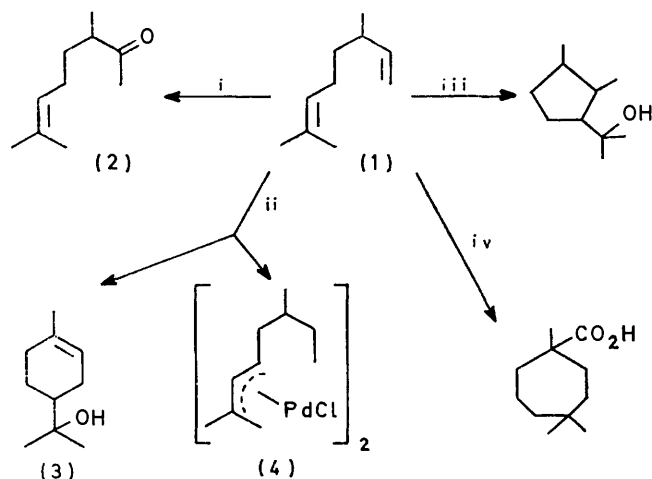


Complexing of Terpenes with Transition Metals. Part IV.† A Comparison of the Reactions of (+)-3,7-Dimethylocta-1,6-diene with Palladium(II) and with Mercury(II)

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With palladium(II) chloride (+)-3,7-dimethylocta-1,6-diene may, depending on the conditions, undergo Wacker oxidation to 3,7-dimethyloct-6-en-2-one, or yield a Pd π -allyl derivative of 2,6-dimethyloct-2-ene and α -terpineol (*p*-menth-1-en-8-ol) by a process of intermolecular hydrogen transfer. Conversely, mercury(II) acetate in aqueous tetrahydrofuran initiates Markownikoff cyclisation to give, after reduction, isomeric 2-(2,3-dimethylcyclopentyl)propan-2-ols, the stereochemistry of which is deduced. Mercury(II) acetate in methanol or propan-2-ol leads mainly to acyclic products. Strongly acidic conditions cyclise 3,7-dimethylocta-1,6-diene to a trimethylcycloheptyl cation which may be trapped under the conditions of the Koch reaction.

We previously surveyed the transformations which may be induced by Pd-co-ordination of a range of typical mono- and sesqui-terpenes.¹ We now indicate for a single isoprenoid diene how reaction may be directed by choice of the co-ordinating metal or other electrophile. (+)-3,7-Dimethylocta-1,6-diene (1), which is readily available from pyrolysis of (+)-pinane,² was chosen for study, and the principal results are summarised in Scheme 1.



SCHEME 1

Reagents: i, PdCl₂-Cu₂Cl₂-DMF; ii, PdCl₂-aqueous acetone; iii, Hg(OAc)₂, H₂O-THF-NaBH₄; iv, HCO₂H-H₂SO₄

Towards PdCl₂, the diene (1) would be expected to react *via* the less substituted 1,2-olefinic bond, and by hydrolysis and oxidation to yield the ketone (2). With PdCl₂-Cu₂Cl₂ in aqueous dimethylformamide (DMF) in the presence of oxygen,³ or *p*-benzoquinone, 3,7-dimethylocta-6-en-2-one (2) was obtained in good yield. There was, however, evidence for a competing reaction.

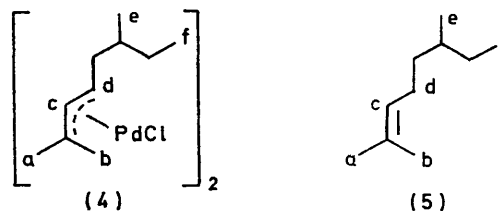
The nature of this second process was elucidated by examining the reaction of (1) with PdCl₂ in the absence of Cu₂Cl₂ using aqueous acetone as solvent. These condi-

tions led to the formation of only small amounts of the ketone (2), and to (-)- α -terpineol (3), [α]_D -7°, and a Pd π -allyl complex, (C₁₀H₁₉PdCl)₂, [α]_D -8° in essentially equal amounts.

α -Terpineol was characterised by spectral data [*m/e* 154 (C₁₀H₁₈O), τ 4.6 (1H), 8.03 (4H), 8.31 (3H), and 8.77 (6H)], and by comparison (n.m.r., g.l.c., i.r.) with an authentic sample. We note however, that the α -terpineol formed is extensively racemised.

The Pd π -allyl complex (C₁₀H₁₉PdCl)₂, which could be purified by chromatography, was characterised by a peak at *m/e* 138 (C₁₀H₁₈), *i.e.* C₁₀H₁₉PdCl - HCl - Pd, and fragment ions *m/e* 123 (138 - 15), and 109 (138 - 29). On the analytical evidence and the n.m.r. and chemical data given below this complex was formulated as (4), protons (c) and (d) being shown to be coupled by double irradiation.

The complex (4), shaken in ether under hydrogen, released a hydrocarbon, *m/e* 140 (C₁₀H₂₀) shown by g.l.c. to contain two components (3:1). The principal hydrocarbon was recognised as (5) from the n.m.r. spectrum, and by comparison with an authentic sample



N.m.r. chemical shifts (τ)

(a), (b) 8.59, 8.77 (s) (a) + (b) 8.3, 8.38 (s)
 (c) 5.09 (d, *J* 12 Hz) (c) 4.8 (t, *J* 6 Hz)
 (d) 6.15 (m), (e) + (f) 9.08 (m) (d) 8.05, (e) + (f) 9.11

obtained by semi-hydrogenation⁴ of 3,7-dimethylocta-1,6-diene.

Decomposition of (4) with aqueous potassium cyanide gave the same hydrocarbon mixture in which, however, (5) formed the minor (10%) constituent. The major

† Part III, K. Dunne and F. J. McQuillin, *J. Chem. Soc. (C)*, 1970, 2203.

