

Manganese(III)-induced Radical Additions to 3,7-Dimethylocta-1,6-diene

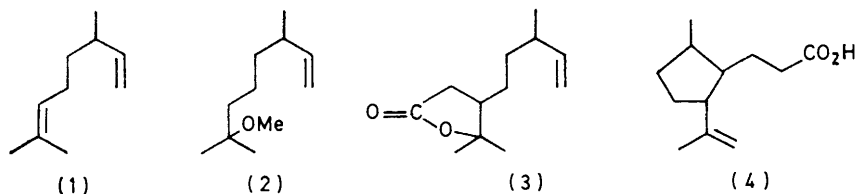
By Francis J. McQuillin and Michael Wood, Department of Organic Chemistry, University of Newcastle upon Tyne NE1 7RU

The reactions of 3,7-dimethylocta-1,6-diene with organic radicals generated by oxidation with manganese(III) acetate of (i) acetic acid, ethyl acetoacetate, and pentane-2,4-dione, and (ii) dimethyl malonate, acetone, cyclopentanone, cyclohexanone, and acetophenone have been examined. Whereas addends in group (i) react mainly at the 6,7-bond, addends in group (ii) react at the 1,2-centre with ring closure to yield cyclopentane derivatives. In competition for the radical $\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_3$, 3,7-dimethyloct-1-ene, 2,6-dimethyloct-2-ene, and 3,7-dimethylocta-1,6-diene react in the ratio 4.8 : 21.4 : 73.8. Competition between acetone and $[\text{}^2\text{H}_6]$ acetone indicates a kinetic isotope effect of *ca.* 3 for the overall process of generation and addition of the radical. The possibility of reversible addition of a radical to an alkene is considered.

In a series of papers¹ we have surveyed the chemistry of transition metal complexing of terpenes, with particular reference to the chemical reactions resulting from transition metal complexing of 3,7-dimethylocta-1,6-diene (1) and the derived methyl ether (2).

In the Wacker type oxidation of the diene (1) induced¹ by Pd^{II} or Rh^{III} , reaction is dependent on electron

characterised as its methyl ester, *m/e* 210 [τ 5.20 (2 H, s), 6.4 (3 H, s), 7.75 (2 H, t, *J* 5 Hz), 8.4 (3 H, s), and 9.0 (3 H, d, *J* 6 Hz)]. Thus both modes of addition are exemplified, but both products arise *via* a tertiary intermediate radical, *i.e.* (3) arises by further oxidation of (5; R = $\text{CH}_2\cdot\text{CO}_2\text{H}$) and (4) by cyclisation and further oxidation of (6; R = $\text{CH}_2\cdot\text{CO}_2\text{H}$).



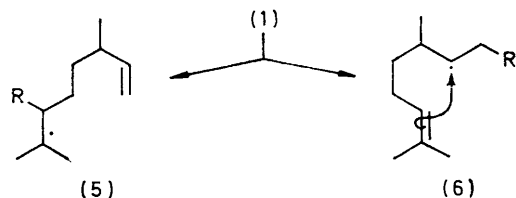
transfer from carbon to Pd^{II} or Rh^{III} . As an extension we have now surveyed the reaction of the diene (1) and the methyl ether (2) with radicals formed by electron transfer from various addends to Mn^{III} .²⁻⁵ Of particular interest was the question whether in the diene (1) the 1,2- or 6,7-centre would prove the principal site of radical addition.

Alkenes with Mn^{III} acetate and acetic acid give products of addition² of the radical $\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$. Under these conditions the diene (1) gave two products, a lactone, ν_{OO} 1760 cm^{-1} , which from its n.m.r. spectrum [τ 4.65, 5.0, and 5.25 (each 1 H, m), 7.65 (2 H, m), 8.65 (3 H, s), 8.79 (3 H, s), and 9.0 (3 H, d, *J* 6 Hz)] clearly has structure (3), and in similar amount an acid (4),

¹ F. J. McQuillin and D. G. Parker, *J.C.S. Perkin I*, 1974, 809; 1975, 2092; K. Dunne and F. J. McQuillin, *J. Chem. Soc. (C)*, 1970, 2196, 2200, 2203.

² J. B. Bush and H. Finkbeiner, *J. Amer. Chem. Soc.*, 1968, 90, 5903; E. I. Heiba, R. M. Dessau and P. G. Rodewald, *ibid.*, 1968, 90, 5905; 1974, 96, 7977; R. E. van der Ploeg and D. W. de Korte, *J. Catalysis*, 1968, 10, 52.

However, it appeared possible that the proportions of reaction at the 1,2- and 6,7-centres in (1) might be



altered with a radical addend more bulky than $\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$. By using dimethyl malonate⁶ in presence of Mn^{III} acetate this appeared to be verified. The reaction gave one major fraction, isolated by g.l.c. and shown to

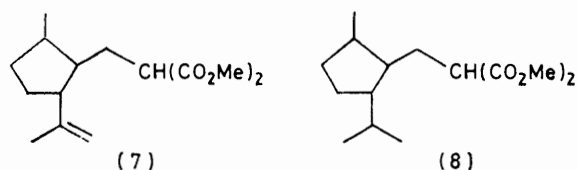
³ E. I. Heiba and R. M. Dessau, *J. Amer. Chem. Soc.*, 1971, 93, 524.

⁴ E. I. Heiba and R. M. Dessau, *J. Amer. Chem. Soc.*, 1972, 94, 2888.

⁵ E. I. Heiba and R. M. Dessau, *J. Org. Chem.*, 1974, 39, 3456, 3457.

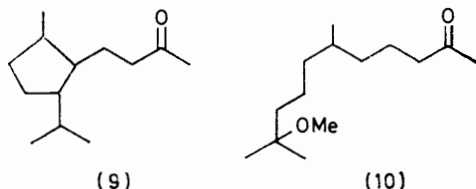
⁶ G. I. Nikishin, M. G. Vinogradov, and T. M. Fedorova, *J.C.S. Chem. Comm.*, 1973, 693.

consist of a mixture of some olefin (7) and mainly the saturated product (8), m/e 268 and 270, τ 5.2. Hydrogenation of the mixture gave (8), m/e 270, τ 6.3 (6 H, s),



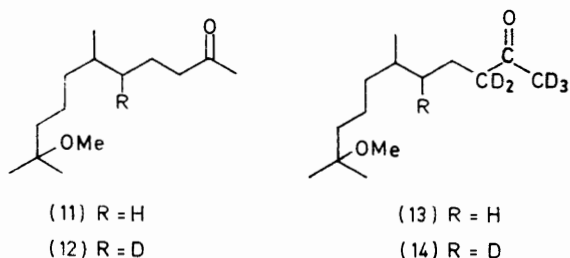
6.65 (1 H, m), and 9.1br (9 H, s). The olefin (7) could, however, be made the sole product by addition of Cu^{II} acetate to the reaction mixture;⁶ the product (7) showed m/e 268, τ 5.25 (2 H, s), 6.3 (6 H, s), 6.7 (1 H, m), 8.4 (3 H, s), and 9.0 (3 H, d, J 6 Hz).

