Factors governing Product Distribution in the Oxidation of Alkenes by Manganese(III) Acetate in Acetic Acid and Acetic Anhydride

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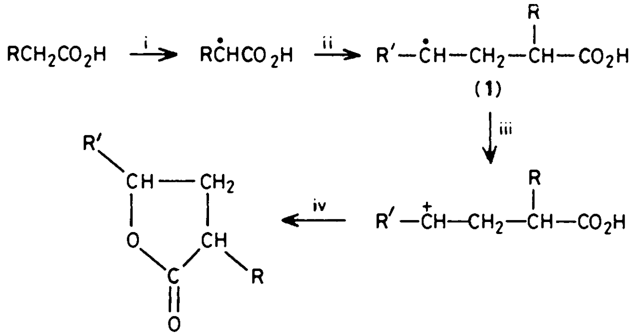
A systematic investigation has been carried out into the effect of different reaction parameters on the oxidation of oct-1-ene by manganese(III) acetate in acetic acid and acetic anhydride. The most important factor in dictating the ratio of products is the composition of the solvent. In the absence of anhydride γ-decanolactone is virtually the sole product. Even small quantitites of anhydride lead to the lactone being replaced by other products derived from cationic intermediates $C_6H_{13}\overset{+}{C}HCH_2COX$ (X = OH or OAc). Further increases in the amount of anhydride encourage the formation of decanoic acid until, in 90% anhydride, this becomes the predominant product. The results cannot be interpreted simply in terms of competition for the alkene by the radicals $\cdot CH_2CO_2H$ and $\cdot CH_2COOCOCH_3$. Decanoic acid formation is also favoured by low temperatures, low concentration of oxidants, and by the addition of acetate ions. A comparision is made of the efficiency of addition when the initiating species is manganese(III) or a peroxide.

The last 30 years have seen a great deal of attention focused on the oxidation of alkenes by metal ions. So fruitful have these investigations proved that many procedures based on such reactions are now of synthetic importance. From this large corpus of work it is apparent that, whilst many metal oxidants can function in more than one way, four general categories of oxidant can be identified: (i) ions which show a propensity for electrophilic attack on alkenes coupled with the ability to undergo a subsequent two-electron reduction; (ii) ions which, with organic substrates of relatively low ionization potential, are capable of undergoing a non-bonded electron-transfer process; (iii) ions which interact with the alkene initially by formation of a tight π-complex; (iv) ions which undergo a one-electron reduction with the concomitant formation of an organic radical able to react with the alkene.

The last class is arguably the least useful from a preparative point of view since such processes often result in the plethora of products so typical of the reactions of radicals with organic substrates. But there are exceptions. For instance the reaction of manganese(III) with alkenes in carboxylic acid solvents has been shown to be a valuable route to γ-lactones.[1,2] The generally accepted mechanism for this oxidation involves addition to the alkene of an initially formed carboxyalkyl species followed by oxidation by manganese(III) of the adduct radical (1) and cyclisation (Scheme 1).


Scheme 1. *Reagents:* i, Mn^{III}, $-Mn^{II} - H^+$; ii, $R'CH{=}CH_2$; iii, Mn^{III}, $-Mn^{II}$; iv, $-H^+$

Other metal ions, *e.g.* cerium(IV),[2] lead(IV),[3] and cobalt(III),[4] can bring about this transformation though usually in lower yields. Even the use of manganese(III) is not without complications since the intermediate (1) can undergo alternative processes such as addition to a further molecule of alkene, leading to telomerisation,[5] or abstraction of a hydrogen atom to give a saturated alkanoic acid.[5,6] This last process is of considerable interest in its own right since it affords a simple route to long-chain carboxylic acids and is, in theory, catalytic on the metal oxidant. Other compounds containing carbonyl groups can react in a similar manner. Thus ketones,[7,8] esters,[8–10] aldehydes,[11] and anhydrides[6] will all form adducts with alkenes in the presence of manganese(III) and in some cases novel cyclisations can be effected.[8,12]

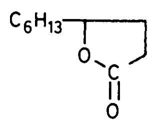
In view of the potential commercial importance of a route to the higher alkanoic acids from alkenes a study was made of the factors governing the types of products obtained and their relative ratios when manganese(III) reacts with alkanoic acids in the presence of alkenes. The results of that work are reported in this paper.