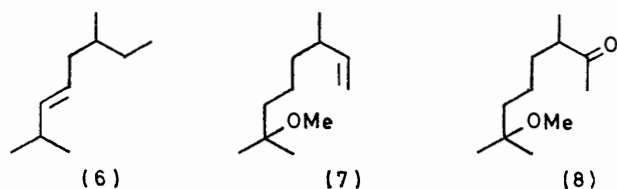
¹ K. Dunne and F. J. McQuillin, *J. Chem. Soc. (C)*, 1970, 2196, 2200, 2203.

² E. Rienacker and G. Ohloff, *Angew. Chem.*, 1961, **73**, 240.

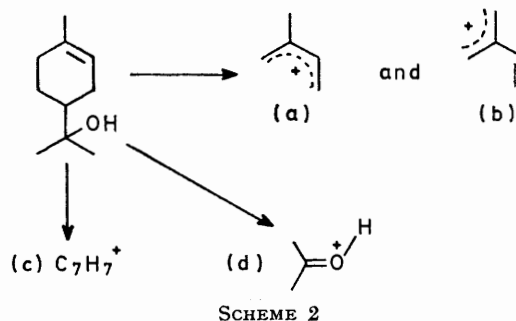
³ W. H. Clement and C. H. Selwitz, *J. Org. Chem.*, 1964, **29**, 241.

⁴ Cf. M. C. Dart and H. B. Henbest, *J. Chem. Soc.*, 1960, 3563.

component was identified as the isomer (6) from the n.m.r. data: τ 4.6 (2H, dt), 8.25 (2H, m), 8.75 (3H, m), and 9.0 (12H, m).

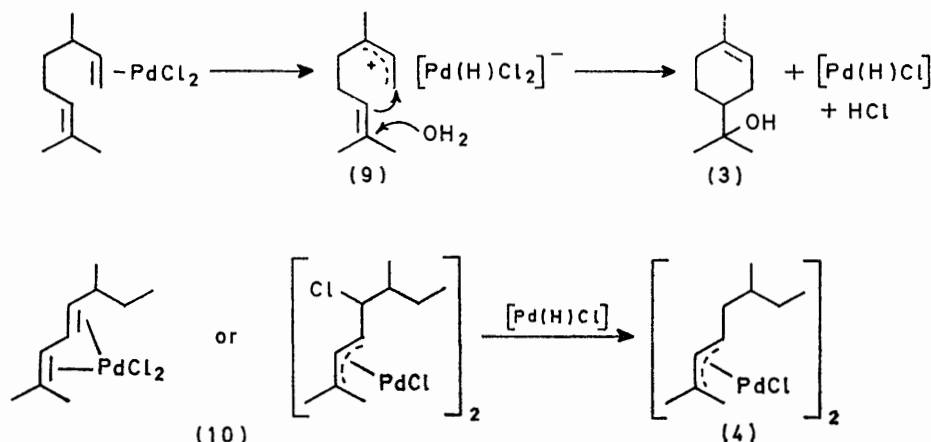


It is of interest that the organic ligand released from (4) by CN^- is protonated preferentially at the more substituted carbon atom of the allyl residue, and at the less substituted carbon atom in the presence of hydrogen (and since palladium is deposited, also with some hydrogen chloride present).



SCHEME 2

The hydrocarbon mixtures from decomposition of (4) could be hydrogenated at platinum to 2,6-dimethyloctane identical (g.l.c., n.m.r.) with an authentic sample obtained from hydrogenation of (1).



SCHEME 3

The reaction leading to (3) and (4) in place of the ketone (2) could be suppressed by acid catalysed addition of methanol to (1). The derived methyl ether (7) with $\text{PdCl}_2\text{-Cu}_2\text{Cl}_2$ in aqueous DMF gave the expected methoxy-ketone (8), *m/e* 186 ($\text{C}_{11}\text{H}_{22}\text{O}$), as sole product in good yield.

⁵ Cf. M. A. Schwartz and T. J. Pines, *J. Amer. Chem. Soc.*, 1972, **94**, 4205.

The unexpected, but not quite unprecedented,⁵ hydrogen transfer involved in the formation of (4) appeared to implicate a palladium-hydride intermediate. The concomitant formation of α -terpineol, which constitutes an oxidation, is the most evident source of such a hydride which has previously been invoked in a number of reactions.⁶

The source of the added hydrogen in the formation of (4) was sought by allowing the diene (1) to react with anhydrous PdCl_2 in D_2O solution. The Pd - π -allyl complex formed in this reaction was identical with (4) on n.m.r. comparison, and contained less than 2% deuterium. The recovered diene (1) contained no deuterium, but the α -terpineol showed: [$^2\text{H}_0$] 30, [$^2\text{H}_1$] 30, [$^2\text{H}_2$] 26.6, and [$^2\text{H}_3$] 11.2%. In the mass spectral breakdown of the [^2H]- α -terpineol (Scheme 2) the ions (a) and (b) appeared at *m/e* 69, 70, and 71, (c) at 91–94, and (d) at *m/e* 59 only. This is consistent with deuterium incorporation in and adjacent to the olefinic bond by exchange catalysed by the rather acidic medium. However, the absence of significant deuterium incorporation into (4) indicates that the hydrogen gained in forming this structure must arise by intermolecular transfer and not from the solvent.

The cyclisation of the diene (1) to α -terpineol involves not only an oxidation, but also an apparently anti-Markownikoff addition. We therefore propose a route (Scheme 3) which involves an intermediate allylic cation (9), formed as an ion-pair with a palladium hydride, most conveniently written as $[\text{Pd}(\text{H})\text{Cl}_2]^-$.

2,6-Dimethyloct-2-ene (5) as expected, did not co-ordinate significantly with PdCl_2 even after several days. It is evident therefore that (4) must arise by sequential

isomerisation of the initially co-ordinated vinylic group to give the strongly co-ordinating diene (10) or an equivalent chloro- Pd - π -allyl,⁷ which, it is suggested, is reduced to (4) by the available palladium hydride as in Scheme 3.

⁶ P. M. Maitlis, 'The Organic Chemistry of Palladium', Academic Press, New York, 1971, vol. I, pp. 21, 57, 103, 142, vol. II, pp. 35, 46, 128, 137.

