. H. Watanabe and L. E. Condon, *ibid.*, 1957, **79**, 2828; D. J. Faulkner and M. R. Petersen, *ibid.*, 1973, **95**, 553.

[6] K. C. Brannock, *J. Amer. Chem. Soc.*, 1959, **81**, 3379; F. Weiss, A. Lantz, and A. Isard, *Bull. Soc. chim. France*, 1965, 3215.

[7] W. G. Young and J. F. Lane, *J. Amer. Chem. Soc.*, 1938, **60**, 847.

[8] W. G. Young and J. S. Franklin, *J. Amer. Chem. Soc.*, 1966, **88**, 785.

[9] R. C. Fahey, *Topics Stereochem.*, 1968, **3**, 237.

chemically pure) could be obtained. The Claisen rearrangements of (5) and (6) to (7) and (8) respectively, previously studied by Schmid,[3] were carried out with neat liquid samples in silanised tubes sealed under
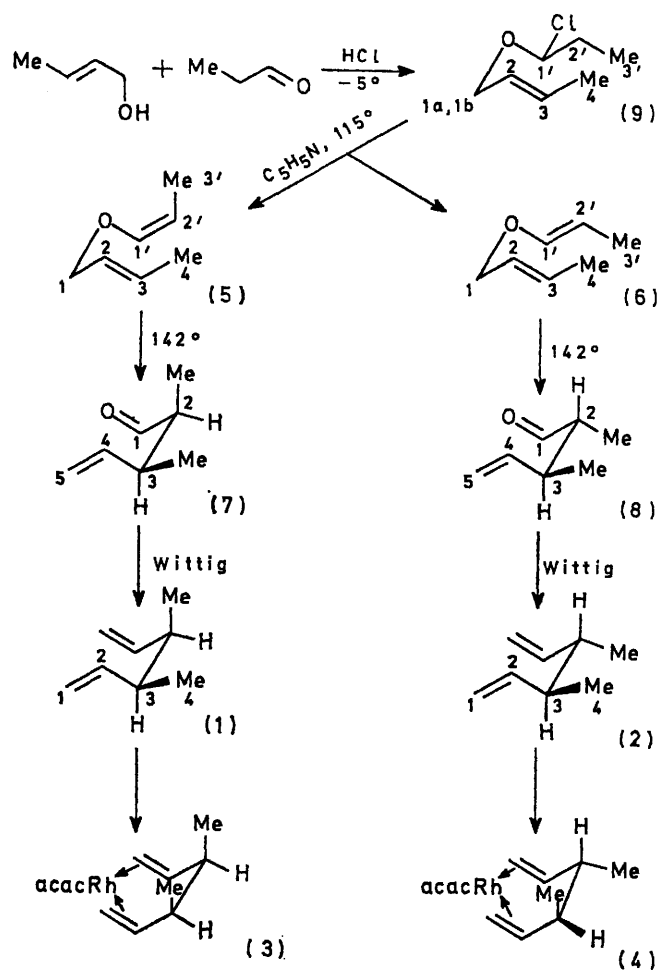
acac = acetylacetonato

SCHEME

nitrogen. The aldehydes so produced were used without further purification.

Epimerisation and other reactions involving deprotonation adjacent to a carbonyl function are a potential problem in Wittig reactions[10] and initial attempts to carry out this procedure for (7) with methylenetriphenylphosphorane in ether solution led to mixtures of (1) and (2) in approximately equal proportions. Much less epimerisation attended the corresponding reaction in dimethyl sulphoxide, and it was found that competition could be eliminated by conducting the reaction at the lowest possible temperature, using an excess of phosphonium salt to buffer the reaction mixture, and employing sodium rather than

potassium as the counter-ion of the deprotonating base. In this way (1) and (2) could be produced from (7) and (8) respectively; spinning-band fractional distillation and selection of a centre cut afforded a further slight, but significant, improvement in stereochemical purity.

The [1]H n.m.r. spectra of the compounds in this synthetic sequence are unexceptional, but demonstrate the high stereochemical purity at intermediate stages. The spectra of the product dienes are virtually identical, any differences in chemical shift or couplings being too slight to be of any diagnostic value. In contrast, the corresponding [13]C n.m.r. spectra are quite distinct, with three of the four resonances separated by more than 0·5 p.p.m. Since ^{13}C chemical shifts are governed by a rather small number of additive factors,[11] these differences may reflect variations in preferred conformation between the isomers.