With acetone as addend³ the diene (1) gave, however, as sole product a material for which the n.m.r. spectrum indicated the cyclic structure (9). This brings into question the importance of the steric bulk of the addend in directing reaction at the 1,2- or 6,7-centre. The product (9) showed m/e 196, τ 7.6 (2 H, m), 8.4–8.7 (10 H, m), 7.9 (3 H, s), and 9.1br (9 H, s).



Under the same conditions the methyl ether (2) gave the expected adduct (10), m/e 228, τ 6.9 (3 H, s), 7.6 (2 H, t, J 6 Hz), 7.7 (3 H, s), 8.4 (1 H, m), 8.7br (10 H), 8.9 (6 H, s), and 9.15 (3 H, d, J 4 Hz).

We also carried out a competition experiment involving the methyl ether (2) and equimolar amounts of acetone and $[\text{2H}_6]$ acetone, with Mn^{III} acetate in dioxan as solvent. The product (by mass spectrometric analysis of the $M - 15$ ions) contained compounds (11)–(14) in the ratio 8 : 1.5 : 1.5 : 1, *i.e.* CH or CD bond rupture is rate limiting with a kinetic isotope effect of *ca.* 3, which is of appropriate magnitude.⁷

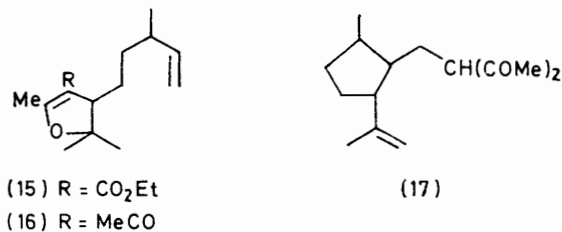


The evident influence of the nature of the addend in determining the production of an acyclic product such as (3) or cyclic products such as (4), (7), (8), or (9) led us to examine as addends also ethyl acetoacetate and pentane-2,4-dione in comparison with the non-enolic ketones cyclopentanone, cyclohexanone, and acetophenone.

The two groups were found to exhibit different behaviour. Ethyl acetoacetate and pentane-2,4-dione with

the diene (1) and Mn^{III} acetate yield adducts at the 6,7-bond with ring closure of oxygen onto C-7. The non-enolic ketones on the other hand yield products of type (4), (7), (8), and (9) by selective addition to the 1,2-bond.

The adduct of ethyl acetoacetate and the diene (1) was given structure (15) on the basis of spectroscopic

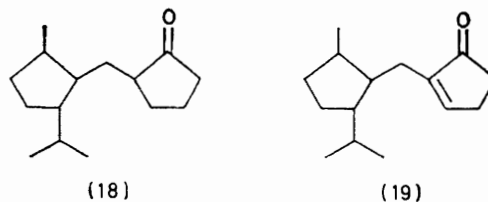


data: m/e 266, τ 4.6 (1 H, m), 5.0 (1 H, m), 5.2 (1 H, m), 5.9 (2 H, q., J 7 Hz), 7.4 (1 H, m), 8.66 (3 H, s), 8.68 (9 H, s and t), and 9.0 (3 H, d, J 6 Hz).

Pentane-2,4-dione gave as main product the dihydrofuran (16), m/e 236, τ 4.5 (1 H, m), 5.0 (1 H, m), 5.25 (1 H, m), 7.5 (1 H, t, J 4 Hz), 7.4 (6 H, s), 8.7 (3 H, s), 8.76 (3 H, s), and 9.05 (3 H, d, J 6 Hz). There was, however, a second product in smaller amount for which the data indicate structure (17), *viz.* m/e 236, τ 5.25 (2 H, s), 6.4 (1 H, t, J 10 Hz), 7.9 (6 H, s), 8.4 (3 H, s), and 9.05 (3 H, d, J 6 Hz).

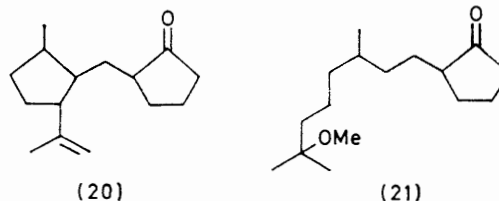
Formation of the products (15)–(17) replicates the behaviour of acetic acid in yielding compounds (3) and (4).

With cyclopentanone and Mn^{III} acetate the diene (1) gave adducts (18) and (19) in similar amounts. G.l.c. separation afforded (18), m/e 222, τ 8.0 (6 H, m), 8.5 (9 H, m), and 9.0br (9 H, s), ν_{CO} 1735 cm^{-1} , and (19), m/e 220, τ 3.0br (1 H, s), 7.5–7.9 (2 H, m), 8.0



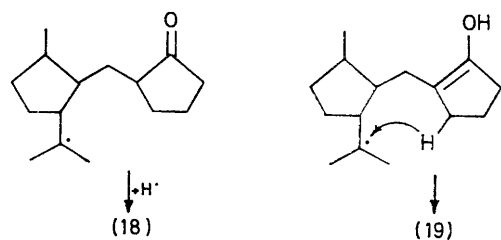
(2 H, m), 8.1 (2 H, m), 8.5 (5 H, m), and 9.0br (9 H, s), ν_{CO} 1710 cm^{-1} .

Addition of Cu^{II} acetate in the reaction of the diene (1) with cyclopentanone did not raise the proportion of unsaturated product (19), but led to the isomeric (20) as sole product; ν_{CO} 1735 cm^{-1} , m/e 220, τ 5.24 (2 H, s), 7.95 (7 H, s), 8.33 (3 H, s), and 9.0 (3 H, d, J 6 Hz).