Results and Discussion

The initial reaction chosen for study was the oxidation of oct-1-ene by two equivalents of manganese(III) acetate dihydrate in acetic acid at 100 °C. Both the alkene and the expected products have volatility characteristics which simplify handling and analysis. As the anhydrous form of the metal salt is both troublesome to prepare and is highly deliquescent[13,14] the dihydrate was employed as oxidant.

The mixture was heated under nitrogen (to preclude the trapping of carbon-centred radicals by oxygen) until the dark brown colouration of the metal ion was discharged. Excess of solvent was removed and the crude product treated with *NN*-dimethylformamide dimethyl acetal to methylate any carboxylic acids before analysis by g.c. Five significant products were detected. These were shown, by comparison with authentic samples, to be the lactone (**2**) and the methyl esters of decanoic acid (**3**), the unsaturated acids (**4**) and (**5**), and the acetoxy-acid (**6**). The yields are set out in Table 1 (experiment 1). Test experiments showed that concentration of the solution before analysis did not result in any detectable loss of products and that methylation of the free acids was quantitative. A small amount of an additional product was also noted (see later).

Problems were experienced in obtaining complete separation by g.c. of the isomers (**4**) and (**5**) and in differentiating between them. In order to confirm the location of the double bonds and to determine the relative proportions of the two compounds a sample of the unmethylated product was cleaved by reductive ozonolysis. By determining the amounts of hexanal and



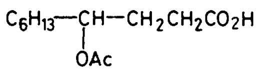
(2)

$C_5H_{11}CH{=}CHCH_2CH_2CO_2H$

(4)

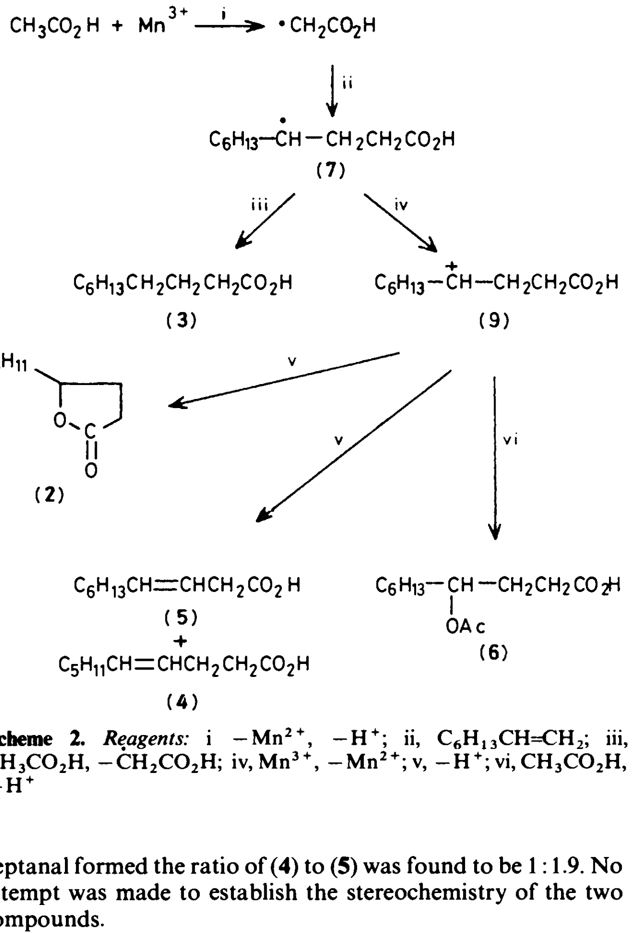
$C_6H_{13}CH{=}CHCH_2CO_2H$

(5)



