Selectivity of Radical Formation in the Reaction of Carbonyl Compounds with Manganese(III) Acetate

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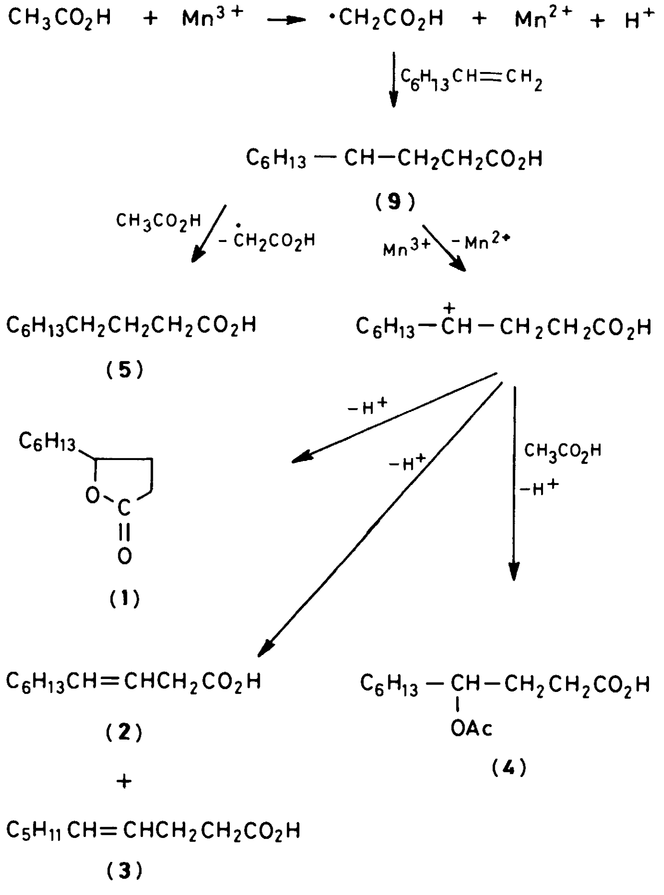
The selectivity of radical generation in the oxidation of carbonyl compounds by manganese(III) has been studied in two ways. Competitive reaction of acetic and propionic acids under conditions in which the resultant radicals are trapped efficiently by an alkene suggests that propionic acid reacts some 3.8 times more readily than does acetic acid. Oxidation of butanone under similar conditions gives products in the formation of which reaction has occurred 2.9 times more readily at C-3 of butanone than at C-1. However, this ratio reflects a combination of chain propagation and of initiation by manganese(III) oxidation. When propagation is effectively eliminated, the C-1 position is the more reactive. The significance of these observations on the mechanism of oxidation of carbonyl compounds by manganese(III) is discussed. It is suggested that enol radical-cations can be formed in the reaction but that these do not give carbonyl-stabilised radicals by deprotonation.

Recently we reported the influence of a number of reaction parameters on the product distribution in the reaction, catalysed by manganese(III) salts, of an alkene with acetic acid derivatives under an inert atmosphere.[1] The most important factor is solvent composition. We found, using oct-1-ene as the trap, that, in acetic acid, the lactone (**1**) is virtually the sole product but inclusion of limited amounts of acetic anhydride in the solvent leads to a switch to unsaturated acids (**2**) and (**3**) and the acetoxy-substituted acid (**4**) whilst the use of anhydride alone results in decanoic acid (**5**) as the major product. The yield of this last product can be improved greatly by maintaining very low concentrations of manganese(III) during the reaction.

All the products are accountable in terms of addition to the alkene of a carboxy-substituted methyl radical derived from acetic acid or its anhydride (*e.g.* Scheme 1),[1–3] but the means by which this radical is formed are unclear. One route, observed with some other one-electron oxidants, is the decarboxylation of the acid followed by hydrogen abstraction from a second molecule of acid by the resultant methyl radical (Scheme 2).[4] However, such a sequence is inconsistent with the low yields of methane relative to other products when manganese(III) acetate and acetic acid react alone[5] and with the reaction not being confined to carboxylic acids but occurring also with anhydrides[5,6] (which might contain some acid), ketones,[7,8] aldehydes,[9,10] and esters,[8,11,12] none of which would be expected to undergo processes akin to decarboxylation.

Other suggestions have included a concerted mechanism,[13] the intermediacy of a manganese–enolate complex,[14] and a proposal involving acetoxyl radicals stabilised within a manganese(III) complex.[6] Perhaps the most plausible idea has been that reaction occurs, not on the acid itself, but on an enol tautomer of the acid,[2] even though evidence for the existence of such a species is lacking. Certainly the rates of reactions of ketones and aldehydes with manganese(III) correlate well with the rates of enolisation of these carbonyl compounds and are independent of the metal ion concentration.[7,15]

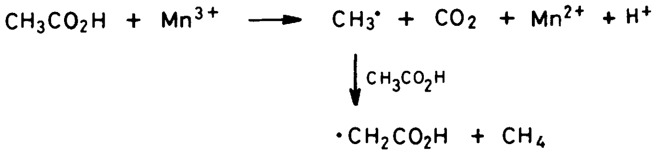
In an attempt to clarify the mode by which carbonyl-stabilised radicals are formed in reactions of manganese(III) with carbonyl compounds we investigated the effect of structure in the carbonyl substrate on its ability to react with an alkene in the presence of manganese(III). The results are reported in this paper.



Scheme 1.