We are led to infer that conditions leading to rapid oxidation of the intermediate radical adduct, *i.e.* in
⁷ H. J. Den Hertog and E. C. Kooyman, *J. Catalysis*, 1966, **6**, 357.

presence of Cu^{II} , lead to compound (20) by proton loss, but that with insufficient oxidising agent there is competitive hydrogen abstraction from the proximate oxocyclopentyl residue, giving (19), or from cyclopentanone in the medium, giving (18) (see Scheme 1). Some

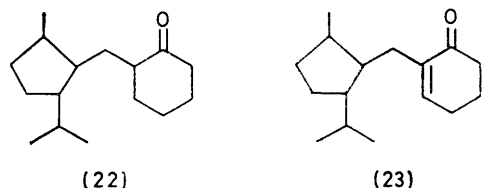


SCHEME 1

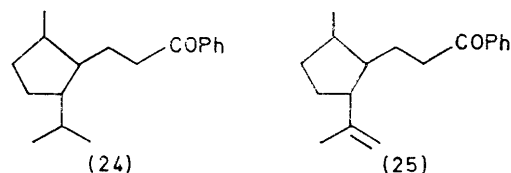
precedent for intramolecular hydrogen transfer of this kind is found in a related photochemical transformation.⁸

Cyclopentanone with Mn^{III} acetate and the methyl ether (2) gave the adduct (21), m/e 239 ($M - 15$), τ 6.9 (3 H, s), 6.85–7.2 (7 H, m), 8.7br (10 H, s), 8.93 (6 H, s), and 9.1 (3 H, d, J 6 Hz).

Cyclohexanone with the diene (1) in the presence of Mn^{III} acetate gave a product consisting of (22) and (23), corresponding to (18) and (19).



Acetophenone similarly gave an adduct with the diene (1) by reaction at the 1,2-centre followed by cyclisation to (24). Reaction in presence of Cu^{II} acetate gave (25).

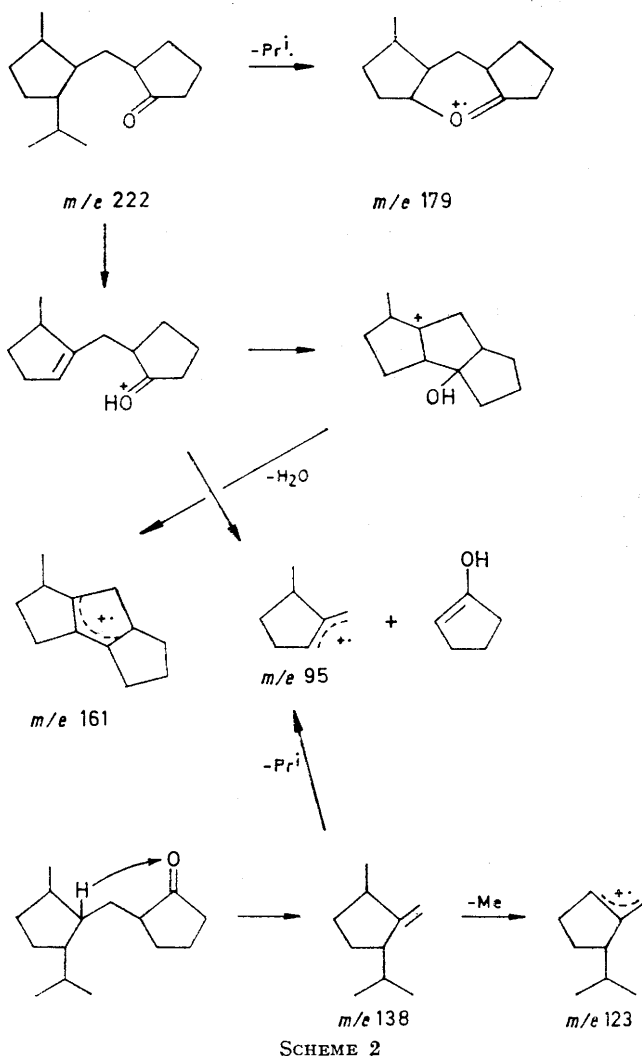


The structures of the cyclic products such as (4), (7), (8), (9), etc. were deduced from n.m.r. spectra. However, the pattern of mass spectral breakdown also lent support to these structures. For example the cyclopentanone adduct (18), m/e 222, showed loss of 43 mass units (Pr^{\cdot}) to give an ion the further fragmentation of which is rationalized in Scheme 2.

The structures of these cyclic products could also be independently confirmed and the stereochemistry ascertained. It was shown previously¹ that the diene (1) with Hg^{II} acetate in aqueous tetrahydrofuran gives an adduct (26; $\text{R} = \text{HgOAc}$), reduced by sodium borohydride to a mixture of 2-(*t*-2,*t*-3-dimethyl-*r*-1-cyclopentyl)propan-2-ol (27) and the *t*-2,*c*-3-dimethyl isomer (28) (mainly the latter).

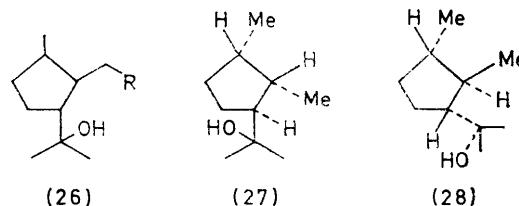
⁸ A. B. Smith and W. C. Agosta, *J. Amer. Chem. Soc.*, 1974, **96**, 3289.

The Hg^{II} acetate adduct (26) could be converted into the corresponding bromide ($\text{R} = \text{HgBr}$), and this with



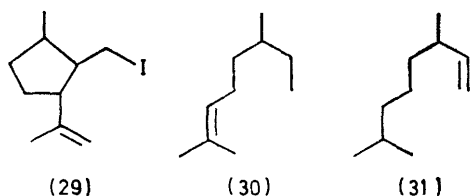
SCHEME 2

iodine in carbon tetrachloride gave an iodide (26; $\text{R} = \text{I}$) which by chromatography on silica suffered dehydration to give (29) (as a mixture of isomers). Condensation of (29) with ethyl 2-oxo-1-sodiocyclopentanecarboxylate, hydrolysis, and decarboxylation gave (20),

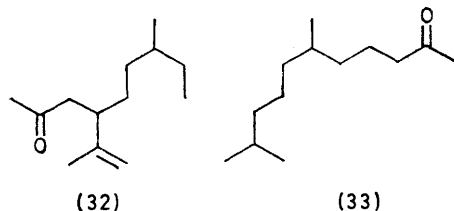


which was hydrogenated to give compound (18), identical (g.l.c., n.m.r., and comparison of 2,4-dinitrophenylhydrazones) with that obtained previously. Similar condensation of (29) with dimethyl sodiomalonate led to compound (7) identified by n.m.r., and mass spectra and t.l.c.