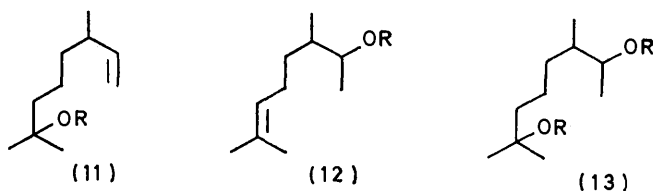
⁷ S. D. Robinson and B. L. Shaw, *J. Chem. Soc.*, 1963, 4806.

The olefinic bond migration may well involve an allylic cation intermediate such as (9), but the mechanism is tentative, and will require further study. It is, however, evident that competition between a process as in Scheme 3 and Wacker oxidation of (1) to (2) will depend on the number and nature of the ligands co-ordinated to palladium, and hence upon the solvent system.

The diene (1) with PdCl_2 in methanol gave the π -allyl complex (4) together with α -terpinyl (*p*-menth-1-en-8-yl) methyl ether. Reaction in dry acetone led to (4), limonene, a chloromethane, and a little *p*-cymene. Reaction with PdCl_2 in acetic acid-potassium acetate led to (4) and α -terpinyl acetate as main products, accompanied by limonene and the ketone (2) with *p*-cymene in small yield. In CDCl_3 the reaction was followed by n.m.r. changes which showed initial loss of the vinyl proton signal at τ 4.2 (100 min) followed by modification of the τ 9.05 doublet due to CH_3CH , whereas the τ 5.09 and 6.15 signals due to (4) became prominent only after ca. 20 h.

Since the interesting reaction sequence outlined in Scheme 3 is dependent on intervention of olefinic bond migration and metal hydride formation we thought it appropriate to examine the behaviour of the diene (1) towards a co-ordinating metal cation with which hydride formation is unlikely. We chose mercury(II) acetate and what emerged was a very significant difference in the reaction of the diene (1) with Hg^{2+} in methanol, or other alcohols, and in aqueous tetrahydrofuran.

With mercuric acetate in methanol followed by borohydride reduction,⁸ the diene (1) led to four methyl ethers separated by g.l.c. Three of these were identified as (11) 12%, (12) (18%), and (13; R = Me) 24%, by n.m.r. and mass spectrometry. The fourth constituent,



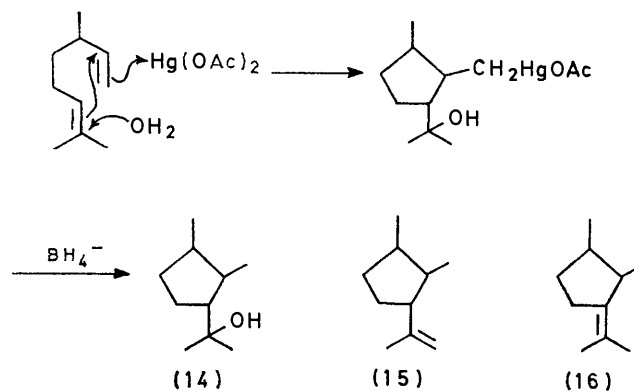
24%, m/e 170 ($\text{C}_{11}\text{H}_{22}\text{O}$) differed (g.l.c., n.m.r.) from α -terpinyl methyl ether, and its structure emerged most clearly from a study of the reaction of the diene (1) with mercuric acetate in aqueous tetrahydrofuran. This gave two major products (3:1), separated by g.l.c., each showing m/e 156 ($\text{C}_{10}\text{H}_{20}\text{O}$), and in the n.m.r. no olefinic or $-\text{CH}-\text{O}-$ signal, *i.e.* representing a pair of monocyclic tertiary alcohols most rationally formulated as isomers of structure (14). These substances were shown (g.l.c., n.m.r.) to differ from menthan-1-ol and menthan-8-ol.

Alcohols of structure (14) are in principle available

⁸ H. C. Brown and Min-Hon Rei, *J. Amer. Chem. Soc.*, 1969, **91**, 5646; H. C. Brown and P. J. Geoghegan, *ibid.*, 1967, **89**, 1522.

⁹ N. N. Ipatiev, W. D. Huntsman, and H. Pines, *J. Amer. Chem. Soc.*, 1953, **75**, 6222; G. Pines, N. E. Hoffman, and V. N. Ipatiev, *ibid.*, 1954, **76**, 4412.

from the ene-cyclisation products derived from the diene (1), known⁹ to constitute a pair of isomers of (15). In fact, the two 1,2-dimethyl-3-isopropenylcyclopentanes obtained in this way and separated by g.l.c., on reaction



with $\text{Hg}(\text{OAc})_2$ - NaBH_4 gave a pair of isomeric 2-(1,2-dimethylcyclopentyl)propan-2-ols each of which was shown by g.l.c. and n.m.r. to be very similar, but not identical with either of the pair of alcohols from hydroxy-mercuration of the diene (1). However, the problem was clarified by dehydration of the latter propan-2-ols by means of potassium hydrogen sulphate. This gave three olefins, separated by g.l.c., each showing m/e 138, and characterised by n.m.r.: (a) τ 9.24 (3H, d), 9.06 (3H, d), 8.43 (3H, s), and 8.34 (3H, s), clearly an isomer of (16), and (b) 9.23 (3H, d, J 6 Hz) 9.06 (3H, d, J 6 Hz), 8.36 (3H, s), and 5.3 (2H, s), and (c) 9.05 (6H, d), 8.34 (3H, s), and 5.3 (2H, s), isomers of (15).

The stereochemistry of the 1,2-dimethyl-3-isopropenylcyclopentanes (b) and (c) emerged from the observation that the corresponding 1,2-dimethyl-3-isopropenylcyclopentanes from the ene-cyclisation of (1) show the n.m.r. olefinic proton signal as a doublet whereas for (b) and (c) this signal appears as a singlet. Two of the four isomeric 1,2-dimethyl-3-isopropenylcyclopentanol,^{10,11} and their acetates,¹⁰ are similarly distinguished by an n.m.r. doublet for the olefinic protons.