Acetylacetonatorhodium(I) *Complexes.*—Both (1) and (2) react rapidly with acetylacetonato(bis-ethylene)-rhodium(I) to produce nicely crystalline chelating 1 : 1 complexes. The *meso*-compound (3) had the simpler n.m.r. spectrum, consistent with the expected plane of symmetry equivalencing the two halves of the ligand. The spectrum of the (±)-isomer (4) is much more complex, and is consistent with the two halves of the ligand being non-identical, and non-interconverting on the n.m.r. time scale at 35°. The spectra are only consistent with the ligand binding in a boat configuration, since the corresponding twist-configurations (10) and (11) would result in a centrosymmetric (±)-compound with a correspondingly simple spectrum and a non-symmetric *meso*-compound with a complex spectrum, in contrast to observation. This is in accord with the limited number of examples of Group VIII hexadiene complexes for which crystallographic structures are available.[12] Furthermore, the boat–twist interconversion must be slow on the n.m.r. time scale, since a sequence of two such steps interchanges the environment of the two halves of the (±)-complex and would
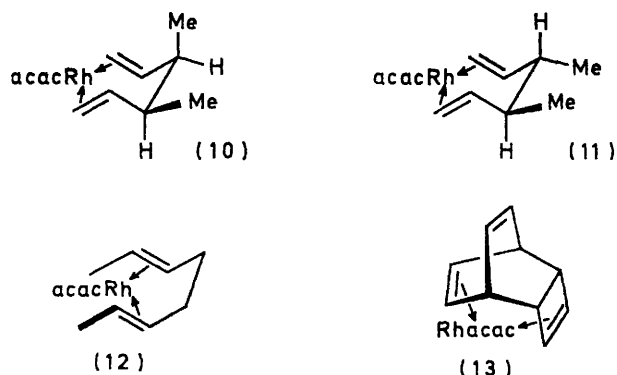
lead to spectral simplification at rapid reaction rates and line-broadening at slow rates. Since the sharper lines in the spectrum of (4) are less than 1 Hz wide, we

[10] C. H. Heathcock and R. Ratcliffe, *J. Amer. Chem. Soc.*, 1971, **93**, 1746.
[11] J. Mason, *J. Chem. Soc.* (*A*), 1971, 1038; G. C. Levy and G. L. Nelson, 'Carbon-13 Nuclear Magnetic Resonance for Organic Chemists,' Wiley-Interscience, New York, 1972.
[12] I. A. Zakhorova, G. A. Kukina, T. S. Kuli-Zade, I. I. Mosieev, G. Yu-Pek, and M. A. Porai-Koshits, *Zhur. neorg. Khim.*, 1966, **11**, 433.

conclude that the process of boat–twist interconversion has an activation energy of at least 16—17 kcal mol^{-1} and *probably considerably* more. The simplicity of the spectrum of (3) suggests that only one of the two possible boat configurations is important; more probably this is the *transoid* form as drawn,† which minimises interactions between the methyl- and vinyl-groups. Both *cisoid* and *transoid* forms engender considerable torsional strain, however.

It was of interest to determine the relative stability of complexes (3) and (4). In (3) there is an eclipsed-butane interaction which can only be relieved by rotation about the C(3)–C(4) bond at the expense of weakening metal–ligand bonding. This is to be compared with two *gauche*-butane interactions in (4) together with a destabilising H–H interaction between one of the vinyl groups and the corresponding *cisoid* methyl group. One might predict that the ($\pm$)-isomer (4) would be more stable ‡ (assuming equal ground-state energies for the two olefins) and this was found to be the case in two separate experiments. In the first, the n.m.r. spectrum of an equimolar mixture of (2) and (3) showed substantial conversion into (1) and (4) after 10 min, with no further change. The *mese* : ($\pm$) ratio was estimated to be 15 : 85 from the spectrum. The second experiment involved treating an equimolar mixture of (1) and (2) with a deficiency of acetylacetonato(bis-ethylene)rhodium(I) in toluene. Distillation from the reaction mixture and g.l.c. analysis showed a 90 : 10 preponderance of *meso*-olefin (1) on recovery.
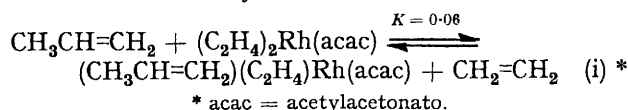
The complexes (3) and (4) could not be thermally interconverted or rearranged. Thus, no changes were observed in n.m.r. spectra on maintaining solutions of (3) and (4) sealed under nitrogen in C_6D_6 for 48 h at 120°. At 135° the same situation pertained, except that rhodium metal was slowly deposited. In other systems, the rate of rearrangement is strongly dependent on substitution at rhodium [1,13]