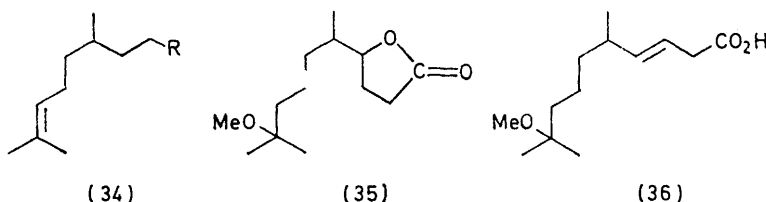
The reactions of the diene (1) with acetic acid, ethyl acetoacetate, and pentane-2,4-dione are rapid, the brown Mn^{III} colour being discharged with precipitation of Mn^{II}



acetate within 10 min. Reactions of (1) with dimethyl malonate, acetone, and the other ketones, however, were noticeably slow. Thus the reactions at the 6,7-centre



are characterised by rapid addition, which becomes irreversible by oxidative addition of a hydroxy-function



to the tertiary radical centre. Addition at the 6,7-bond, which leads to a tertiary radical intermediate, should be the preferred reaction route. There is therefore the implication that addends which do not contain the hydroxy-group may first add reversibly at the 6,7-bond. In the light of this, we compared the reactivity of the alkenes (1), (30), and (31) in competition for addition of acetone in the presence of Mn^{III} acetate sufficient for only partial reaction. The adducts from (30) and (31), *i.e.* (32) and (33), were separately characterised. G.l.c. analysis of the product of the competition study indicated the presence of (9) (73.8), (32) (21.4), and (33) (4.8%). Thus, as expected, the 6,7-double bond does react more rapidly than that at the 1,2-position. However, addition at the 1,2-position in (1) is evidently enhanced by concomitant involvement of the 6,7-double bond in cyclisation and transfer of the radical to the tertiary centre. There is precedent for reversible radical addition,⁹ and the effect of added Cu^{II} ion indicates that hydrogen addition to the intermediate radical or its oxidation to a carbocation by Mn^{III} are relatively slow. In addition, the ligand properties of the CH_2CO_2H , $CH_3COCHCO_2Et$, and $CH_3COCHCOCH_3$ resi-

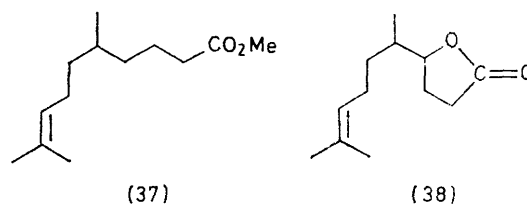
⁹ M. Julia, M. Maumy and L. Liou, *Bull. Soc. chim. France*, 1967, 2641; J. C. Chottard and M. Julia, *Tetrahedron Letters*, 1971, 2561; D. B. Denny and P. P. Klemchuk, *J. Amer. Chem. Soc.*, 1958, 80, 3289; W. H. Urrey, D. J. Trecker, and H. D. Hartzler, *J. Org. Chem.*, 1964, 29, 1663.

dues may facilitate this further oxidation by retaining metal ion in the reaction complex. These addends are therefore well suited to effect rapid and irreversible addition to the 6,7-bond. In the case of $\cdot CH(CO_2Me)_2$ or the various ketone radicals it is possible to consider that the radical formed by addition at the 6,7-double bond is sufficiently long-lived to undergo regression or rearrangement, *i.e.* (5) \rightarrow (6). On this view, adducts such as (3), (15), and (16) may be regarded as products arising from kinetic reaction control, whereas (8), (9), (17), (18), *etc.* are thermodynamic products. In the processes represented by (5) and (6), the second will involve the larger entropy of activation which may, however, be compensated in the smaller steric compression involved in bonding the addend R at a primary rather than at a secondary carbon centre.

The availability of the methyl ether (2) also gives access to a third group of derivatives of the type (34), by radical addition to (2) followed by elimination of the elements of methanol. Several examples of this procedure have been examined. 7-Methoxy-3,7-dimethyloctene (2) with acetic acid and Mn^{III} acetate gave the lactone (35), an unsaturated acid [mainly (36)], and a small amount of an acetoxy-acid related to (36). These

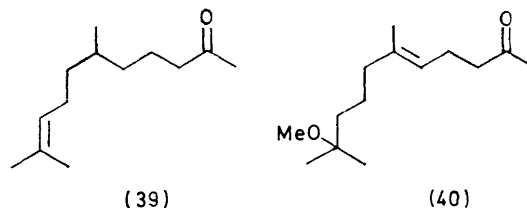
products could be characterised by their n.m.r. spectra. In addition (36) could be hydrogenated to the dihydro-acid.

The methyl ester of dihydro-(36), warmed in the presence of toluene-*p*-sulphonic acid, gave the olefin (37),



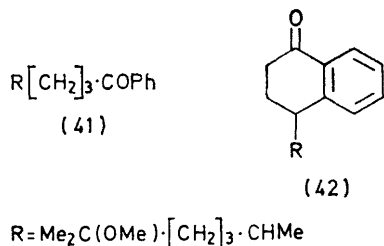
characterised by n.m.r. The lactone (35) could similarly be converted into (38).

The acetone adduct of (2) [*i.e.* (10)] in the same way



yielded (39), or when the radical addition was performed in the presence of Cu^{II} acetate, the ketone (40).

The methoxy-octene (2) with acetophenone gave a mixture of the expected ⁴ products (41) and (42).



EXPERIMENTAL

N.m.r. data are quoted only in cases where the data do not appear in the main text. Reactions with Mn^{III} acetate were carried out under nitrogen. Manganese(III) triacetate was prepared¹⁰ and used as the dihydrate.