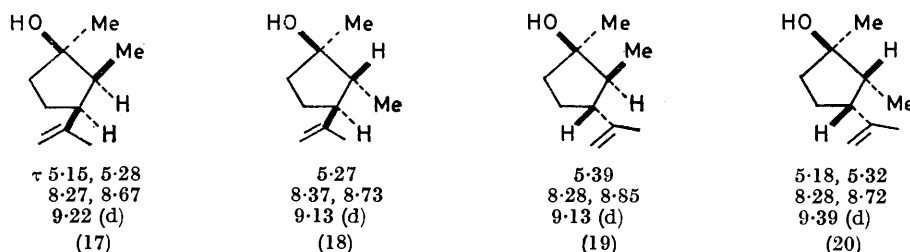
Since the stereochemistry of the four isomeric 1,2-dimethyl-3-isopropenylcyclopentanol is based on thoroughly systematic work¹¹ they offer a reliable basis for comparison, and the n.m.r. data assembled below provide a reasonably unambiguous steric assignment for our products.

Inspection of the n.m.r. data for the isomers (17)–(20) shows that when the 2-methyl and 3-isopropenyl groups are *cis*-related the olefinic signal appears as a doublet, and when all three alkyl groups are *cis*-related the methyl doublet shows marked shielding. On this basis the 1,2-dimethyl-3-isopropenylcyclopentanes from ene-cyclisation of the diene (1) are formulated as (21) and (24). In

¹⁰ J. M. Coxon, R. P. Garland, and M. P. Hartshorn, *Austral. J. Chem.*, 1972, **25**, 353.

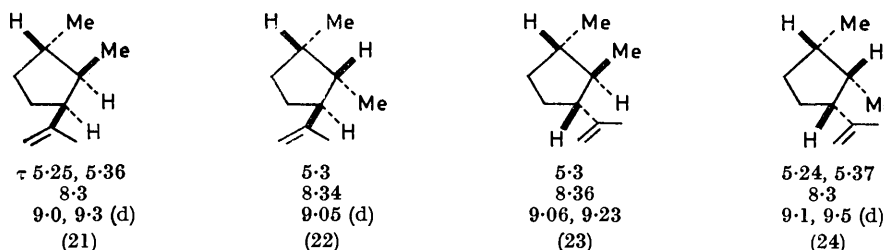
¹¹ von H. Stricher, G. Ohloff, and E. Kovats, *Helv. Chim. Acta*, 1967, **50**, 759.

agreement with the n.m.r. data, the isomeric 1,2-dimethyl-3-isopropenylcyclopentanes arising by hydroxymercuration of the diene (1), BH_4^- reduction, and dehydration, are therefore (22) and (23), the major component being most probably the all-*trans*-isomer (23).

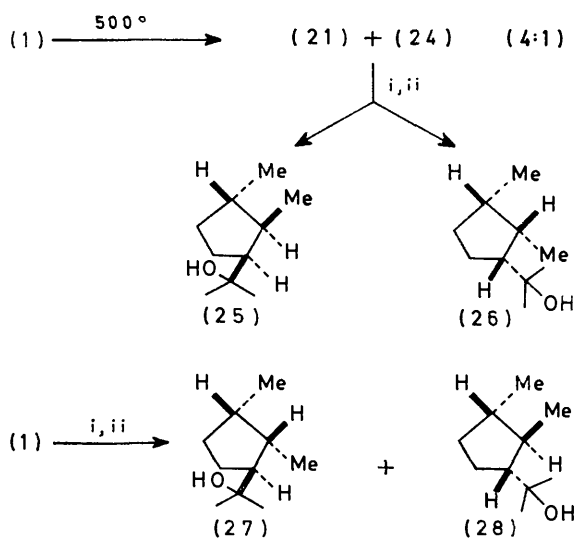


The various 2-(1,2-dimethylcyclopentyl)propan-2-ols synthesised in this work are accordingly as formulated in Scheme 4.

In line with these deductions the unidentified methyl ether derived from methoxymercuration of (1) is regarded as the methyl ether corresponding with (28)



which is the major product from the hydroxymercuration reaction.



SCHEME 4

Reagents: i, $\text{Hg}(\text{OAc})_2\text{-H}_2\text{O-THF}$; ii, NaBH_4

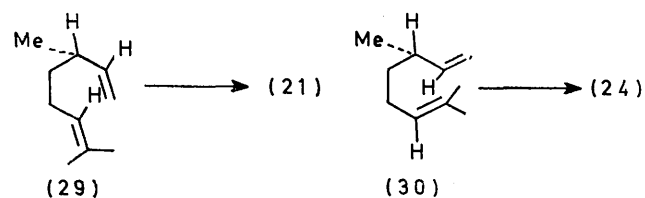
However, although the above data offer a consistent basis for stereochemical assignments, it is important to

note that although Ipatiev, Huntsman, and Pines⁹ designate (24) as the minor product of ene-cyclisation of (1), they regard the major product as (23). We agree in detail with the proportions of cyclisation products reported by these authors, and with their i.r. data. How-

ever, their structure (23) for the major cyclic product was assigned mainly on the basis of i.r. comparisons.⁹ We regard the n.m.r. data as more critical, and the revised formulations as more self-consistent in other ways.

We note, in particular, that in the ene-cyclisation

products from (1), and in the major products of ene-cyclisation of linalool^{10,11} and of linalyl acetate¹¹ the 2-methyl and 3-isopropenyl groups are *cis*-related in agreement with reaction *via* conformations¹² (29) and (30), which from inspection of molecular models permit maximal overlap.