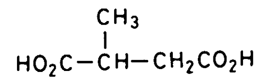
Results and Discussion

An ideal substrate for study would be one possessing two sites at which reaction could occur. Unfortunately, dicarboxylic acids, such as methylsuccinic acid (**6**), and their anhydrides, have relatively high melting points and poor solvent properties



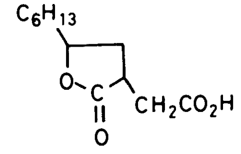
Scheme 2.

toward manganese(III) salts. Despite the report that, using acetic acid as co-solvent, lactone (**7**) is obtained from succinic acid itself and oct-1-ene,[2] we were unable to detect any oxidation product from methylsuccinic acid under similar conditions though some γ-decanolactone (**1**) (from the acetic acid co-solvent) was formed.

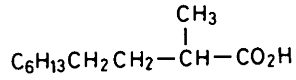


$HO_2C-\overset{\overset{CH_3}{|}}{C}H-CH_2CO_2H$

(**6**)



(**7**)



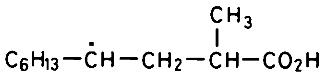
$C_6H_{13}CH_2CH_2-\overset{\overset{CH_3}{|}}{C}H-CO_2H$

(**8**)

Instead we used a mixture of propionic and acetic acids, reaction conditions being chosen [dropwise addition of a solution of manganese(III) acetate in mixed acid to a solution of oct-1-ene in mixed anhydride] such that only a single type of product, the saturated acids, was formed in significant amount. A trial experiment demonstrated that propionic acid and anhydride together gave a yield of 2-methyldecanoic acid (**8**) similar to that of decanoic acid from the acetic system:[1] no undecanoic acid, the product of reaction at C-3 of propionic acid, was formed. However under competitive conditions using equimolar quantities of the two acids and of the two anhydrides the yield of (**8**) was 3.8 times that of (**5**), demonstrating that a methyl substituent at C-2 facilitates reaction. Other products, resulting from oxidation of initial adduct radicals, were present in only trace quantities.

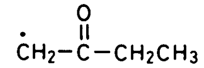
There is one flaw in the foregoing argument that manganese(III) reacts more readily at a site possessing a methyl substituent. The conditions chosen to simplify the range of potential products are such that oxidation is catalytic in manganese(III) (yields are *ca.* 250% based on the metal oxidant[1]). The ratio therefore reflects a combination of the selectivity of initiation by the metal ion and of propagation by the chain-carrying species, carbonyl-substituted radicals such as (**9**). Propagation will be the major contributor to the ratio and, indeed, simple alkyl radicals, which ought to be acceptable models for (**9**) and (**10**), show nucleophilic tendencies on reaction with carboxylic acids, undergoing selective abstraction from the site adjacent to the carbonyl function and reacting more readily with propionic than with acetic acid.[16,17] If conditions are chosen so as to inhibit chain propagation and so provide information on the initiation step, the large number of products makes accurate quantification by gas chromatography impossible. We thus turned our attention to a related system, the manganese(III)-catalysed addition to alkenes of a ketone possessing two potential sites of reaction.

Acetone, when oxidised by manganese(III) in the presence of oct-1-ene, reacts in a similar way to acetic acid.[7] Butanone should thus provide information on the selectivity of manganese(III) toward ketones. Two contradictory reports on related studies have appeared. In one, when alkene was not included as a radical trap, a mixture of 1- and 3-acetoxybutanones was obtained in a ratio of 2.5:1 suggesting that an electron-donating methyl group inhibits reaction at a site adjacent to a carbonyl function.[18] The other,[19] whilst employing alkene, included copper(II) in the system, presumably in order that alkyl radicals would be oxidised readily and hydrogen abstraction precluded. The selectivity found was the opposite of that reported by Okano *et al.* Reaction at C-3 of butanone was favoured over reaction at C-1 by a factor of 4:1. Now copper(II) is a very effective oxidant of carbon-centred radicals even when they possess strongly electron-withdrawing groups.[20] The initial radicals might therefore be oxidised rather than being trapped by the alkene. If the rates of oxidation of (**11**) and (**12**) differ the ratio of adducts would not reflect the relative ease of formation of the two radicals.



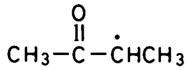
$C_6H_{13}-\dot{C}H-CH_2-\overset{\overset{CH_3}{|}}{C}H-CO_2H$

(**10**)



$\dot{C}H_2-\overset{\overset{O}{\|}}{C}-CH_2CH_3$

(**11**)



$CH_3-\overset{\overset{O}{\|}}{C}-\dot{C}HCH_3$

(**12**)

When we oxidised butanone under conditions similar to those used by Heiba *et al.* for acetone[7] we obtained a complex mixture of products which were identified as the saturated ketones (**13**) and (**14**), the acetoxy ketones (**15**)* and (**16**), and the unsaturated ketones (**17**)—(**20**). The diketones (**21**)* and (**22**), which arise from reactions not involving the alkene, were also present. Similar products have been noted before when alkene has been absent but not previously when a trap has been present.

Now the reaction system includes substantial amounts of potassium acetate, which accelerates the addition but has the drawback that the proportion of saturated adducts is increased.[1] Indeed lower concentrations of potassium acetate reduce the yields of saturated ketones whilst those of the other alkene adducts rise (Table 1). As we have already argued in the case of acids, high yields of the former adducts favour chain propagation as the source of radicals (**11**) and (**12**) and thus mask the selectivity of of radical formation by manganese(III). Table 1 shows a marked change in selectivity in the three reactions. At high acetate concentration products derived from the more substituted radical (**12**) predominate over those from (**11**), but as chain propagation is suppressed so formation of (**11**) is favoured. Thus we conclude that alkyl radicals form selectively (**12**) from butanone but oxidation of the ketone by manganese(III) produces preferentially (**11**).