The observed stability of these particular hexadiene complexes to Cope rearrangement or to [1,3] sigmatropic rearrangements is likely to be kinetic in origin, but the alternative explanation that they are simply more stable than possible rearrangement products must be considered. Cramer [14] has measured the relative thermodynamic stabilities of substituted olefin–rhodium complexes and shown, for example, that propylene complexes less readily than ethylene (equation i). In order to make the proper thermodynamic comparison of (3) or (4) and their rearrangement products such as (12), it is necessary to consider in addition
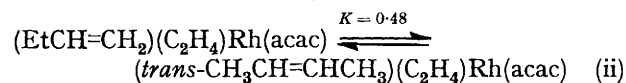
the fact that methyl-substitution stabilises an olefin,

$$CH_3CH{=}CH_2 + (C_2H_4)_2Rh(acac) \underset{}{\overset{K\,=\,0\cdot06}{\rightleftharpoons}}$$
$$(CH_3CH{=}CH_2)(C_2H_4)Rh(acac) + CH_2{=}CH_2 \quad (i)\;*$$

* acac = acetylacetonato.

a factor which might be responsible for driving the equilibrium in (i) to the left. A more pertinent (but hypothetical) equilibrium is (ii), and the value of its equilibrium constant may be derived from Cramer's data, with due reference to thermochemical tables.[15] On this basis, the rearrangement of (3) to (12) should be observable, if kinetically accessible.

$$(EtCH{=}CH_2)(C_2H_4)Rh(acac) \underset{}{\overset{K\,=\,0\cdot48}{\rightleftharpoons}}$$
$$(trans\text{-}CH_3CH{=}CHCH_3)(C_2H_4)Rh(acac) \quad (ii)$$

In conclusion, we note that the rhodium complex of Nenitzescu's hydrocarbon (13) is stable to flow thermolysis at 450° under conditions where the parent hydrocarbon is completely rearranged.[16]

EXPERIMENTAL

^{1}H N.m.r. spectra were recorded in CCl_4 unless stated otherwise, on a Perkin-Elmer R12 machine at 60 MHz and chemical shifts are recorded relative to tetramethylsilane. ^{13}C N.m.r. spectra were recorded in $CDCl_3$ solution at 22·62 MHz employing the Bruker WH-90 FT-system and are recorded in p.p.m. relative to tetramethylsilane. I.r. spectra were taken on a Perkin-Elmer 257 instrument. Nitrogen was purified by passage through chromous chloride, sulphuric acid, and over potassium hydroxide pellets. Thermolysis tubes were pre-treated by washing with a solution of dichlorodimethylsilane in toluene. Spinning-band fractional distillations were effected with a Nester–Faust annular Teflon still.

cis- *and* trans-*Prop*-1-*enyl* trans-*But*-2-*enyl Ether.*— Freshly distilled propionaldehyde (83 g, 1·4 mol) and *trans*-crotyl alcohol (100 g, 1·39 mol) were mixed at —78° with exclusion of moisture and allowed to warm to —20°. Passage of a very slow stream of dry hydrogen chloride gas through the stirred mixture was then commenced, and the solution maintained between —10 and —5°. Samples were removed at intervals and monitored by n.m.r. spectroscopy, following changes in the 4·2—5·2 p.p.m. range. After 8 h two well-defined layers had formed and no further changes in the n.m.r. spectrum could be discerned. The upper layer was separated, and treated sequentially with three portions of anhydrous calcium chloride. The amber liquid was distilled *in vacuo* (bath temperature 19—21° at 10^{-2} mmHg), the receiver flask being maintained at dry-ice temperature to give *trans*-but-2-enyl 1-chloropropyl ether (9) (*ca.* 90 g), δ 5·61 (3H, m, H-2, -3, and -1'), 4·32 (1H, m, H-1a), 4·05 (1H, dd, $J_{1a,1b}$ 11·5, $J_{1,2}$ 6·5 Hz, H-1b), 2·00 (2H, m, $J_{1',2'}$ 6 Hz, H-2'), 1·75 (3H, d, $J_{d,4}$ 5·5 Hz, H-4), and 1·01 (3H, t, $J_{2',3'}$ 7·5 Hz, H-3').