$C_6H_{13}{-}\underset{\displaystyle OAc}{\underset{|}{C}}H{-}CH_2CH_2CO_2H$

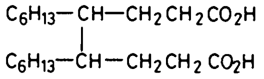
(6)



Scheme 2. *Reagents:* i $-Mn^{2+}$, $-H^+$; ii, $C_6H_{13}CH{=}CH_2$; iii, CH_3CO_2H, $-CH_2CO_2H$; iv, Mn^{3+}, $-Mn^{2+}$; v, $-H^+$; vi, CH_3CO_2H, $-H^+$

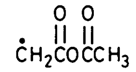
heptanal formed the ratio of (**4**) to (**5**) was found to be 1 : 1.9. No attempt was made to establish the stereochemistry of the two compounds.

The standard mechanism[2,5,6] involving the addition of a carboxymethyl radical to the alkene accounts for the formation of all five products (Scheme 2). A disproportionation reaction between two of the adduct radicals (**7**) offers an alternative route to products (**3**)—(**5**) but is felt to be unlikely on three grounds. First, reaction is relatively slow at 100 °C in acetic acid so that the concentration of radicals will be minimal. Secondly if (**7**) can disproportionate we might expect some relationship between the yields of saturated and of unsaturated acids, evidence for which is not apparent. Finally radicals might be expected to dimerise forming (**8**). No evidence could be found by g.c., at retention times appropriate for C_{20} diesters, for the presence of the dimethyl ester of (**8**) either in this or any subsequent experiment.



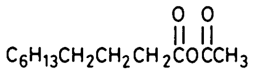
$C_6H_{13}{-}CH{-}CH_2CH_2CO_2H$ over $C_6H_{13}{-}CH{-}CH_2CH_2CO_2H$ (bonded CH–CH)

(8)



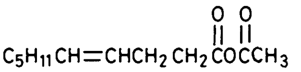
$\dot{C}H_2\overset{\overset{O}{\|}}{C}\overset{\overset{O}{\|}}{C}CH_3$

(10)



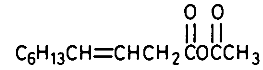
$C_6H_{13}CH_2CH_2CH_2\overset{\overset{O}{\|}}{C}\overset{\overset{O}{\|}}{C}CH_3$

(11)



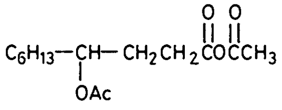
$C_5H_{11}CH{=}CHCH_2CH_2\overset{\overset{O}{\|}}{C}\overset{\overset{O}{\|}}{C}CH_3$

(12)



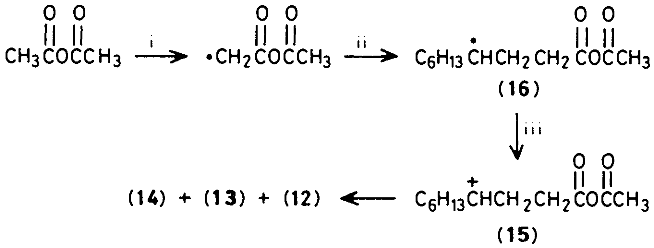
$C_6H_{13}CH{=}CHCH_2\overset{\overset{O}{\|}}{C}\overset{\overset{O}{\|}}{C}CH_3$

(13)



$C_6H_{13}{-}\underset{\displaystyle OAc}{\underset{|}{C}}H{-}CH_2CH_2\overset{\overset{O}{\|}}{C}\overset{\overset{O}{\|}}{C}CH_3$

(14)



Scheme 3. *Reagents:* i, Mn^{3+}, $-Mn^{2+}$ $-H^+$; ii, $C_6H_{13}CH{=}CH_2$; iii, Mn^{3+}, $-Mn^{2+}$