Now the correct ratio of α-oxo radicals formed by reaction of manganese(III) will be obtained when the adduct radicals are absent. Even in the absence of potassium acetate this condition is not met but plotting the collective yield of saturated ketones in Table 1 against the total selectivity and extrapolating to a zero yield, when propagation must be non-existent, gives a ratio of products derived from (**12**) *versus* those derived from (**11**) of *ca.* 0.4:1, *i.e.* $\cdot CH_2COC_2H_5$ is formed some two and a half times as readily as is $CH_3CO\dot{C}HCH_3$. This agrees well with the ratio of acetoxybutanones obtained by Okano when alkene was omitted.[18]

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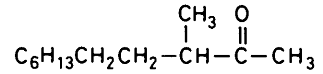
* The two diastereoisomers of this compound were present in the ratio of *ca.* 1:1.

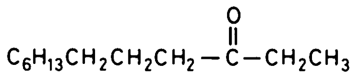
Table 1. Products from the reaction of manganese(III) acetate with butanone and oct-1-ene in acetic acid at 80 °C

[KOAc]/ mol dm^{-3}	Oct-1-ene conversion (%)	Products (% based on alkene)							Product ratio		
		(13)	(14)	(15)[a]	(16)	(17) + (18)	(19) + (20)	(21)[a] + (22)	(13)/(14)	(15)/(16)	(17) + (18)/(19) + (20)
2.5	33	18.5	6.4	3.2	3.0	1.4	0.7	9.2	2.9	1.1	2.0
0.8	35	13.5	7.7	5.6	5.8	1.5	0.8	14.3	1.8	0.97	1.9
0	35	6.2	7.4	5.9	9.9	3.3	2.5	26.5	0.8	0.60	1.3

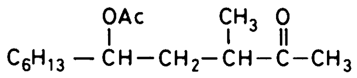
[a] Ratio of diastereoisomers *ca.* 1:1.


$C_6H_{13}CH_2CH_2-\overset{CH_3}{\overset{|}{CH}}-\overset{O}{\overset{\|}{C}}-CH_3$

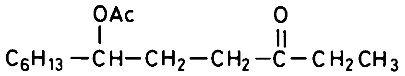
(13)


$C_6H_{13}CH_2CH_2CH_2-\overset{O}{\overset{\|}{C}}-CH_2CH_3$

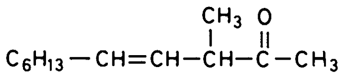
(14)


$C_6H_{13}-\overset{OAc}{\overset{|}{CH}}-CH_2-\overset{CH_3}{\overset{|}{CH}}-\overset{O}{\overset{\|}{C}}-CH_3$

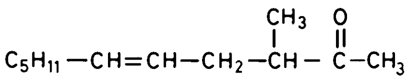
(15)


$C_6H_{13}-\overset{OAc}{\overset{|}{CH}}-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-CH_2CH_3$

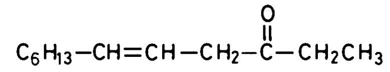
(16)


$C_6H_{13}-CH=CH-\overset{CH_3}{\overset{|}{CH}}-\overset{O}{\overset{\|}{C}}-CH_3$

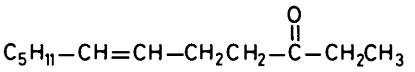
(17)


$C_5H_{11}-CH=CH-CH_2-\overset{CH_3}{\overset{|}{CH}}-\overset{O}{\overset{\|}{C}}-CH_3$

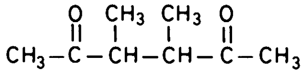
(18)


$C_6H_{13}-CH=CH-CH_2-\overset{O}{\overset{\|}{C}}-CH_2CH_3$

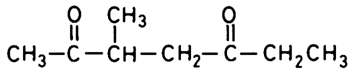
(19)


$C_5H_{11}-CH=CH-CH_2CH_2-\overset{O}{\overset{\|}{C}}-CH_2CH_3$

(20)

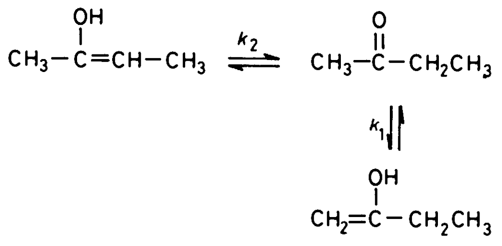

$CH_3-\overset{O}{\overset{\|}{C}}-\overset{CH_3}{\overset{|}{CH}}-\overset{CH_3}{\overset{|}{CH}}-\overset{O}{\overset{\|}{C}}-CH_3$

(21)

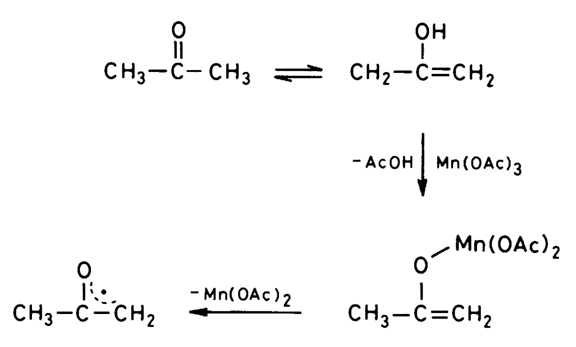

$CH_3-\overset{O}{\overset{\|}{C}}-\overset{CH_3}{\overset{|}{CH}}-CH_2-\overset{O}{\overset{\|}{C}}-CH_2CH_3$