The chloro-ether (9) was dehydrochlorinated in 10 g portions without further purification. Freshly distilled pyridine (15 ml) was heated to reflux and the chloro-ether

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† The n.m.r. spectrum of acetylacetonato(3-methylhexa-1,5-diene)rhodium(I) suggests that two configurational isomers are present, V. Aris, unpublished work.

‡ The Me–H eclipsed conformation is 3·2 kcal mol^{-1} and the Me–Me eclipsed conformation 4·3 kcal mol^{-1} above the ground state conformation of n-butane; J. B. Hendrickson, *J. Amer. Chem. Soc.*, 1967, **89**, 7036. The destabilising effect of vinyl β-methyl interactions may be assessed from heats of formation data;[15] $\delta\Delta H_f$(2,2-dimethylpropane — propane) = 14·85; $\delta\Delta H_f$ (3,3-dimethylbut-1-ene — but-1-ene) = 14·67; $\delta\Delta H_f$(*trans*-3,3-dimethylpent-2-ene — *trans*-pent-2-ene) = 13·87 kcal mol^{-1}. A value of $\leqslant 1$ kcal mol^{-1} is therefore indicated.

[13] J. A. Conneely, unpublished work.

[14] R. Cramer, *J. Amer. Chem. Soc.*, 1967, **89**, 4621.

[15] S. W. Benson, F. R. Cruickshank, D. M. Golden, G. R. Haugen, H. E. O'Neal, A. S. Rodgers, R. Shaw, and R. Walsh, *Chem. Rev.*, 1969, **69**, 279.

[16] W. Grimme, personal communication, October 1970.

(10 g) added rapidly in one portion. Cloudiness was immediately noted and two layers were formed. After 90 s the mixture was cooled and poured into water. The upper layers from nine such procedures were combined, washed with an equal volume of water six times, and dried (CaCl₂). N.m.r. analysis of the crude reaction mixture showed a *cis* : *trans* ratio of 1·6 : 1·0. Fractional distillation gave first a substantial fore-run, b.p. 37—44° at 40 mmHg, which was rejected. Material boiling in the range 45—50° at 40 mmHg was collected and combined for redistillation. Slow distillation allowed the separation of two distinct fractions (collection rate 1 drop per 40 s). The first was *trans*-but-2-enyl *cis*-prop-1-enyl ether (5) (21 g), b.p. 39·5° at 33 mmHg, δ * 5·79 (1H, dq, $J_{1',2'}$ 5·8, $J_{1',3'}$ 1·6 Hz, H-1), 5·55 (2H, m, H-2 and -3), 4·24 (1H, dq, H-2'), 4·08 (2H, d, $J_{1,2}$ 4 Hz, H-1), 1·69br (3H, d, $J_{3,4}$ 5 Hz, H-4), and 1·51 (3H, dd, $J_{2',3'}$ 6·7 Hz, H-3'), $\nu_{max.}$ (film) 3030m, 2920s, 2850s, 1665m, 1450m, 1410m, 1390m, 1360s, 1265s, 1100br,s, 970s, and 730m cm⁻¹. Following an intermediate fraction of b.p. 40—42° at 33 mmHg, there was obtained *trans*-but-2-enyl *trans*-prop-1-enyl ether (6) (12 g), b.p. 43·0 at 33 mmHg, δ * 6·06 (1H, dd, $J_{1',2'}$ 12 $J_{1'3'}$ ~1 Hz, H-1'), 5·52 (2H, m, H-2 and -3), 4·61 (1H, dq, $J_{2',3'}$ 6·5 Hz, H-2'), 3·99 (2H, d, $J_{1,2}$ 3·5 Hz, H-1), 1·79 (3H, d, $J_{3,4}$ 5 Hz, H-4), and 1·50 (3H, dd, H-3'), $\nu_{max.}$ (film) 3025m, 2920s, 2850s, 2740w, 1660s, 1450s, 1380m, 1260m, 1160br,s, 1115s, 965s, 925s, 780w, and 660w cm⁻¹.