3,7-Dimethylocta-1,6-diene and Acetic Acid.—3,7-Dimethylocta-1,6-diene (1 g) in acetic acid (20 ml) and acetic anhydride (10 ml) with Mn^{III} triacetate (3.9 g, 2 equiv.) was heated under reflux. After 10 min Mn^{II} diacetate was filtered off and the products were recovered from the filtrate by addition of water and ether. Neutral materials were separated by heating with methanolic sodium hydroxide, dilution with water, and extraction with ether. Acidification of the alkaline solution (12% HCl) gave a product separated by aqueous sodium hydrogen carbonate into an acid and a neutral component. The former, esterified by diazomethane, gave *methyl 3-(2-isopropenyl-5-methylcyclopentyl)propanoate* (4), apparently as a single substance (t.l.c. on silica gel in benzene, R_F 0.75), m/e 210, 195, 179, and 168 (Found: C, 74.25; H, 10.5. $\text{C}_{12}\text{H}_{20}\text{O}_2$ requires C, 74.3; H, 10.3%). The neutral material showed one peak on g.l.c. (6 ft silicone SE30; 80–160 °C) m/e 196, 181, and 153, ν_{CO} 1760 cm^{-1} , corresponding with *5,5-dimethyl-4-(3-methylpent-4-enyl)tetrahydrofuran-2-one* (3) (Found: C, 73.2; H, 10.1. $\text{C}_{12}\text{H}_{20}\text{O}_2$ requires C, 73.5; H, 10.2%). This lactone (0.3 g) could be hydrogenated over platinum dioxide in ether (uptake 34.2 ml; calc. 33.2 ml). The dihydro-derivative showed m/e 198, 183, and 155, τ 7.6 (2 H, m), 8.65 (3 H, s), 8.73 (3 H, s), and 9.05br (6 H, s).

3,7-Dimethylocta-1,6-diene and Dimethyl Malonate.—(a) 3,7-Dimethylocta-1,6-diene (1 g), dimethyl malonate (25 ml), and Mn^{III} acetate (3.9 g) were heated under gentle reflux for 12 h. Recovery as above and removal of the excess of dimethyl malonate by distillation left a residue which by preparative g.l.c. (80–190 °C; 10 ft silicone SE30) gave (7) and (8) as a mixture, m/e 268 and 270, τ 5.2. Hydrogenation (PtO_2 ; Et_2O) gave a single product, m/e 270, 238, and 227, *dimethyl (2-isopropyl-5-methylcyclopentylmethyl)malonate* (8) (Found: C, 66.5; H, 9.3. $\text{C}_{15}\text{H}_{26}\text{O}_4$ requires C, 66.6; H, 9.6%).

(b) 3,7-Dimethylocta-1,6-diene (1 g) and dimethyl malonate (1 g) with Mn^{III} acetate (3.9 g) and Cu^{II} acetate (1.45 g) in acetic acid (25 ml) were heated until the brown Mn^{III} colour had disappeared (10 min). Isolation by filtration *etc.*, gave a product which was chromatographed on a silica gel column. Benzene–light petroleum (1:1) eluted *dimethyl (2-isopropenyl-5-methylcyclopentylmethyl)malonate* (7), m/e 268, 225, 196, and 143 (Found: C, 67.7; H, 8.9. $\text{C}_{15}\text{H}_{24}\text{O}_4$ requires C, 67.2; H, 8.95%).

3,7-Dimethylocta-1,6-diene with Acetone.—3,7-Dimethylocta-1,6-diene (1 g), acetone (25 ml), and Mn^{III} acetate (3.9 g)

were heated for 24 h. Recovery gave material (0.8 g) showing one main component [t.l.c. on silica gel in benzene–chloroform (10:1), R_F 0.76; or g.l.c. on 10 ft silicone SE30, 80–190 °C]. Preparative g.l.c. gave *4-(2-isopropyl-5-methylcyclopentyl)butan-2-one* (9), m/e 196, 178, 153, 138, and 123 (Found: C, 79.1; H, 12.5. $\text{C}_{13}\text{H}_{24}\text{O}$ requires: C, 79.5; H, 12.25%).

7-Methoxy-3,7-dimethyloctene with Acetone or [²H₆]Acetone.—(a) *7-Methoxy-3,7-dimethyloctene* (3 g) with acetone (25 ml) and Mn^{III} acetate (9.45 g) was refluxed for 24 h. Recovery gave a residue (3.55 g) which g.l.c. showed to contain one main component. This was isolated by preparative g.l.c. (10 ft silicone SE30; 80–190 °C) as a liquid, R_F 0.39 (CHCl_3 ; SiO_2), m/e 213 ($M - 15$), 196, 163, and 73, *10-methoxy-6,10-dimethylundecan-2-one* (10) (Found: C, 73.7; H, 12.1. $\text{C}_{14}\text{H}_{28}\text{O}_2$ requires C, 73.6; H, 12.3%).

(b) *7-Methoxy-3,7-dimethyloctene* (1 g) with acetone (0.343 g), [²H₆]acetone (0.343 g), and Mn^{III} acetate (3.15 g, 2 equiv.) in dioxan (25 ml) was refluxed for 24 h. Recovery gave a product which g.l.c. showed to contain a single component (silicone SE30; 80–160 °C). Preparative g.l.c. gave a product comprising compounds (11)–(14) (mass spectral data as above).

3,7-Dimethylocta-1,6-diene and Ethyl Acetoacetate.—3,7-Dimethylocta-1,6-diene (1 g) in acetic acid (25 ml) with ethyl acetoacetate (1 g) and Mn^{III} acetate (5 g) was heated under reflux for 10 min. Recovery gave a residue (1.48 g) which was chromatographed on silica gel. Elution with benzene–light petroleum (1:1) gave a product, R_F 0.33 (silica gel; same solvent), m/e 266, 251, 237, 221, 209, 196, and 183, *ethyl 4,5-dihydro-2,5,5-trimethyl-4-(3-methylpent-4-enyl)furan-3-carboxylate* (15) (Found: C, 72.35; H, 9.85. $\text{C}_{16}\text{H}_{26}\text{O}_3$ requires C, 72.2; H, 9.7%).

3,7-Dimethylocta-1,6-diene with Pentane-2,4-dione.—3,7-Dimethylocta-1,6-diene (1 g) in acetic acid (25 ml) with pentane-2,4-dione (1 g) and Mn^{III} acetate (3.9 g) was heated under reflux for 10 min. Recovery gave material (1.23 g) from which unchanged diene was removed by distillation. The residue (0.9 g), chromatographed on silica gel (elution with benzene) gave a mixed product, separated by preparative t.l.c. into materials of R_F 0.37 and 0.17 in benzene. The former was *3-(2-isopropenyl-5-methylcyclopentylmethyl)pentane-2,4-dione* (17), m/e 236, 193, and 222, and showing a red colour reaction in alcoholic iron(III) chloride (Found: C, 75.7; H, 10.0. $\text{C}_{15}\text{H}_{24}\text{O}_2$ requires C, 76.2; H, 10.2%). The component of R_F 0.17, m/e 236, 221, 203, 179, and 153, was *4-acetyl-2,3-dihydro-2,2,5-trimethyl-3-(3-methylpent-4-enyl)furan* (16), λ_{max} 275 nm (ϵ 1770), unchanged on addition of aqueous sodium hydroxide, and showing no colour with alcoholic iron(III) chloride (Found: C, 75.7; H, 10.3. $\text{C}_{15}\text{H}_{24}\text{O}_2$ requires C, 76.2; H, 10.2%).