Effect of Solvent Composition.—In acetic acid oxidation of manganese(III) results in a high conversion of oct-1-ene into the lactone as reported earlier.[1,2] However, de Klein noted that, in pure acetic anhydride, excellent yields, based on oxidant, of decanoic acid can be obtained[5] whilst Okano, using hex-1-ene as the alkene, obtained 4-acetoxyoctanoic acid as the major product in a mixed solvent of acid and anhydride.[6] Solvent composition obviously is important in dictating the course of the reaction. We therefore carried out a series of oxidations in which the proportions of acetic acid and acetic anhydride were varied. The results in Table 1 demonstrate the profound effect that the nature of the solvent has upon both the product distribution and the time required for complete reduction of manganese(III).

When anhydride is present not only can the carboxymethyl radical be generated from acetic acid but the anhydride-derived radical (**10**) may also be formed. If this were trapped by the alkene we might expect to find amongst the products before work-up anhydride analogues of (**3**)—(**6**), namely (**11**)—(**14**). The normal method of work-up results in such compounds being converted into the methyl esters. Unfortunately, direct analysis before work-up is not feasible. Unsymmetrical anhydrides exist at higher temperatures in equilibrium with their symmetric analogues.[15] The detection of (**11**)—(**14**) in the system would not, therefore, prove that (**10**) had been generated.

However, that (**10**) is formed and trapped in mixed solvents is suggested by the manner in which (**2**) decreases when anhydride is present to be replaced by (**4**)—(**6**). The carbonium ion (**15**) derived from the radical (**16**) is unable to cyclise and would react either by loss of a proton or by nucleophilic attack (Scheme 3).

One of the more unexpected features in Table 1 is the great reduction in reaction time brought about by relatively small amounts of anhydride whilst increasing proportions have no further effect. This we believe to be due to the use of the

Table 1. Products from the oxidation of oct-1-ene by manganese(III) acetate dihydrate in acetic acid–anhydride mixtures at 100 °C

Experiment	Solvent composition (v/v AcOH–Ac_2O)	Reaction time (h)	Alkene conversion (%)[a]	Products (% based on alkene)			
				(3)	(4) + (5)	(6)	(2)
1	100—0	95	64	0.1	2.4	3.9	57
2	98—2	85	55	0.5	2.3	4.4	48
3	88.5—11.5[b]	6.5	66	1.4	10	38	16
4	80—20	2.5	76	2.9	22	35	15
5	70—30	2.0	78	4.5	25	36	13
6	50—50	2.0	66	5.2	10	40	11
7	30—70	2.0	61	14	7.1	31	9.4
8	20—80	2.0	61	15	trace	35	10
9	2—98	2.0	54	29		19	6.0
10	0—100	2.5	56	29		21	6.0

[a] Does not include any telomer formed. [b] This solvent composition corresponds to the theoretical absence of water.

dihydrate of manganese(III) acetate. With the volume of solvent employed in the system no water of crystallisation would remain at the composition used in experiment 3. It seems to be at this composition that the increase in the rate of oxidation is most marked. With a greater proportion of acid effectively no anhydride will be present in the system. One might suggest, therefore, that the change results from the anhydride being oxidised to (**10**) much more readily than is acetic acid to the carboxymethyl radical. It is notable that at the composition of experiment 3 the yield of lactone, a product which cannot result from reaction of (**10**) with alkene, is markedly depleted. Rather surprisingly the reverse situation seems to hold in cobalt(III) oxidations of related systems.[4] The yield of lactone increases as the proportion of anhydride is increased. Equally surprisingly no acid products analogous to (**3**) to (**6**) were noted. However, the ease of oxidation of acetic anhydride cannot be the full story. Even when the anhydride is by far the major component in the solvent (experiment 10) significant quantities of lactone are still formed implying that the generation of carboxymethyl radicals remains competitive.