erythro- *and* threo-2,3-*Dimethylpent-4-enal.*—*trans*-But-2-enyl *cis*-prop-1-enyl ether (1·72 g) was sealed under nitrogen in a small pre-treated glass ampoule and maintained in an oil-bath at 142·5° for 150 min. At the end of this period a sample was monitored by n.m.r. spectroscopy and showed no detectable residual vinyl ether. The procedure was repeated several times and the resulting *erythro*-2,3-dimethylpent-4-enal used without further purification, δ 9·53 (1H, d, $J_{1,2}$ 1·5 Hz, H-1), 5·54 [1H, ddd, $J_{4,5}$ 10 (*cis*) and 17 (*trans*), $J_{3,4}$ 6·5 Hz, H-4], 4·97 (2H, m, J_{gem} 1·0 Hz, H-5), 2·50, and 2·16 (2H, pent overlapping q, $J_{2,3}$ 6 Hz, H-2 and -3), and 1·00 (6H, d, J 6·5 Hz, 2 × Me), $\nu_{max.}$ (film) 3075w, 2960s, 2920m, 2860m, 2700w, 1730vs, 1645w, 1460m, 1390w, 1090w, 1000w, and 905s cm⁻¹. Similar thermolysis of the *trans*-vinyl ether at 142·5° for 60 min gave rise to *threo*-2,3-dimethylpent-4-enal, δ 9·52 (1H, d, $J_{1,2}$ 2·0 Hz, H-1), 5·68 [1H, ddd, $J_{4,5}$ 10 (*cis*) 17 (*trans*), $J_{3,4}$ 7 Hz, H-4], 5·07 (2H, m, J_{gem} 1·0 Hz, H-5), 2·52 and 2·20 (2H, pent overlapping q, $J_{2,3}$ 7 Hz, H-2 and -3), and 1·10 (6H, d, 6·5 Hz, 2 × Me), $\nu_{max.}$ (film) 3080w, 2960s, 2860m, 2700w, 1730vs, 1645w, 1460m, 1385m, 1080w, 1000w, and 290s cm⁻¹.

meso-3,4-*Dimethylhexa-1,5-diene* (1).—Methyltriphenylphosphonium iodide (12·4 g, 30·6 mmol) was stirred under nitrogen with degassed dimethyl sulphoxide (35 ml) at 20° until almost completely dissolved. A solution of sodium dimsyl † (14 ml; 1·3M-solution in Me₂SO; 19·2 mmol) was added by syringe over 5 min with vigorous stirring, and the resulting deep yellow solution was cooled to 10°. Isopentane (10 ml) was added, and the mixture stirred until partial emulsification had occurred. A solution of *erythro*-2,3-dimethylpent-4-enal (1·72 g, 15·3 mmol) in isopentane (20 ml) was added over 20 min when the colour was virtually discharged. After a further 15 min the isopentane layer was separated by syringe, water (5 ml) was added, and the dimethyl sulphoxide layer again extracted with isopentane (10 ml). The combined

isopentane solutions were washed with water and dried over a little anhydrous K₂CO₃. The product from four similar runs was combined, and solvent removed by careful fractionation. The resulting residue was fractionated at 83 mmHg, the fraction of b.p. 38·1—38·8° (3·5 ml) being collected to give *meso*-3,4-dimethylhexa-1,5-diene, which was stored under nitrogen in sealed ampoules prior to further reaction, δ 5·52 [2H, ddd, $J_{1,2}$ 10 (*cis*) and 17 (*trans*), $J_{2,3}$ 6·5 Hz, H-2], 4·87 (4H, m, J_{gem} 2·5 Hz, H-1), 2·04 (2H, dq, $J_{3,4}$ 6·5 Hz, H-3), and 0·90 (6H, d, H-4), δ (¹³C) 142·05 (C-2), 112·91 (C-1), 42·85 (C-3), and 17·37 (C-4) p.p.m. G.l.c. showed the presence of 5·0% (±)-isomer and no other impurity (20 ft Squalene column, 100°).

(±)-3,4-*Dimethylhexa-1,5-diene* (2).—Methyltriphenylphosphonium iodide (23 g, 57·3 mmol), sodium dimsyl (31 ml; 1·3M-solution in Me₂SO; 39·3 mmol), and *threo*-3,4-dimethylpent-4-enal were treated in the same manner. The product of two such reactions was fractionated at 100 mmHg, the fraction of b.p. 45·5—46·1° (2·5 ml) giving (±)-3,4-dimethylhexa-1,5-diene, δ 5·50 [2H, ddd, $J_{1,2}$ 10 (*cis*) and 17 (*trans*), $J_{2,3}$ 6·5 Hz, H-2], 4·90 (4H, m, J_{gem} 2·5 Hz, H-1), 2·00 (2H, dq, $J_{3,4}$ 6·5 Hz, H-3), and 0·91 (6H, d, H-4), δ (¹³C) 141·59 (C-2), 113·07 (C-1), 42·51 (C-3), and 16·70 (C-4) p.p.m. G.l.c. (20 ft Squalane column, 100°) showed the presence of 3·5% of the faster-running *meso*-isomer and no other impurity.