(22)

The same regioselectivity is not shown in the formation of diketones. In none of the reactions was octane-3,6-dione found (0.3% would have been detected). The principal components of this type were the two diastereoisomers of (**21**). A third compound, unresolved by g.l.c. from one of the isomers of (**21**), was tenatatively identified as the unsymmetrical diketone (**22**) on the basis of ions in the mass spectrum of the inhomogeneous g.l.c. peaks at *m/z* 57 ($EtCO^+$) and 113 (*M* − Et) which were absent from the spectrum of the second isomer of (**21**). There were also signals in the ^{13}C n.m.r. spectrum of the mixture, isolated by preparative g.l.c., at 45.1 and 235.2 p.p.m. Whilst the amount of (**22**) could not be quantified it was small compared with that of (**21**).



Scheme 3.



Scheme 4.

Enolisation is said to be the rate-determining step in the generation of radicals from ketones by manganese(III).[15] Whilst for butanone such a rate is a composite of two processes (Scheme 3) and does not provide information on regioselectivity in the system, the ratio $k_1:k_2$ has been determined, in water, to be about 1:1.[21] If conversion of enols into products is indeed rapid compared with their rates of formation the ratio of products derived from (**11**) to those from (**12**) should also be about 1:1, as is found, for instance, in the bromination of butanone,[22] a process known to involve slow rate-determining enolisation. Our results then would imply that enolisation cannot be rate-determining in the manganese(III) oxidation.

An enol might still be the reactive entity rather than the ketone itself if the slow step follows enolisation. Thus slow decomposition of an enol–manganese(III) complex[14] could lead to carbonyl-stabilised radicals (*e.g.* Scheme 4), the proportions of (**11**) and (**12**) being dependent either on the relative rates of complex formation or on the rates of destruction. Of the other suggestions for initiation, steric factors might favour hydrogen transfer in a concerted process[13] from the less crowded site, *i.e.* lead to preferential formation of (**11**), but a mechanism involving acetoxyl radicals[6] could not explain the selectivity observed. Hydrogen abstraction by oxygen-centred radicals not only occurs more readily from a methylene group than from an analogous methyl group[23] but also favours sites distant from the carbonyl function.[24]

In a recent paper we demonstrated that one-electron metal oxidants can effect electron-transfer from alkenes of sufficiently low ionization potential.[25] With manganese(III) acetate in acetic acid, radical-cations are formed when this potential is less than *ca.* 8.5 eV. Now, whilst ionisation potentials of enols are obviously not available, those of enol ethers, which should be suitable models for enols, are low enough to suggest that electron transfer is a possibility (Table 2).[26,27] From the values for phenol and anisole the ionisation potential of an enol should lie above that of the corresponding ether by *ca.* 0.25 eV and, whilst the ionisation potentials of 2-alkoxybutenes have not been determined, a figure of about 8.5 eV for butenols would not be unreasonable. Proton loss by a radical-cation could then give a carbonyl-stabilised radical (*e.g.* Scheme 5).

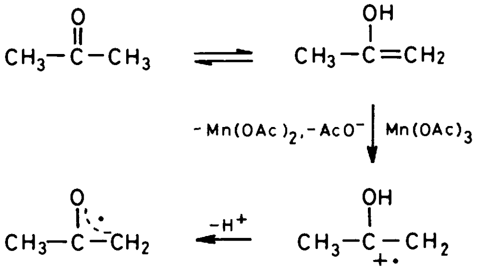
Unfortunately for this argument, the radical (**12**) might be expected to form more readily than (**11**) since the ionisation potential of but-2-en-2-ol should be lower than that of but-1-en-2-ol.[28] The reverse seems to be true. In contrast the relative amounts of diketones are consistent with the view that but-2-en-2-ol undergoes electron transfer more readily than but-1-en-2-ol. Nucleophilic attack on the predominant but-2-en-2-ol radical-cation by un-ionised enol molecules would then lead to the preferential formation of (**21**) with some (**22**) and little octane-3,6-dione (Scheme 6).

An alternative route for formation of dimeric products from ketones, the simple combination of the carbonyl-stabilised radicals (**11**) and (**12**), seems to us unable to explain the product distribution on its own. Given the relatively slow consumption of the oxidant (> 1 h) the concentration of (**11**) and (**12**) should be very low. It is therefore unlikely that such a high yield of dimers could result from radical–radical coupling. In addition, since radical dimerisation is diffusion-controlled, the ratios (**21**):(**22**):octane-3,6-dione would provide a measure of the relative concentrations of (**11**) and (**12**). From the results we obtained this would be at least 1 : 10. To account for the ratio of products obtained from the trapping of the two radicals by oct-1-ene requires then that (**11**) reacts with the alkene at least 13 times more rapidly than does (**12**). Given the similar natures of the two species we believe this value to be excessively large.