If it is assumed that the products (**2**) and (**4**)—(**6**) stem from common carbonium ion precursors (**9**) and (**15**), a large proportion of anhydride is required before the formation of these ions is repressed and significant quantitites of the hydrogen-abstraction product (**3**) obtained. An explanation for this may be the much lower solubility of manganese(III) in acetic anhydride (see later). Less manganese(III) is available to oxidise a radical adduct whilst the total concentration of hydrogen donors remains constant. This same factor may also explain why the time taken for complete destruction of manganese(III) remains roughly constant over large changes in solvent ratio. Whilst more anhydride is present to form (**10**) less manganese(III) is available to initiate the reaction.

The one remaining aspect of the data in Table 1 for which no obvious explanation can be offered is the very rapid fall off in the yield of (**4**) and (**5**) between experiments 5 and 8 whilst that of (**6**) undergoes virtually no change. It cannot be that the first two compounds result from loss of acetic acid from (**6**) [or even elimination from (**2**)] since check experiments showed (**2**) and (**6**) to be stable to the reaction conditions. Nor does the reverse process of addition to the double bond in the unsaturated adducts seem plausible since there appears no reason why electrophilic addition should lead to highly selective nucleophilic attack on C-4; we were unable to detect any isomeric forms of (**2**) and (**6**). The remaining possibility, suggested by a referee, is that the relative rates of proton loss from, and of nucleophilic attack on, (**9**) and (**15**) are strongly solvent dependent.

The solvent composition under which reaction proceeds at an acceptable rate and all four types of product are formed in reasonable yields are those of experiment 6. Equal volumes of acetic acid and anhydride were therefore employed in subsequent examinations of other reaction parameters.

Table 2. Product distribution during the reaction of manganese(III) acetate dihydrate with oct-1-ene in acetic acid–acetic anhydride at 100 °C

Reaction time (h)	Alkene conversion (%)	Oxidant conversion (%)	Product distribution (%)			
			(3)	(4) + (5)	(6)	(2)
0.17	8.5	19	1.4	23	48	28
0.30	18	58	2.6	21	46	28
0.58	32	77	3.4	20	48	28
1.6	50	86	4.4	20	44	32
2.0	56	100	6.7	19	54	21

[a] Determined by iodometry.

Table 3. Effect of concentration of oxidant on product distribution in the oxidation of oct-1-ene by manganese(III) acetate dihydrate in acetic acid–acetic anhydride at 100 °C

Initial concentration of oxidant (mol dm^{-3})	Time taken for decolourisation (h)	Alkene conversion (%)	Product distribution (%)			
			(3)	(4) + (5)	(6)	(2)
0.50	2.0	66	6.5	15	61	17
0.35	1.0	41	7.3	21	53	18
0.25	0.8	32	9.3	18	54	19
0.125	0.8	16	15	15	56	15
0.050	0.3	6.6	29	11	45	15
0.025	0.25	3.0	43	6.7	33	17

Effect of Oxidant Concentration.—The effect on product distribution of manganese(III) concentration is clearly shown in Tables 2 and 3. In Table 2 are listed the results of monitoring the product ratio during the course of a single oxidation, portions being withdrawn at fixed intervals. Given that the relative yields of the five principal products is largely dictated by the ratio of hydrogen donor to oxidant and that the concentration of donor solvent remains effectively constant throughout the reaction whilst that of manganese(III) should fall, it is not surprising that the proportion of decanoic acid rises steadily. The same effect is observed when the initial concentration of oxidant is lowered, other reaction parameters being kept constant (Table 3).

One interesting point from Table 2 is that the reduction of manganese(III) appears to run ahead of the conversion of alkene. Thus, after 0.3 h 58% of the oxidant has disappeared whilst less than one-third of the final products has been formed.