Hexadiene–*Acetylacetonatorhodium*(I) *Complexes.*—Acetylacetonato(bis-ethylene)rhodium(I) (258 mg, 1 mmol.) was maintained under nitrogen in a Schlenck tube and (±)-3,4-dimethylhexa-1,5-diene (120 mg, 1·09 mmol) was added by syringe in one portion. Immediate and vigorous evolution of ethylene was observed, and the tube was agitated occasionally and maintained at room temperature for 30 min. Isopentane (1 ml) was added, and after a further 30 min removed *in vacuo* together with excess of olefin. The crude product (300 mg) was recrystallised from isopentane at −78° to give acetylacetonato[(±)-3,4-*dimethylhexa*-1,5-*diene*]*rhodium*(I), m.p. 114—115°, δ (C₆D₆) 5·25 (1H, s, CH in acac), 4·86 [1H, dddd, $J_{1,2}$ 8 (*cis*) and 13 (*trans*), $J_{2,3}$ 6, J_2,¹⁰³Rh 2 Hz, H-2], 4·12 [1H, dddd, $J_{5,6}$ 7·5 (*cis*) and 12 (*trans*), $J_{4,5}$ 7, J_5,¹⁰³Rh 2 Hz, H-5], 4·02 (1H, dt, H-6-*cis*), 3·05 (1H, dd, H-1-*cis*), 2·75 (1H, dt, H-6-*trans*) obscuring *ca.* 2·50 (1H, m, H-3 or -4), 1·93 (6H, s, Me in acac), part obscuring 1·87 (1H, d, H-1-*trans*), and 1·02 and 1·00 (6H, d and d, 2 × Me), part obscuring 0·70 (1H, m, H-4 or -3) (Found: C, 50·15, H, 6·75, Rh, 32·85. C₁₃H₂₁O₂Rh requires C, 50·0; H, 6·75; Rh, 33·0%).

Acetylacetonato(meso-3,4-*dimethylhexa*-1,5-*diene*)*rhodium*(I) was similarly obtained, m.p. 52—53°, δ (C₆D₆) 5·20 (1H, s, CH in acac), 4·35 [2H, dddd, $J_{1,2}$ 8·5 (*cis*) and 12·5 (*trans*), $J_{2,3}$ 4, J_2,¹⁰³Rh 2 Hz, H-2], 3·51 (2H, dd, H-1 and -6-*cis*), 2·38br (2H, H-1 and -6-*trans*), 1·86 (6H, s, Me in acac), *ca.* 1·50 (2H, m, H-3 and -4, part obscured), and 1·25 (6H, d, $J_{3,Me}$ 6 Hz, 2 × Me) (Found: C, 50·1; H, 6·8; Rh, 32·6. C₁₃H₂₁O₂Rh requires C, 50·0; H, 6·75; Rh, 33·0%).

Competition between meso- *and* (±)-3,4-*Dimethylhexa*-1,5-*diene for Acetylacetonatorhodium*(I).—(a) (±)-3,4-Dimethylhexa-1,5-diene (11·0 mg, 0·1 mmol) was added to a solution of acetylacetonato(*meso*-3,4-dimethylhexa-1,5-diene)rhodium(I) (31·2 mg, 0·1 mmol) in C₆D₆ (0·5 ml) and the n.m.r. spectrum recorded immediately.‡ Monitoring at

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* *Cf.* data in ref. 3.
† Methylsulphinylmethylsodium.
‡ Taken at 100 MHz.

δ 3·05 [($\pm$), H-1] *versus* δ 3·5 (*meso*, H-2) allowed the estimation of a mixture of 85% ($\pm$)-complex, 15% *meso*-complex, unchanged after 48 h.

(*b*) A solution of acetylacetonato(bis-ethylene)rhodium(I) (52 mg) in toluene (1 ml) was held at 0° whilst a 1 : 1 mixture of *meso*- and ($\pm$)-3,4-dimethylhexa-1,5-diene (44 mg) was added. After 30 min at 0°, toluene and residual olefin were recovered by trap-to-trap distillation and analysed by g.l.c. (20 ft Squalane column, 100°) showing the recovered olefin to be 90% *meso*- and 10% ($\pm$)-isomer.