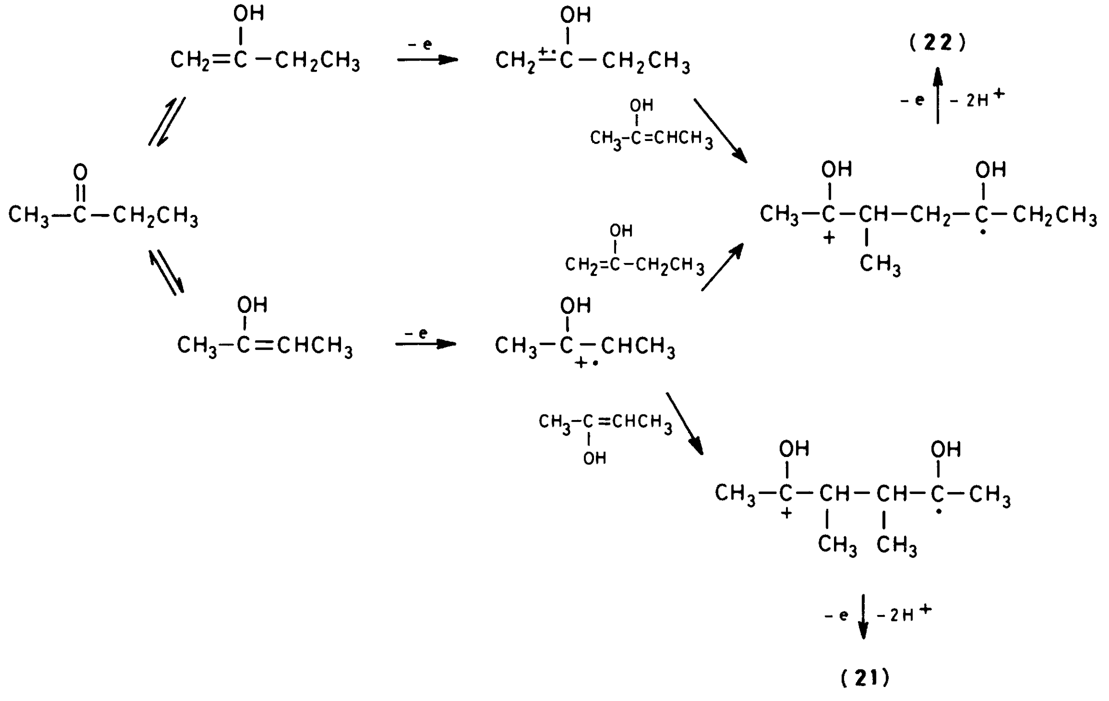
We believe then that the enolic forms of ketones can produce radical-cations under the reaction conditions. The majority of, if not all, diketonic product is likely to arise by this route. However, the selectivity observed in the generation of carbonyl-stabilised radicals from butanone when initiation predominates is not consistent with their precursor being a radical-cation, though none of the alternative proposals for radical formation

Table 2. Ionisation potentials of some compounds related to enols

Compound	I.P. (eV)	Ref.
PhOH	8.50	26
PhOMe	8.22	26
$CH_2=CH-OCH_3$	8.93	26
$CH_2=CH-OC_2H_5$	8.95	27
$CH_3-CH=CH-OC_2H_5$	8.47	27
$(CH_3)_2C=CH-OC_2H_5$	8.04	27



Scheme 5.



Scheme 6.

offers a fully acceptable explanation of the selectivity. If electron transfer is significant in the oxidation of ketones, then carboxylic acids and their derivatives, which give similar products, would also have to undergo tautomerisation. Whilst such a process is not excluded theoretically and has been widely cited in standard texts (*e.g.* ref. 29), we are not aware of direct evidence for the formation of 'enol' forms of such compounds in solution.

Experimental

The general procedures employed for oxidation and for analysis have been described previously[1] as have the preparations of some of the materials. Propionic acid and anhydride (B.D.H.) were distilled before use whilst butanone (B.D.H. AnalaR reagent) was used without further purification.

Methylsuccinic Acid.—This acid was made by a standard method[30] and had m.p. 108—109 °C (from chloroform) (lit.,[30] 110—111 °C).

Methylsuccinic Anhydride.—A mixture of methylsuccinic acid (40 g) and acetyl chloride (70 cm^3) was refluxed gently on a steam-bath for 2.5 h. After acetic acid and excess of acetyl chloride were removed under reduced pressure, the residue was distilled to give methylsuccinic anhydride (30.5 g, 88%) as a colourless viscous oil, b.p. 91—93 °C at 0.3 mmHg; m.p. 30—32 °C (lit.,[31] 33 °C); δ_H 3.5—2.5 (3 H, m, $COCH_2CHCO$) and 1.27 (3 H, t, *J* 6.5 Hz, CH_3).

2-*Methyldecanoic Acid*.—To a solution of sodium (6 g) in dry butan-1-ol (140 cm^3) maintained at 70—80 °C was added rapidly diethyl methylmalonate (45.4 g). 1-Bromo-octane (51.3 g) was then added at such a rate that the solution boiled gently and the mixture was then heated for 5 h under reflux. Excess of alcohol was removed by distillation; the crude ester was refluxed with sodium hydroxide solution [44 g of hydroxide in water (35 cm^3)], the acid was liberated by addition of concentrated hydrochloric acid (150 cm^3), and the mixture was extracted with diethyl ether. The extracts were washed with dilute hydrochloric acid, dried ($MgSO_4$), and evaporated, and the residue was decarboxylated by heating at 200 °C for 6 h. Distillation of the black oil gave 2-methyldecanoic acid (31.2 g, 64%) as a colourless liquid, b.p. 105—106 °C at 0.3 mmHg (lit.,[31] 137—139 °C at 14 mmHg); δ_H 11.65 (1 H, s removed by D_2O, CO_2H), 2.42 (1 H, q of t, $J = J' = 7$ Hz, CHCO), and 1.6—0.7 (20 H, aliphatic envelope).