Table 4. Effect of temperature on the products of oxidation of oct-1-ene by manganese(III) acetate dihydrate in acetic acid–acetic anhydride

			Products (% based on alkene)			
T/°C	Reaction time (h)	Alkene conversion (%)	(3)	(4) + (5)	(5)	(2)
63	84	54	9.9	3.0	32	9.1
85	6.5	59	6.5	6.3	36	11
100	2.0	66	5.2	10	40	11
115	0.4	83	5.6	11	52	15

Table 5. Effect of potassium acetate on the oxidation of oct-1-ene by manganese(III) acetate dihydrate in acetic acid–acetic anhydride at 100 °C

			Product distribution (%)			
[KOAc]/ mol dm^{-3}	Reaction time (h)	Alkene conversion (%)	(3)	(4) + (5)	(6)	(2)
0.0	2.0	60.0	5.5	18	57	19
0.1	1.2	64.5	8.1	15	60	17
0.3	1.1	66.9	10	12	62	16
0.5	0.9	63.5	13	12	58	16
0.75	0.9	56.9	14	9.3	61	16
1.5	0.8	60.2	16	5.5	64	14

This does not result from utilisation of alkene being more efficient at lower oxidant levels since Table 3 shows there to be an essentially linear relationship between alkene conversion and initial concentration of oxidant. One possibility is that manganese(II) is effective in favouring the formation of carboxyalkyl radicals or their analogues. Certainly the reduction of manganese(III) is inhibited by manganese(II), the production of a bridged complex having been suggested as an explanation of this observation.[16]

Even at relatively low concentrations of manganese(III) oxidation of adduct radicals (**7**) and/or (**16**) is still an important process. If the reaction is to be an efficient route to saturated acids some means must be found of repressing radical oxidation. In theory the manganese salt simply serves as a source of initiating radical in a chain reaction. The concentrations used above are still greatly in excess of those normally employed with radical initiators. We therefore sought to improve conversion of oct-1-ene into decanoic acid by adding a solution of the oxidant dropwise to a solution of the alkene in acetic anhydride at 100 °C thus ensuring a constant but very low concentration of magnanese(III).* Analysis of the product showed virtually exclusive formation of decanoic acid under these conditions, no unsaturated acids and only traces of (**2**) and (**6**) being detected.

Effect of Temperature.—In Table 4 is set out the effect on product distribution of varying the temperature of reaction. Naturally the rate of consumption of oxidant increases rapidly with temperature but so does the overall conversion of alkene. However, hydrogen abstraction by adduct radicals is less able to compete with oxidation at higher temperatures.† Of those products derived by oxidation of adduct radicals the unsaturated acids are most favoured by higher temperatures as might be expected if these arise by elimination from a carbonium ion intermediate.

Table 6. Effect of alkene concentration on the yield of decanoic acid in the oxidation of oct-1-ene by manganese(III) acetate dihydrate in acetic acid–acetic anhydride at 100 °C

Initial concentration of oct-1-ene (mol dm^{-3})	Yield of (3) based on alkene (%)	Yield of (3) based on oxidant (%)
0.5	5.3	53
0.25	11	111
0.125	24	236
0.0625	29	294

Effect of Added Acetate Ion.—In manganese(III) oxidations the addition of sodium or potassium acetate has often been found to bring about a beneficial reduction in reaction time.[2,3,14,17] In some cases the effect can be ascribed to the raising of the b.p. of the solvent[2] but in other instances, where the reaction temperature has been held constant, acceleration has still been observed.[14,17] As Table 5 shows, not only is reaction time shortened but the product ratio is also changed. The formation of decanoic acid is greatly faciliated by the presence of the anion whilst the yield of unsaturated acids and, less markedly, the lactone fall. It is perhaps not surprising that the products from the carbonium ions (**9**) and (**15**) are diverted to (**6**) since acetate will prove an effective nucleophile. However, we would have anticipated that acetate would also function as a base in this solvent system and hence lead to a greater reduction in the yield of (**2**) than (**4**) and (**5**) if we accept that the last two compounds result from proton loss.