3,7-Dimethylocta-1,6-diene with Cyclopentanone.—(a) 3,7-Dimethylocta-1,6-diene (2.43 g) in dioxan (100 ml) with Mn^{III} acetate (9.43 g) was heated at 110 °C, and cyclopentanone (2.46 g) was added dropwise during 6 h. After heating for 24 h, recovery, after removal of unchanged diene, gave a residue (2.02 g) which was separated by preparative g.l.c. (10 ft Apiezon; 190 °C) into two components (*ca.* 1:1). The first was *2-(2-isopropyl-5-methylcyclopentylmethyl)cyclopentanone* (18), m/e 222, 179, 123, and 81, ν_{CO} 1735 cm^{-1} (Found: C, 81.2; H, 11.3. $\text{C}_{15}\text{H}_{26}\text{O}$ requires C, 81.1; H, 11.7%). The second was *2-(2-isopropyl-5-methylcyclopentylmethyl)cyclopent-2-enone* (19), m/e 220, 177, 123, and 81, ν_{CO} 1710

¹⁰ O. T. Christiansen, *Z. anorg. Chem.*, 1901, **27**, 325.

cm^{-1} , λ_{max} 235 nm (ϵ 9350) (Found: C, 81.9; H, 10.55. $\text{C}_{15}\text{H}_{24}\text{O}$ requires C, 81.9; H, 10.9%).

(b) A similar reaction with the diene (1), acetic acid (25 ml), Mn^{III} acetate (3.9 g), Cu^{II} acetate (1.45 g), and cyclopentanone (0.61 g) (reaction time 15 min) gave a product (0.81 g), purified by chromatography on silica gel. Elution with benzene gave a substance, m/e 220, 177, 123, and 81 corresponding in its n.m.r. spectra (see main text) with 2-(2-isopropenyl-5-methylcyclopentylmethyl)cyclopentanone (20) (Found: C, 81.9; H, 10.5. $\text{C}_{15}\text{H}_{24}\text{O}$ requires C, 81.9; H, 10.9%).

7-Methoxy-3,7-dimethyloctene with Cyclopentanone.—The product obtained from 7-methoxy-3,7-dimethyloctene (0.5 g), cyclopentanone (0.25 g), and Mn^{III} acetate (3.16 g) in dioxan (25 ml) was chromatographed on silica gel. Elution with benzene gave 2-(7-methoxy-3,7-dimethyloctyl)cyclopentanone (21), m/e 239 ($M - 15$), 222, 189, 149, and 73 (Found: C, 75.3; H, 11.4. $\text{C}_{16}\text{H}_{30}\text{O}_2$ requires C, 75.5; H, 11.8%).

3,7-Dimethylocta-1,6-diene and Cyclohexanone.—3,7-Dimethylocta-1,6-diene (2.47 g) with cyclohexanone (1.73 g) and Mn^{III} acetate (9.65 g) in dioxan (100 ml), heated for 12 h, gave on recovery a residue (1.34 g) (after removal of unchanged materials by distillation). This residue was distilled at 110 °C (0.5 mmHg) and the distillate separated by preparative g.l.c. (10 ft Apiezon; 190 °C) into two components. The first (57.2%) was 2-(2-isopropyl-5-methylcyclopentylmethyl)cyclohexanone (22) (Found: m/e 236.212 $\text{C}_{16}\text{H}_{28}\text{O}$ requires M , 236.214), τ 7.8 (10 H, m), 8.4 (10 H, m), and 9.1br (8 H, s), ν_{CO} 1710 cm^{-1} . The second component was 2-(2-isopropyl-5-methylcyclopentylmethyl)cyclohex-2-enone (23) (Found: m/e 234.1964. $\text{C}_{16}\text{H}_{26}\text{O}$ requires M , 234.1984), τ 3.0br (1 H, s), 7.8 (4 H, m), 8.5 (9 H, m), and 9.1 (6 H, s), ν_{CO} 1685 cm^{-1} .

3,7-Dimethylocta-1,6-diene and Acetophenone.—(a) 3,7-Dimethylocta-1,6-diene (1 g) with acetophenone (1.74 g) and Mn^{III} acetate (3.9 g) in dioxan (25 ml) was heated for 12 h. Recovery (removal by distillation of unchanged materials) gave a residue which was chromatographed on silica gel. A product eluted by light petroleum-benzene (9 : 1) was shown to be a single substance by t.l.c. (R_F 0.69 in benzene). This was 3-(2-isopropyl-5-methylcyclopentyl)propiofenone (24) m/e 258, 240, 133, 119, and 105, τ 2.4 (2 H, m), 3.47 (3 H, m), 7.1 (2 H, m), 7.7 (2 H, m), and 9.1 (9 H), λ_{max} 241 nm (ϵ 1238) (Found: C, 83.75; H, 9.7. $\text{C}_{18}\text{H}_{26}\text{O}$ requires C, 83.7; H, 10.1%).

(b) 3,7-Dimethylocta-1,6-diene (1 g), acetophenone (0.87 g), Mn^{III} acetate (3.9 g), and Cu^{II} acetate (1.45 g) in acetic acid (25 ml) were heated for 12 h. Isolation by chromatography on silica gel gave a product (eluted by benzene-light petroleum, 1 : 1) shown by t.l.c. to be a single substance, R_F 0.69 in benzene. This was 3-(2-isopropenyl-5-methylcyclopentyl)propiofenone (25), m/e 256, 213, 238, 154, and 138, τ 2.9 (2 H, m), 3.45 (3 H, m), 5.3 (2 H, s), 7.2 (2 H, t, J 8 Hz), 7.8 (2 H, m), 8.4 (3 H, s), and 9.1 (3 H, d, J 6 Hz) (Found: C, 84.1; H, 9.7. $\text{C}_{18}\text{H}_{24}\text{O}$ requires C, 84.5; H, 9.4%).

Competition of Alkenes for Addition of Acetone.—(a) 2,6-Dimethyloct-2-ene (30) was prepared by semihydrogenation of 3,7-dimethylocta-1,6-diene as previously described.¹

3,7-Dimethyloct-1-ene (31) was prepared from citronellol (3,7-dimethyloct-6-en-1-ol) (3 g), which was hydrogenated over platinum oxide (0.1 g) in ethanol (25 ml) (uptake 470 ml). The product was distilled from boric acid (2 g) through a Vigreux column¹¹ to give the olefin (31), m/e 140, τ 4.5

(1 H, m), 5.0 (1 H, m), 5.2 (1 H, m), 8.1 (1 H, m), 8.7br (7 H, s), and 9.03 (9 H, s).