Dodecan-3-*one*.—Phosphorus tribomide (35 g) was added to nonan-1-ol (50 g) cooled to −10 °C at such a rate that the temperature of the mixture remained below −4 °C. After 3 h the mixture was allowed to warm to room temperature and left overnight. The resulting liquid was distilled; the fraction of b.p. 63—64 °C at 1.8 mmHg was washed with ice-cold concentrated sulphuric acid (3 × 5 cm^3) and finally shaken with solid potassium carbonate. Distillation gave 1-bromononane (37.4 g, 52%) as a colourless liquid, b.p. 73—74 °C at 3.5 mmHg (lit.,[31] 93—97 °C at 13 mmHg); δ_H 3.37 (2 H, t, *J* 6.5 Hz, CH_2Br), 1.82 (2 H, quintet, *J* 7 Hz, CH_2CH_2Br), and 1.56—0.6 (15 H, aliphatic envelope).

The Grignard reagent prepared from 1-bromononane (18 g) and magnesium (2.2 g) in dry diethyl ether (85 cm^3) was added dropwise to a solution of propionic anhydride (23 cm^3) in dry diethyl ether (50 cm^3) at −70 °C under nitrogen over 1.5 h, after which the solution was stirred for 2 h at −70 °C and finally overnight at room temperature. Saturated aqueous ammonium chloride (50 cm^3) was added; the ether layer was separated, the aqueous layer was extracted with more ether, and the combined extracts were washed with water and dried ($MgSO_4$). Removal of the solvent and distillation of the residue gave dodecan-3-one (10.1 g, 83%) as a colourless liquid, b.p. 87—89 °C at 1 mmHg (lit.,[32] 134 °C at 18 mmHg); δ_H 2.70—2.15 (4 H, m, CH_2COCH_2), and 1.75—0.65 (20 H, aliphatic envelope); *m/z* 184 (2.6%, $M^{+\cdot}$), 155 (27, *M* − Et), 85 (26, $C_5H_9O^+$ and/or $C_6H_{13}^+$), 73 (28, $C_4H_9O^+$), 72 (100, $C_4H_8O^{+\cdot}$), 71 (28, $C_4H_7O^+$), 57 (69, $EtCO^+$), 55 (20, $C_4H_7^+$), 43 (50, $C_3H_7^+$), and 41 (31, $C_3H_5^+$).

3-*Methylundecan*-2-*one*.—2-Bromodecane was prepared in similar manner to 1-bromononane using decan-2-ol as substrate in a yield of 64% and had b.p. 68—70 °C at 1.5 mmHg (lit.,[33] 111 °C at 11 mmHg), δ_H 4.08 (1 H, quintet, *J* 7 Hz, CHBr), 1.67 (5 H, d, *J* 7 Hz, and m, $CH_2CHBrCH_3$), and 1.40—0.65 (15 H, aliphatic envelope). A Grignard reagent was prepared from 2-bromodecane (5.2 g) and magnesium (0.61 g) in diethyl ether (35 cm^3) and added dropwise to acetic anhydride [6 cm^3 in diethyl ether (15 cm^3)] in the way described for the synthesis of dodecan-3-one. Work-up in the same manner gave, on distillation, a fraction (0.83 g), b.p. 70—72 °C at 1.0 mmHg. Gas chromatographic analysis showed this to be a mixture of unchanged 2-bromodecane and 3-methylundecan-2-one (*ca.* 3:2). From this was isolated by preparative g.l.c. 3-methylundecan-2-one, δ_H 2.13 (4 H, s and m, $CHCOCH_3$) and 1.5—0.65 (20 H, aliphatic envelope); *m/z* 184 (0.9%, $M^{+\cdot}$), 141 (2, *M* − CH_3CO), 72 (100, $C_4H_8O^{+\cdot}$), 71 (8, $CH_3COCHCH_3^+$), 57 (20, $C_3H_5O^+$ and/or $C_4H_9^+$), 55 (11, $C_4H_7^+$), 43 (34, CH_3CO^+ and $C_3H_7^+$), and 41 (17, $C_3H_5^+$).

(E)-*Dodec*-6-*en*-3-*one*.—(*E*)-Dec-4-enoyl chloride, prepared from (*E*)-dec-4-enoic acid by the method of Ireland *et al.*,[34] had b.p. 67—68 °C at 0.8 mmHg (lit.,[34] 50—55 °C at 0.05 mmHg). To a solution of the acid chloride (2.0 g) in benzene (15 cm^3) cooled at 0 °C was added a solution of diethylcadmium in benzene [prepared from bromoethane (1.5 g) and magnesium (0.32 g) in diethyl ether (20 cm^3) to which anhydrous cadmium chloride (1.30 g) had been added; the ether was then replaced by benzene as solvent]. The mixture was warmed and stirred at 35 °C for 2 h. Sulphuric acid (20 cm^3; 0.5 mol dm^{-3}) was added, the mixture was stirred for 10 min; the benzene layer was separated, and the aqueous layer extracted with more benzene. The combined extracts were washed with sodium carbonate solution and water, dried ($MgSO_4$), and evaporated. Gas chromatography–mass spectrometry showed the product to contain two components, ethyl (*E*)-dec-4-enoate and (*E*)-dodec-6-en-3-one. The ester was removed by stirring the product with a solution of potassium hydroxide (2.8 g) in 1:1 ethanol–water (50 cm^3) at 100 °C for 5 h. Extraction of the cooled solution with ether gave (E)-*dodec*-6-*en*-3-*one* (0.73 g), which was purified by preparative gas chromatography; δ_H 5.6—5.3 (2 H, m, HC=CH), 2.6—2.1 (6 H, m, CH_2COCH_2-CH_2C=), 2.1—1.8 (2 H, m, H_2CCH=), and 1.5—0.8 (12 H, aliphatic envelope); *m/z* 182 (2.4%, $M^{+\cdot}$), 153 (2.4, *M* − Et), 125 (1.4, *M* − Et − CO). 111 (4, *M* − C_5H_{11} and/or $C_8H_{15}^+$), 110 (6, $C_8H_{14}^{+\cdot}$), 81 (6, $C_6H_9^+$), 69 (16, $C_5H_9^+$), 57 (100, $EtCO^+$ and C_4H_9), 55 (18, $C_4H_7^+$), and 41 (21, $C_3H_5^+$) (Found: C, 78.4; H, 12.0. $C_{12}H_{22}O$ requires C, 79.1; H, 12.1%).