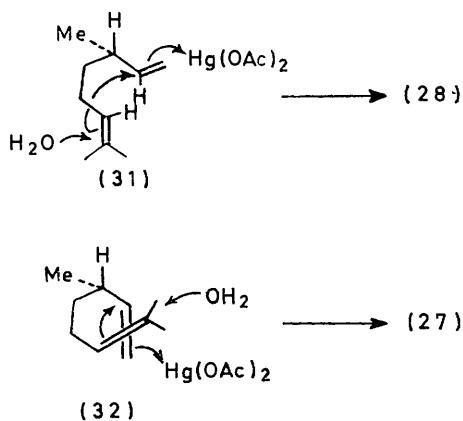


Conversely, it is clear that the *trans*-related 2-Me and 3-Me₂C(OH) groups of (27) and (28) arising from Hg^{2+} induced cyclisation derive from reaction *via* (31) and (32) which permit maximal separation of groups not engaged in carbon-carbon bond formation.

The Table summarises the yields of products from reaction of (1) with mercuric acetate in methanol and propan-2-ol followed by reduction. In general acyclic

¹² J. A. Berson, R. G. Wall, and H. D. Perlmuter, *J. Amer. Chem. Soc.*, 1966, **88**, 187; R. K. Hill and M. Rabinovitz, *ibid.*, 1964, **86**, 965.

ethers are the main product, and it is clear that in water-tetrahydrofuran cyclisation to give (27) and (28) is dependent on a water-THF interaction which retards entry of the water nucleophile.

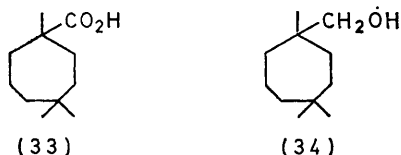


In the diene (1) the 6,7-olefinic bond with the lower ionisation energy should be the more reactive towards a small electrophile, and acid catalysed addition gave the

Yields (%) of products from reaction of diene (1) with $\text{Hg}(\text{OAc})_2$ in methanol and propan-2-ol

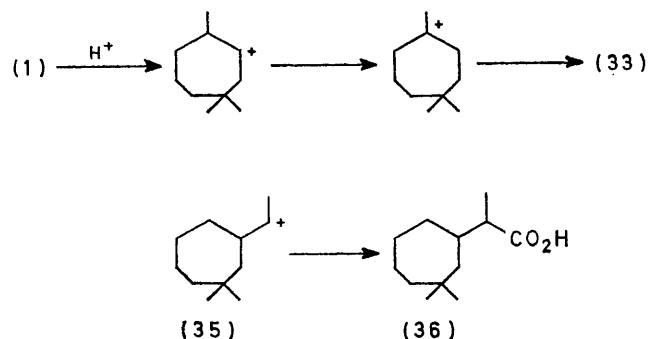
	(11)	(12)	(13)	Cyclic product
MeOH	12	18	24	24
Pr ⁱ OH	5	37	4	18

derivatives (11; R = H, Me, Prⁱ, or Ac). In the absence of a strong nucleophile, however, cyclisation should lead to a cycloheptane derivative. This was tested



under the conditions of the Koch reaction¹³ which gave an acid, the methyl ester of which was homogeneous on g.l.c., and which could also be obtained by Koch synthesis from 2,6,6-trimethylcycloheptanol. This product is most reasonably formulated as (33). There is, however, precedent¹⁴ for also considering a carbonium ion rearrangement to (35) and thence (36). We therefore converted the ester of (33) into the carbinol (34). This again appeared homogeneous on g.l.c., and the characteristic CH_2OH n.m.r. signals at τ 6.51 and 6.65 were moved together by $\text{Eu}(\text{dpm})_3$ without relative displace-

ment. The Koch reaction product therefore appears to be essentially one substance, clearly (33).



It thus is possible to convert 3,7-dimethylocta-1,6-diene (1) into acyclic or into 5-, 6-, or 7-membered carbocyclic products by choice of the initiating electrophile.

EXPERIMENTAL

Reaction products were in general purified by preparative g.l.c. and characterised by n.m.r. and mass spectroscopy.*

G.l.c. was carried out using an Aerograph model 700 instrument with hydrogen as carrier gas and using a 7 ft column with either (a) 15% Apiezon or (b) 15% polyethylene glycol succinate on Celite. The column material and temperature are indicated for individual cases in the text.

N.m.r. spectra were recorded at 60 MHz using a Varian EM360 or at 90 MHz using a Bruker spectrometer.

Mass spectra were obtained on an A.E.I. MS9 instrument at 70 eV.

3,7-Dimethyloct-6-en-2-one (2).—(a) (+)-3,7-Dimethylocta-1,6-diene (1) (1.1 g) in dimethylformamide (5 ml) and water (1 ml) with palladium(II) chloride (0.1 g) and copper(I) chloride (0.2 g) was shaken under oxygen for 2 h. Water was added, and the products, extracted into ether, were separated on a silica gel column. Elution with light petroleum gave a hydrocarbon fraction containing recovered diene (1), benzene eluted the Pd π -allyl complex (4), benzene-ether mixture gave the ketone (2), and ether eluted α -terpineol (3).

The 3,7-dimethyloct-6-en-2-one (2) was shown to be a single substance by g.l.c. (15% Apiezon; 130°), and was characterised by peaks at m/e 154 (M^+), 136, 121, 109, 96, and 95, τ 4.6 (1H, t, J 6 Hz), 7.62 (1H, m), 7.85 (3H, s), 8.06 (2H, m), 8.28 (3H, s), 8.40 (3H, s), 8.63 (2H, m), and 8.85 (3H, d, J 7 Hz).

Characterisation of the other products is considered below.

(b) A similar experiment carried out at 70° gave a smaller yield of the ketone (2) and an additional, yellow, rather water soluble product recognised as bis(dimethylamine)-dichloropalladium(II) (Me_2NH)₂PdCl₂, m/e 268, 232, and 196, τ 7.5 (d, J 6 Hz) and 6.8 (m) ratio 6 : 1; ν_{NH} 3220 cm^{-1} .

(c) Use of *p*-benzoquinone (1 mol. equiv.) as oxidant in place of Cu_2Cl_2 gave (2), (3), and (4) as in (a).