(b) 2,6-Dimethyloct-2-ene (0.5 g) in acetone (25 ml) with Mn^{III} acetate (3.0 g) was heated for 24 h. Recovery gave a product which by g.l.c. (6 ft silicone SE30; 80–150 °C) or t.l.c. (silica gel; benzene-chloroform, 9 : 1) was shown to contain two components. One product, R_F 0.6, isolated by column chromatography on silica gel was 4-isopropenyl-7-methylnonan-2-one (32), m/e 196, 181, and 153, τ 5.2 (2 H, s), 7.6 (2 H, m), 7.95 (3 H, s), 8.35 (3 H, s), 8.75br (7 H), and 9.0br (6 H, s), $\nu_{\text{C=O}}$ 890, ν_{CO} 1710 cm^{-1} . The second product, R_F 0.2, eluted with ether, was 4-(1-hydroxy-1-methylethyl)-7-methylnonan-2-one, m/e 196 ($M - 18$) and 181, ν_{OH} 3400, ν_{CO} 1710 cm^{-1} , τ 7.6 (2 H, m), 7.9 (3 H, s), 8.6 (3 H, s), 8.7 (3 H, s) and 9.05br (6 H) (Found: C, 73.2; H, 10.0. $\text{C}_{13}\text{H}_{26}\text{O}_2$ requires C, 73.0; H, 10.15%).

(c) 3,7-Dimethyloct-1-ene with acetone, treated as in (b), gave one major product, isolated by chromatography on silica gel. Elution with benzene gave 6,10-dimethylundecan-2-one (33), m/e 198, 180, 165, and 155, τ 7.5 (2 H, t, J 6 Hz), 7.9 (3 H, s), 8.7br (12 H), and 9.05 (9 H, m).

(d) 3,7-Dimethyloct-1-ene, 2,6-dimethyloct-2-ene, and 3,7-dimethylocta-1,6-diene (each 0.25 g) in acetone (25 ml) with Mn^{III} acetate (1 g), heated for 12 h, gave a product, g.l.c. analysis (6 ft silicone SE30; 80–160 °C) of which showed three components, corresponding to (32), (33), and (9) in the ratio 21.4 : 4.8 : 73.8.

2-Iodomethyl-1-isopropenyl-3-methylcyclopentane (29).—3,7-Dimethylocta-1,6-diene (10 g) in tetrahydrofuran (50 ml) and water (50 ml) with Hg^{II} acetate (23.1 g) was set aside for 0.5 h. Recovery by dilution with water and extraction with ether gave the Hg^{II} adduct (26; $R = \text{HgOAc}$), τ 4.9br (HO), 7.9 (3 H, s), 8.1 (2 H, m), 8.63 (3 H, s), 8.73 (3 H, s), and 9.0 (3 H, d, J 6 Hz). Without further purification this material (21.4 g) was taken up in water (100 ml) and treated with sodium bromide (6 g) in water (20 ml). After 2 h, a little mercury was filtered off and the filtrate extracted with ether. This gave material which was chromatographed on silica gel. Elution with benzene gave 2-bromomercuriomethyl-1-(1-hydroxy-1-methylethyl)-3-methylcyclopentane (26; $R = \text{HgBr}$), m/e 219, 221, 201, 203, 173, 175, 96, 81, and 54, τ 7.5br (HO), 8.0–8.6 (9 H, m), 8.7 (3 H, s), 8.76 (3 H, s), and 9.0 (3 H, d, J 6 Hz) (Found: C, 28.1; H, 4.5. $\text{C}_{10}\text{H}_{19}\text{BrHgO}$ requires C, 27.6; H, 4.35%).

This material (1 g) in carbon tetrachloride (25 ml) was slowly treated with a solution of iodine (0.59 g) in the same solvent (25 ml). After several hours the cream-coloured precipitate was filtered off and the filtrate washed with aqueous sodium thiosulphate. Recovery gave the hydroxyiodide (26; $R = \text{I}$), m/e 267 ($M - 15$), 155, 137, and 97, τ 6.5 (2 H, d, J 4 Hz), 8.1–8.6 (7 H, m), 8.8 (3 H, s), 8.9 (3 H, s), and 9.0 (3 H, d, J 6 Hz). Chromatography of this material on silica gel and elution with light petroleum gave the iodide (29), m/e 264 and 137, τ 5.3 (2 H, s), 6.7 (2 H, d, J 4 Hz), 8.33 (3 H, s), and 9.0 (3 H, d, J 6 Hz), $\nu_{\text{C=O}}$ 890 cm^{-1} (Found: C, 45.1; H, 6.9%; m/e 264.038. $\text{C}_{10}\text{H}_{17}\text{I}$ requires C, 45.5; H, 6.5%; M , 264.0377).

Synthesis of the Cyclopentanone Derivatives (18) and (20).—The iodide (29) (0.5 g) was added to ethyl 2-oxo-1-sodio-cyclopentanecarboxylate [from the ester (0.6 g) and sodium hydride (0.1 g) in dioxan (10 ml)]. After heating overnight the product was isolated by adding water and ether, and

¹¹ W. Brandenburg and A. Galat, *J. Amer. Chem. Soc.*, 1950, **72**, 3275.

chromatographed on silica gel. Elution with light petroleum removed unchanged material, and ether eluted the required ester, which was boiled in 10% hydrochloric acid (2 h). Recovery gave material (Found: *m/e* 220.1827. Calc. for $C_{15}H_{24}O$: *M*, 220.1822), τ 5.2br (2 H, s), 8.0br (7 H), 8.33 (3 H, s), and 9.0 (3 H, d), corresponding with (18). Hydrogenation (PtO_2 ; Et_2O) of this material gave a product (Found: *m/e*, 222.1984. Calc. for $C_{15}H_{26}O$: *M*, 222.1904), τ 8.0 (7 H, m), and 9.1br (9 H) with the same retention time on g.l.c. (10 ft silicone SE30) as (20); this product and (20) gave the same 2,4-dinitrophenylhydrazone, m.p. and mixed m.p. 60°, R_F 0.265 on silica gel in light petroleum-ether (5:1).