Octane-3,6-*dione*.—This compound was prepared using the method developed by Larcheveque *et al.* for the synthesis of 1,4-diketones.[35] A mixture obtained from diethylamine (2.68 g), hexamethylphosphoramide (8 cm^3), dry benzene (7.5 cm^3), and fresh lithium wire (0.26 g) was stirred under nitrogen until the metal had completely dissolved. The temperature of the mixture was maintained at 20 °C while dry tetrahydrofuran (10 cm^3) was added to the dark red solution; the mixture was then cooled to −30 °C and a solution of 2-(*N*-cyclohexyl)iminobutane (5.1

g) in tetrahydrofuran (10 cm^3) was added slowly with stirring. The solution was then kept for 1 h at -5 °C. 1,2-Epoxybutane (2.54 g) was added dropwise at -15 °C, and the mixture kept at room temperature for 4 h. The solution was poured into water and extracted with ether; the extracts were washed with dilute hydrochloric acid and dried ($MgSO_4$). Removal of the solvent left crude 6-hydroxyoctan-3-one (1 g, 21%), which was oxidised without purification using sodium dichromate (0.6 g) in water (3 cm^3) containing concentrated sulphuric acid (0.64 g). Preparative g.l.c. afforded octane-3,6-dione, m.p. 29—31 °C (lit.,[31] 34—35 °C); δ_H 2.70 (4 H, s, $COCH_2CH_2CO$), 2.48 (4 H, q, J 7.5 Hz, CH_2CH_3), and 1.05 (6 H, t, J 7.5 Hz, CH_3CH_2); m/z 142 (1.1, $M^{+\cdot}$), 113 (100, $M - C_2H_5$), 95 (9, $M - C_2H_5 - H_2O$), 85 (14, $M - C_2H_5 - CO$), and 57 (92, $EtCO^+$).

Reaction of Oct-1-ene with Manganese(III) *Acetate Dihydrate*.—(a) *In the presence of acids*. The reaction of manganese(III) acetate with oct-1-ene in methylsuccinic acid was carried out as described by Heiba and Dessau for succinic acid.[2] A mixture of methylsuccinic acid (39.2 g), acetic acid (15 cm^3), potassium acetate (2 g), oct-1-ene (0.75 g), and manganese(III) acetate dihydrate (2.7 g) was heated under nitrogen at reflux for 1.5 h, during which time the brown colour of manganese(III) was discharged (*ca.* 20 min). The product mixture was stirred with water (150 cm^3) and extracted with several portions of ether. The combined extracts were washed with water, dried, and evaporated to give a dark oil (0.5 g), which was methylated as described previously[1] before analysis by gas chromatography.

In determining the selectivity of formation of radicals at low concentrations of manganese(III), the following solvent mixtures were employed: (i) acetic acid (6.01 g) and propionic acid (7.41 g), (ii) acetic anhydride (30.63 g) and propionic anhydride (39.05 g). A solution of manganese(III) acetate dihydrate (0.168 g) in a mixture of the acids (5 cm^3) diluted with the anhydride mixture (5 cm^3) was added dropwise to a stirred solution of oct-1-ene (0.7 g) in the anhydride solvent mixture (50 cm^3). The conditions and work-up procedure were the same as those used previously.[1]

(b) *In the presence of butanone or acetone*. To a mixture of manganese(III) acetate dihydrate (4.02 g), acetone (11.6 g) or butanone (14.4 g), and acetic acid (40 cm^3) was added a requisite amount of oven-dried potassium acetate. The apparatus was flushed with nitrogen and the stirred mixture warmed on a water-bath at 80 °C for 3—4 min, until a dark-brown homogeneous solution was obtained.* Oct-1-ene (0.86 g) was then added, and the mixture stirred for a further 1.25 h, until all the oxidant had been consumed. The solution was cooled, and most of the solvent removed by evaporation. Water was added to the residue, and the mixture extracted with several portions of diethyl ether. The combined extracts were washed with sodium carbonate solution and water, and dried ($MgSO_4$). Removal of the solvent afforded a viscous yellow oil, which was analysed directly by gas chromatography. In one reaction with butanone, low concentrations of oxidant were maintained by dropwise addition of a solution of manganese(III) acetate (0.67 g, 0.5 mol equiv.) in acetic acid (25 cm^3) to a solution of oct-1-ene (0.56 g) in butanone (50 cm^3). After 2.5 h the product was isolated in the usual way.