* For compounds marked with a dagger (†), low resolution mass spectra are recorded in Supplementary Publication No. SUP 20925 (11 pp., 1 microfiche) (for details of Supplementary Publications see Notice to Authors No. 7 in *J.C.S. Perkin I*, 1972, Index issue).

¹³ H. Koch and W. Haaf, *Annalen*, 1958, **618**, 251; 1960, **638**, 122; W. Haaf, *Org. Synth.*, 1966, **46**, 72; J. A. Olah, 'Friedel-Crafts and Related Reactions,' Wiley-Interscience, New York, vol. 3, 1964, p. 1284; D. R. Kell and F. J. McQuillin, *J.C.S. Perkin I*, 1972, 2096.

¹⁴ J. B. Hall and L. K. Lala, *J. Org. Chem.*, 1972, **37**, 920.

Bis[chloro(2-4- η -2,6-dimethyloct-2-ene)palladium(II)] (4).†
 —(a) The diene (1) (2 g) was stirred with palladium(II) chloride (0.6 g) in acetone (10 ml) and water (1 ml) for 40 h. The products isolated by chromatography on silica gel comprised (i) recovered diene, (ii) a yellow complex (4), soluble in benzene, ether, and chloroform, and less soluble in alcohol, *m/e* 138 (Found: C, 42.6; H, 6.8. C₁₀H₁₈ClPd requires C, 42.75; H, 6.75%), [α]_D -8°, n.m.r. as in the text under (4), and (iii) a liquid fraction, b.p. 120° at 15 mmHg, *m/e* 154 (C₁₀H₁₈O) identified as α -terpineol,† [α]_D -7° by comparison of i.r., mass, and n.m.r. spectra [τ 4.6 (1H, m), 8.03 (4H, m) 8.31 (3H, s), and 8.77 (6H, s)] with those of authentic material.

(b) Use of disodium tetrachloropalladium(II) in acetone gave a similar result, *i.e.* α -terpineol and complex (4) as major, and the ketone (2) as minor products.

(c) Reaction with disodium tetrachloropalladium(II) in methanol (for 25 h) gave the complex (4) and a liquid, τ 6.78 (3H, s) and 8.8 (6H, s) recognised as α -terpinyl methyl ether by comparison with authentic material.

(d) The diene (1) (1 g) and palladium(II) chloride (0.37 g) in D₂O (1 ml) was stirred for 60 h. A little palladium was deposited and the solution became very acidic. Ether extraction gave a product separated on a silica gel column to give (i) recovered diene, *m/e* 138, *i.e.* with no ²H-incorporation, (ii) complex (4), *m/e* 139 (intensity only 2% that of *m/e* 138), and (iii) α -terpineol, *m/e* 141 (1.43%), 140 (3.84), 139 (11.2), 138 (26.6), 137 (29.9), and 136 (29.4), and fragmentation discussed in the text. The recovered D₂O showed proton incorporation.

Reaction of the Diene (1) with PdCl₂ in Acetic Acid.—The diene (1) (1.6 g) with palladium(II) chloride (0.5 g) and potassium acetate (2 g) in acetic acid (10 ml) was stirred for 48 h. The product obtained by chromatography on silica gel showed small amounts of 3,7-dimethyloctan-2-one eluted by benzene, with the Pd- π -allyl complex (4) eluted by benzene-ether and α -terpinyl acetate as main products. The latter was characterised by *m/e* 196, τ 4.6br (1H), 8.07 (3H, s), 8.4 (3H, s), and 8.6 (6H, s).

Decomposition of the Allyl Complex (4).—(a) The complex (4) (0.4 g) with potassium cyanide (2 g) in water (10 ml) was warmed for 2 h. The organic product, taken into ether, formed an oil which by g.l.c. (15% Apiezon on Celite at 130°) revealed two components (9 : 1). The mixture was characterised by *m/e* 140 (C₁₀H₂₀), 125, 111, *etc.*, and τ 4.6 (2H, dt), 8.25 (2H, m) 8.75 (3H, m), 9.05 (6H, d, *J* 6 Hz), *i.e.* principally (6).†

(b) The complex (4) (0.4 g) in ether (5 ml) was shaken under hydrogen until uptake ceased. The organic product by g.l.c. analysis as above showed the same components as the product from (a), but in the ratio 1 : 3, and *m/e* 140, τ 4.8 (1H, m), 8.3 (3H, s), 8.4 (3H, s), 8.75br (5H), and 9.1 (6H, d), corresponding with (5).†

(c) The diene (1) (1 g) in ether (5 ml) with platinum oxide (0.1 g) and sodium nitrite (0.03 g) was shaken under hydrogen, and after absorption of 170 ml H₂ the organic product was recovered, b.p. 71° at 22 mmHg, *m/e* 140, τ 4.8 (1H, t), 8.05 (2H), 8.3 (3H, s), 8.4 (3H, s), and 8.75 (3H, m). This material was shown by g.l.c. and n.m.r. comparison to be identical with the principal component of the product obtained under (b). Complete hydrogenation of the latter over platinum in ether gave a material, *m/e* 142, identical (g.l.c., n.m.r.) with an authentic sample of 2,6-dimethyloctane from hydrogenation of (1).

7-Methoxy-3,7-dimethyloct-1-ene (7), 7-Methoxy-3,7-di-

methyloctan-2-one (8),† and 7-Methoxy-3,7-dimethyloctan-2-ol.†—(a) The diene (1) (2 g) in methanol (5 ml) with conc. H₂SO₄ (0.2 g) was kept for 5 h. Recovery by g.l.c. (Apiezon column at 130°) or column chromatography on silica gel gave the methoxy-olefin (7), *m/e* 170, τ 4.3 (1H, m, *J* 12, 7, and 7 Hz), 4.98 (1H, dd, *J* 12 and 2.5 Hz), 5.18 (1H, dd, *J* 7 and 2.5 Hz), 6.92 (3H, s), 8.4 (1H, m), 8.7 (6H), 8.95 (6H, s), and 9.02 (3H, d, *J* 8 Hz), by elution with benzene-ether.