When alkali-metal acetates are added to a solution of manganese(III) acetate in acetic acid a new peak appears in the absorption spectrum at 417 nm.[14] This has been attributed to the formation of an acetato-complex, $Mn(OAc)_4^-$. The accelerating of the oxidation by acetate ion is probably due to a modification of the oxidising species just as we earlier accounted for the effect on reaction time of relatively small quantities of acetic anhydride.

The increasing preference for hydrogen abstraction over radical oxidation as the concentration of acetate ion rises could be explained either by the presence of a new oxidising entity or by the active participation of acetate ion in the abstraction process. We have seen that, at least as regards reaction with the solvent, formation of an acetato-complex increases the oxidising power rather than decreasing it as required by the first explanation. We therefore favour the acceleration of hydrogen donation to (**7**) as explaining the improved yield of decanoic acid. This view is supported by evidence from e.s.r. spectroscopy showing that acetate is a more efficient hydrogen donor to the hydroxyl radical than is acetic acid.[18]

Accountability of Alkene.—One final parameter was investigated. A series of reactions was carried out by dropwise addition of the oxidant at varying initial concentrations of the alkene. Low alkene concentrations favour the formation of decanoic acid (Table 6). It is also apparent that this reaction is indeed a radical chain process with yields, based on oxidant, of up to 295%.

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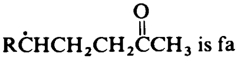
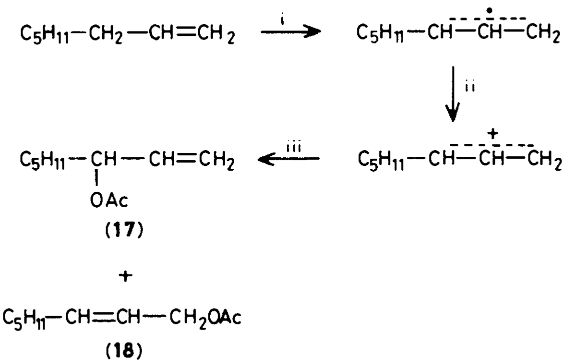
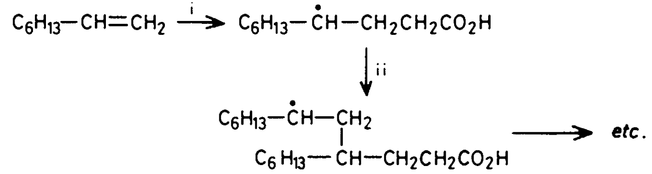
* Manganese(III) has a very limited solubility in acetic anhydride. Homogeneous conditions cannot be maintained unless acetic acid is used as the solvent for the oxidant.

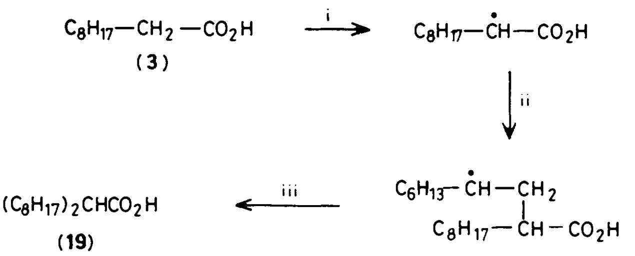
† The temperature effect on the abstraction:oxidation ratio of adduct radicals appears to be variable. When acetone is the source of carboxy-substituted radicals and manganese(III) the oxidant, hydrogen abstraction by the species  $R\dot{C}HCH_2CH_2\overset{\overset{\displaystyle O}{\|}}{C}CH_3$ is facilitated by raising the temperature. If the oxidant is cerium(IV), however, abstraction is favoured by lower temperatures.[7]