From one reaction was isolated by preparative gas chromatography a sample of one of the diastereoisomers of 3,4-dimethylhexane-2,5-dione; δ_H 3.16—2.70 (2 H, m, CHCO), 2.20 (6 H, s, CH_3CO), and 1.10 (6 H, d, CH_3CH); δ (^{13}C) 212.2 (CO), 48.45 (CHCO), 28.73 (CH_3CO), and 13.80 (CH_3CH); m/z 142 (2.4%, $M^{+\cdot}$), 100 (25, $M - CH_2CO$), 85 (40, $M - CH_2CO - CH_3$), 72 (6, $C_4H_8O^{+\cdot}$), and 43 (100, CH_3CO^+) (Found: C, 67.4; H, 10.1. $C_8H_{14}O_2$ requires C, 67.6; H, 9.9%).

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References

1 G. Midgley and C. B. Thomas, *J. Chem. Soc., Perkin Trans. 2*, 1984, 1537.
2 E. I. Heiba, R. M. Dessau, and P. G. Rodewald, *J. Am. Chem. Soc.*, 1974, **96**, 7977.
3 W. J. de Klein, *Recl. Trav. Chim. Pays-Bas*, 1975, **94**, 48.
4 J. M. Anderson and J. K. Kochi, *J. Am. Chem. Soc.*, 1970, **92**, 2450.
5 W. J. de Klein, *Recl. Trav. Chim. Pays-Bas*, 1977, **96**, 22.
6 M. Okano, *Bull. Chem. Soc. Jpn.*, 1976, **49**, 1041.
7 E. I. Heiba and R. M. Dessau, *J. Am. Chem. Soc.*, 1971, **93**, 524.
8 F. J. McQuillin and M. Wood, *J. Chem. Soc., Perkin Trans. 1*, 1976, 1762.
9 G. I. Nikishin, M. G. Vinogradov, S. P. Verenchikov, I. N. Kostyukov, and R. V. Kereselidze, *Zh. Org. Khim.*, 1972, **8**, 539.
10 G. I. Nikishin, M. G. Vinogradov, and G. P. Il'ina, *Zh. Org. Khim.*, 1972, **8**, 1404.
11 F. J. McQuillin and M. Wood, *J. Chem. Res.*, 1977, (*S*) 61; (*M*), 0752.
12 G. I. Nikishin, M. G. Vinogradov, and T. M. Fedorova, *J. Chem. Soc., Chem. Commun.*, 1973, 693.
13 R. Van der Ploeg, R. W. de Korte, and E. C. Kooyman, *J. Catal.*, 1968, **10**, 52.
14 J. B. Bush and H. Finkbeiner, *J. Am. Chem. Soc.*, 1968, **90**, 5903.
15 Y. Yamiya and M. Kotake, *Bull. Chem. Soc. Jpn.*, 1973, **46**, 2780.
16 B. C. Gilbert, R. O. C. Norman, G. Placucci, and R. C. Sealey, *J. Chem. Soc., Perkin Trans. 2*, 1975, 885.
17 M. J. Davies, B. C. Gilbert, C. B. Thomas, and J. Young, *J. Chem. Soc., Perkin Trans. 2*, 1985, 1199.
18 M. Okano and T. Aratoni, *Bull. Chem. Soc. Jpn.*, 1976, **49**, 2811.
19 M. G. Vinogradov, S. P. Verenchikov, T. M. Fedorova, and G. I. Nikishin, *Zh. Org. Khim.*, 1975, **11**, 947.
20 J. K. Kochi and D. M. Mog, *J. Am. Chem. Soc.*, 1965, **87**, 522.
21 J. Warkentin and O. S. Tee, *J. Am. Chem. Soc.*, 1966, **88**, 5540; A. A. Bothner-By and C. Sun, *J. Org. Chem.*, 1967, **32**, 492.
22 J. W. Thorpe and J. Warkentin, *Can. J. Chem.*, 1972, **50**, 3229.
23 B. C. Gilbert, R. O. C. Norman, G. Placucci, and R. C. Sealy, *J. Chem. Soc., Perkin Trans. 2*, 1975, 885.
24 B. C. Gilbert, R. O. C. Norman, and R. C. Sealy, *J. Chem. Soc., Perkin Trans. 2*, 1973, 2174.
25 J. A. Norman, C. B. Thomas, and M. J. Burrow, *J. Chem. Soc., Perkin Trans. 1*, 1985, 1087.
26 K. Watanabe, T. Nakayama, and J. Mottl, *J. Quant. Spectrosc. Radiat. Transfer*, 1961, **2**, 369.
27 R. Huisgen and H. Mayr, *Tetrahedron Lett.*, 1975, 2965.
28 J. L. Holmes and F. P. Lossing, *J. Am. Chem. Soc.*, 1980, **102**, 1591.
29 J. March, 'Advanced Organic Chemistry,' McGraw-Hill, New York, 1985, 3rd edn., p. 531.
30 G. B. Brown, *Org. Synth.*, 1955, **3**, 615.
31 'Dictionary of Organic Compounds,' 5th edn., ed. J. Buckingham, Chapman and Hall, New York, 1982.
32 D. Savoia, C. Trombini, and A. Umani-Ronchi, *J. Org. Chem.*, 1978, **43**, 2907.
33 F. S. Prout, J. Cason, and A. W. Ingersoll, *J. Am. Chem. Soc.*, 1948, **70**, 298.
34 R. E. Ireland, R. H. Mueller, and A. K. Willard, *J. Org. Chem.*, 1976, **41**, 986.
35 M. Larcheveque, G. Vallette, T. Cuvigny, and H. Normant, *Synthesis*, 1975, 256.

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* A check experiment demonstrated that a minimal amount of dimer (*ca.* 0.3%) was formed during this period.