(b) This material (7) (0.9 g) with palladium(II) chloride (0.1 g) and copper(II) chloride (0.2 g) in DMF (5 ml) and water (1 ml) was shaken under oxygen for 2 h. Recovery gave the methoxy-ketone (8)† isolated by g.l.c. (15% Apiezon at 150°), *m/e* 186, τ 6.82 (3H, s), 7.85 (3H, s), 8.86 (6H, s), and 8.9 (3H, d, *J* 7 Hz), ν_{\max} 1715 cm⁻¹.

(c) The ketone (8) (0.3 g) was reduced with excess of sodium borohydride in ethanol (10 ml) for 1 h. Recovery gave 7-methoxy-3,7-dimethyloctan-2-ol which was purified by g.l.c. (15% Apiezon at 150°), and characterised by *m/e* 173 (*M* - 15), ν 3400 and 1090 cm⁻¹, τ 6.25 (1H, m), 6.81 (3H, s), 8.85 (6H, s), 8.85 (3H, d, *J* 6 Hz), and 9.1 (3H, d, *J* 6 Hz).

Alkoxymercuration of the Diene (1).—The diene (1) (1.5 g) and mercury(II) acetate (3.2 g) in methanol were allowed to react with stirring for 10 min, when sodium hydroxide solution (3M; 10 ml) followed by sodium borohydride (0.5M in 3M-NaOH; 10 ml) was added. The product isolated in ether showed by g.l.c. (15% Apiezon column at 130°) four major and two minor constituents, as well as a little recovered diene (16%). G.l.c. separation on Apiezon at 130° gave (i) the methoxy-olefin (7) (13%), *m/e* 170, identical with an authentic sample prepared as above, τ 4.98 (1H, dd, *J* 12 and 2.5 Hz), 5.18 (1H, dd, *J* 7 and 2.5 Hz), 4.3 (1H, m, *J* 12, 7, and 7 Hz), 6.92 (3H, s), 8.4br (1H), 8.7 (6H, m), 8.95 (6H, s), and 9.02 (3H, d, *J* 8 Hz), ν 1085 and 1640 cm⁻¹; (ii) 7-methoxy-2,6-dimethyloct-2-ene (18%) (12; R = Me), *m/e* 170, τ 4.95 (1H, t, *J* 7 Hz), 6.77 (3H, s), 8.34 (3H, s), and 8.41 (3H, s); (iii) a methyl 1-methyl-1-(2,3-dimethylcyclopentyl)ethyl ether (16%) regarded as the methyl ether of (28),† *m/e* 170, τ 6.96 (3H, s), 8.94 (6H, s), and 9.12 (6H, d, *J* 4 Hz); and (iv) 2,7-dimethoxy-2,6-dimethyloctane (13; R = Me),† (24%), *m/e* 202, τ 6.39 (1H, m), 6.77 (3H, s), 6.92 (3H, s), 8.92 (6H, s), and 9.07 (6H, m), and some small unidentified fractions.

(b) A similar preparation using propan-2-ol gave by g.l.c. separation (15% Apiezon, 130°) (i) recovered diene (27%); (ii) 7-isopropoxy-2,6-dimethyloct-2-ene (12; R = Prⁱ)† (36%), *m/e* 198, τ 4.9 (1H, t, *J* 6 Hz), 6.4 (2H, m), 8.05 (2H, m), 8.3 (3H, s), 8.4 (3H, s), 8.7 (3H, m), and 9.0 (12H, m); (iii) an unidentified product (18%), *m/e* 198, τ 6.4 (1H, septet), 8.9 (6H, s), and 9.05 (12H, m); and (iv) 2,7-diisopropoxy-2,6-dimethyloctane (4%) (13; R = Prⁱ),† *m/e* 258.

Hydroxymercuration of the Diene (1).—(a) Mercury(II) acetate (3.2 g) in water (10 ml) and tetrahydrofuran (10 ml) was treated with the diene (1) (1.5) with stirring when the yellow colour of the solution faded. After a further 0.5 h, 3M-aqueous NaOH (10 ml) followed by 0.5M-NaBH₄ in 3M-NaOH (15 ml) was added. The organic layer was separated after adding salt, and the aqueous layer extracted with ether. The product separated by g.l.c. (15% Apiezon on Celite at 150°) gave two main components (70 : 30), *viz.* (i) 2-(*t*-2,*t*-3-dimethyl-*r*-1-cyclopentyl)propan-2-ol (27),† *m/e* 156, τ 8.76 (6H, s) and 9.05 (6H, d, *J* 7 Hz) and (ii) 2-(*t*-2,*c*-3-dimethyl-*r*-1-cyclopentyl)propan-2-ol (28),† *m/e* 156, τ 8.8 (6H), 8.94 (3H, d, *J* 6 Hz), and 9.0 (3H, d, 6 Hz).

(b) The mixture of alcohols (i) and (ii) above (2 g) was dehydrated by heating (for 1 h) with potassium hydrogen sulphate (3 g) and the product separated by g.l.c. (15% Apiezon on Celite at 100°) to yield (i) a product (28%) regarded as a 1-isopropylidene-2,3-dimethylcyclopentane (16),[†] m/e 138, τ 8.3 (3H, s), 8.43 (3H, s), 9.06 (3H, d, J 6 Hz), and 9.24 (3H, d, J 6 Hz); (ii) *r*-1-isopropenyl-*t*-2,*c*-3-dimethylcyclopentane (23) [†] (53.5%), m/e 138, n.m.r. as in the text; and (iii) *r*-1-isopropenyl-*t*-2,*t*-3-dimethylcyclopentane (22) [†] (18.5%), m/e 138, n.m.r. as in the text.