Synthesis of the Malonate Derivative (7).—The iodide (29) (0.427 g) was added to a hot solution of dimethyl malonate (0.21 g) in methanolic sodium methoxide [sodium (0.03 g) in 25 ml], and the solution was refluxed until neutral (2 h). Recovery gave material (0.256 g) which was chromatographed on silica gel. After elution with light petroleum, elution with benzene-ether (20:1) gave a product identical with (7), R_F 0.43 (silica gel; benzene), *m/e* 268, τ 5.25 (2 H, s), 6.3 (6 H, s), 6.7 (1 H, m), 8.4 (3 H, s), and 9.0 (3 H, d, *J* 6 Hz) (Found: C, 67.5; H, 8.7. Calc. for $C_{15}H_{24}O_4$: C, 67.2; H, 8.9%).

Additions to 7-Methoxy-3,7-dimethyloct-1-ene.—(a) *Acetic acid*. The methoxyoctene (2) (6.42 g) in acetic acid (36 ml) and acetic anhydride (18 ml) with Mn^{III} acetate (8.0 g) was heated at 140 °C for ca. 1 h. Separation of the acidic product (aqueous sodium hydrogen carbonate) gave 9-methoxy-5,9-dimethyldec-3-enoic acid (36), *m/e* 213 (*M* - 15), τ 4.7 (2 H, m), 6.8 (3 H, s), 7.7 (2 H, m), 8.4 (1 H, m), 8.7 (6 H, m), 8.8 (6 H, s), 9.1 (3 H, d), and 1.4 (1 H) (Found: C, 68.6; H, 11.0. $C_{13}H_{24}O_3$ requires C, 68.4; H, 10.6%). 9-Methoxy-5,9-dimethyldecanoic acid, obtained on hydrogenation, showed a similar n.m.r. spectrum lacking the τ 4.7 signal, and yielded a *methyl ester* (Found: *m/e* 244.2040. $C_{14}H_{28}O_3$ requires *M*, 244.2038). Refluxed in benzene with a little toluene-*p*-sulphonic acid (2 h) this ester gave methyl 5,9-dimethyldec-8-enoate (37), *m/e* 212, τ 4.95 (1 H, m), 6.39 (3 H, s), 8.33 (3 H, s), 8.43 (3 H, s), and 9.15 (3 H, d, *J* 6 Hz).

The methoxyoctene-acetic acid reaction also yielded 5-(5-methoxy-1,5-dimethylhexyl)tetrahydrofuran-2-one (35), which was extracted into aqueous sodium hydroxide solution and recovered by acidification; ν_{CO} 1760 cm^{-1} , *m/e* 213 (*M* - 15), τ 5.7 (1 H, m), 6.9 (3 H, s), 7.6 (2 H, m), 8.4br (1H), 8.7br (6 H, s), 8.9 (6 H, s), and 9.1 (3 H, d, *J*

6 Hz) (Found: C, 68.8; H, 10.3. $C_{13}H_{24}O_3$ requires C, 68.4; H, 10.55%).

Toluene-*p*-sulphonic acid in hot benzene (3 h) with the lactone (35) gave 5-(1,5-dimethylhex-4-enyl)tetrahydrofuran-2-one (38), *m/e* 196 (*M* - 15), τ 5.0 (1 H, t), 5.7 (1 H, m), 8.4 (6 H), and 9.1 (3 H, d) (Found: C, 74.0; H, 10.0. $C_{12}H_{20}O_2$ requires C, 73.5; H, 10.2%).

Lithium aluminium hydride in ether reduced the lactone (35) to 9-methoxy-5,9-dimethyldecane-1,4-diol, τ 6.3-6.6 (3 H, m) and 6.9 (3 H, s) (Found: C, 67.05; H, 11.4. $C_{13}H_{28}O_3$ requires C, 67.2; H, 12.0%).

(b) *Acetone*. (i) 10-Methoxy-6,10-dimethylundecan-2-one (10) in benzene with a crystal of toluene-*p*-sulphonic acid gave 6,10-dimethylundec-9-en-2-one (39), *m/e* 194, τ 7.9 (3 H, s), 7.7 (2 H, m), 5.0 (1 H, m), 8.39 (3 H, s), 8.46 (3H, s), and 9.1 (3 H, d, *J* 6 Hz) (Found: C, 79.65, H, 12.35. $C_{13}H_{24}O$ requires C, 79.6; H, 12.25%).

(ii) 10-Methoxy-6,10-dimethylundecan-2-one with sodium borohydride in ethanol gave 10-methoxy-6,10-dimethylundecan-2-ol, *m/e* 215 (*M* - 15), τ 8.8 (3 H, s), 7.5br (1 H), 6.4br (1 H, m), 6.9 (3 H, s), 8.7 (6 H, s), and 9.1 (3 H, d, *J* 6 Hz) (Found: C, 73.2; H, 12.85. $C_{14}H_{30}O_2$ requires C, 73.6; H, 12.4%).

(iii) 7-Methoxy-3,7-dimethyloct-1-ene (3 g) in acetone (25 ml) with Mn^{III} acetate (9.45 g) and Cu^{II} acetate (3.4 g) gave a product from which preparative g.l.c. afforded 10-methoxy-6,10-dimethylundec-5-en-2-one (40), *m/e* 211 (*M* - 15), τ 7.9 (3 H, s), 4.7 (1 H, t), 6.9 (3 H, s), 8.4 (3 H, s), and 8.9 (6 H, s) (Found: C, 74.7; H, 11.4. $C_{14}H_{28}O_2$ requires C, 74.3; H, 11.5%).

(c) *Acetophenone*. 7-Methoxy-3,7-dimethyloct-1-ene (2) with acetophenone (20 g) and Mn^{III} acetate (9.43 g) was heated for 24 h. G.l.c. indicated two products, which were separated by chromatography on alumina. Light petroleum-ether (1:1) eluted 9-methoxy-5,9-dimethyl-1-phenyldecane-1-one (41), *m/e* 275 (*M* - 15), τ 2.2 (2 H, m), 2.7 (3 H, m), 7.2 (2 H, t), 7.0 (3 H, s), 9.0 (6 H, s), and 9.1 (3 H, d), followed by 3,4-dihydro-4-(5-methoxy-1,5-dimethylhexyl)naphthalen-1(2H)-one (42), *m/e* 288 and 273, τ 2.1 (1 H, d), 2.7 (3 H, m), 7.3 (2 H, t), 6.9 (3 H, s), 8.9 (6 H, s), and 9.1 (3 H, d, *J* 6 Hz) (Found: C, 79.65; H, 9.4. $C_{19}H_{28}O_2$ requires C, 79.2; H, 9.75%).

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