Ene-cyclisation of the Diene (1) and Hydroxymercuration of the 1-Isopropenyl-2,3-dimethylcyclopentanes formed.—(a) The diene (1) was heated and the vapour passed over copper turnings in a 25 × 3 cm tube at 550° in a stream of nitrogen. The product by g.l.c. (15% Apiezon on Celite at 100°) showed (i) recovered diene (21.5%); (ii) *r*-1-isopropenyl-*c*-2,*t*-3-dimethylcyclopentane (21) [†] (59%), m/e 138, n.m.r. as in the text, ν_{\max} 3090, 2970, 2880, 1648, 1455, 1375, 1290, 1130, 1090, 1025, 1000, 975, 890, and 730 cm^{-1} ; and (iii) *r*-1-isopropenyl-*c*-2,*c*-3-dimethylcyclopentane (24) [†] (14%), m/e 138, n.m.r. as in the text, ν_{\max} 3090, 2970, 2880, 1645, 1473, 1455, 1437, 1337, 1263, 1240, 1153, 1135, 960, and 890 cm^{-1} .

(b) Hydroxymercuration of these products, which had been separated by preparative g.l.c., gave (i), from (21), 2-(*c*-2,*t*-3-dimethyl-*r*-1-cyclopentyl)propan-2-ol (25),[†] m/e 156, 141, 129, and 59 (base peak), τ 8.74 (3H, s), 8.77 (3H, s), 9.04 (3H, d, J 7 Hz), and 9.15 (3H, d, J 7 Hz), ν_{\max} 3460 and 1155 cm^{-1} ; (ii) from (24), 2-(*c*-2,*c*-3-dimethyl-*r*-1-cyclopentyl)propan-2-ol (26),[†] m/e 156 absent, 141, 138, 95 (base peak), and 59, τ 8.71 (3H, s), 8.81 (3H, s), 9.06 (3H, d, J 8.5 Hz), and 9.23 (3H, d, J 8.5 Hz), ν_{\max} 3420 and 1160 cm^{-1} .

Acid Catalysed Additions to the Diene (1).—*General method.* The diene (1) (2 g) in propan-2-ol, acetic acid, or water (10 ml) with conc. H_2SO_4 (0.5 ml) was kept for 5 h. The products, isolated by g.l.c. (15% Apiezon, 140°), were characterised by n.m.r. and mass spectra: (a) 7-isopropoxy-3,7-dimethyloct-1-ene (11; R = Prⁱ),[†] m/e 198, τ 6.2 (1H, sept, J 6 Hz), 8.65 (6H), 8.91 (6H, d, J 6 Hz), 8.88 (6H, s), and 9.0 (3H, d, J 7 Hz), with lower field signals at τ 4.3, 4.98, and 5.18 as for the methoxy-analogue (7) above; (b) 7-acetoxy-3,7-dimethyloct-1-ene (11; R = Ac), m/e 198 (M^+) absent, 183 ($M - 15$), and 138 ($M - 60$), τ 4.3 (1H,

m , J 12, 7, and 7 Hz), 4.98 (1H, dd, J 12 and 2.5 Hz), 5.18 (1H, dd, J 7 and 2.5 Hz), 8.04 (3H, s), 8.58 (6H, s), and 9.01 (3H, d, J 7 Hz); (c) 2,6-dimethyloct-7-en-2-ol (11; R = H), m/e 157 ($M + 1$), 141, and 138, τ 4.3 (1H, m), 4.98 (1H, dd, J 12 and 2.5 Hz), 5.18 (1H, dd, J 7 and 2.5 Hz), 8.6 (6H), 8.8 (6H, s), and 9.03 (3H, d, J 7 Hz), ν_{\max} 3400 cm^{-1} .

Koch Reaction with the Diene (1) and with 2,6,6-Trimethylcycloheptanol.—(a) To sulphuric acid (93%; 34 g) and formic acid (0.2 ml) was added with stirring a solution of the diene (1) (2.5 g) and formic acid (3.1 g) in carbon tetrachloride (36 ml) during 1 h. The organic acid product (1.6 g) was esterified with diazomethane to give methyl 1,4,4-trimethylcycloheptane-1-carboxylate (33),[†] b.p. 120° at 15 mmHg, and a little of the methyl ester of a dimeric acid, b.p. 230° at 15 mmHg, m/e 336 ($\text{C}_{24}\text{H}_{40}\text{O}_2$). The lower boiling ester was characterised by m/e 198 ($\text{C}_{12}\text{H}_{22}\text{O}_2$), 183, 166, 139, etc., τ 6.3 (3H, s) and 9.1 (9H, s), ν_{\max} 1700, 1220, and 1155 cm^{-1} .

(b) Eucarvone¹⁵ was hydrogenated (PtO₂, ether) and reduced to 2,6,6-trimethylcycloheptanol (NaBH_4), and this alcohol (3 g) was treated with formic acid and sulphuric acid as in (a) to obtain methyl 1,4,4-trimethylcycloheptane-1-carboxylate (1.3 g), b.p. 120° at 15 mmHg, identical (m.s., n.m.r., g.l.c., and i.r.) with the ester prepared in (a).

(c) Methyl 1,4,4-trimethylcycloheptane-1-carboxylate was reduced with lithium aluminium hydride in ether to give (1,4,4-trimethylcycloheptyl)methanol (34) [†] which was purified by g.l.c. (5% SE 30, 130°) or column chromatography on silica gel from which elution with chloroform gave a product, m/e 152 ($M - 18$), 139 ($M - \text{CH}_2\text{OH}$), 138, 123, etc., τ 6.48, 6.58 (2H), 9.08 (9H, s), 8.71 (10H), and 8.55br (1H). In the presence of $\text{Eu}(\text{dpm})_3$ in CDCl_3 the τ 6.48 and 6.58 signals were moved downfield by 2 p.p.m., but maintained their separation, and the τ 9.08 proton signal was resolved.

We are grateful to the S.R.C. for a CAPS award to D. G. P. and to Bush, Boake, Allen Ltd., for interest and for gifts of materials.

[3/1180 Received, 7th June, 1973]

¹⁵ E. J. Corey and H. J. Burke, *J. Amer. Chem. Soc.*, 1956, **78**, 174; E. J. Corey, H. J. Burke, and W. A. Remers, *ibid.*, p. 180.