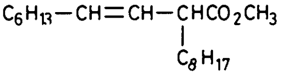
Scheme 4. *Reagents:* i, Mn^{3+}, $-Mn^{2+}$ $-H^+$; ii, Mn^{3+}, $-Mn^{2+}$; iii, AcOH, $-H^+$



Scheme 5. *Reagents:* i, Mn^{3+}, CH_3CO_2H; ii, $C_6H_{13}CH{=}CH_2$

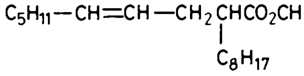


Scheme 6. *Reagents:* i, Mn^{3+}, $-Mn^{2+}$ $-H^+$; ii, $C_6H_{13}CH{=}CH_2$; iii, CH_3CO_2H, $-\dot{C}H_2CO_2H$



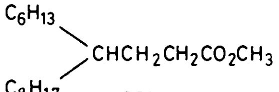
$C_6H_{13}{-}CH{=}CH{-}CH(C_8H_{17})CO_2CH_3$

(20)



$C_5H_{11}{-}CH{=}CH{-}CH_2CH(C_8H_{17})CO_2CH_3$

(21)



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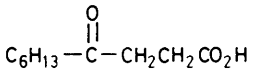


$C_6H_{13}{-}CO{-}CH_2CH_2CO_2H$

(23)

Table 7. A comparison of the addition of acetic anhydride to oct-1-ene initiated by manganese(III) acetate dihydrate and by di-t-butyl peroxide

Initiator	Ratio initiator: alkene	T/°C	Addition time (h)	Yield of decanoic acid based on alkene (%)	Yield of decanoic acid based on oxidant (%)
$Mn(OAc)_3{\cdot}2H_2O$	0.1	100	2	29	290
$(Bu^tO)_2$[a]	0.15	140	6	72	240[b]

[a] Ref. 20. [b] Assuming 1 mol peroxide initiates the formation of 2 mol decanoic acid.

In most of the experiments described above the accountability of alkene is only moderate. There is certainly some unchanged oct-1-ene at the end of the reaction though the method of work-up meant that this was removed during the concentration step. Quantification by g.c. of the more volatile components before removal of the solvent is not easy but it was demonstrated in experiment 6 that *ca.* 20% of the alkene remained after oxidation was complete. In one instance the unchanged alkene was determined by a more accurate iodometric procedure. Prior to removal of solvent bromine in acetic acid was added followed, after 15 min, by potassium iodide solution. The liberated iodine was titrated against sodium thiosulphate. Based on results from standard solutions of oct-1-ene in acetic anhydride the method was estimated to have an accuracy of ±3% after allowance for the presence of (**4**) and (**5**) and for the reaction of bromine with acetic anhydride. The accountability of products plus unchanged alkene was calculated to be 89%. Of the missing 11% some might be lost by evaporation or condensation above the hot solution leaving very little to be accounted for by reactions not so far discussed.

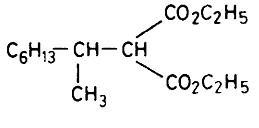
Two such routes which immediately spring to mind are allylic substitution (Scheme 4) and telomerisation (*e.g.* Scheme 5). The first process can be of importance when halide ions are present in the system[19] but in their absence allylic products have not been found in other than trace amounts.[1,2] In none of the reactions reported here were the allylic acetates (**17**) and (**18**) detected.

The occurence of telomerisation is more difficult to demonstrate. The C_{18} esters resulting from the coupling of two alkene molecules should be amenable to analysis by g.c. though products of higher molecular weight pose problems. The presence of small amounts of minor products was noted earlier. The major one of long retention time (present in *ca.* 1.6% yield) in a reaction in which decanoic acid was produced in large amounts was tentatively identified, by g.c.—m.s., as methyl 2-octyldecanoate. The acid (**19**) from which this is derived (or the corresponding anhydride) does not arise *via* Scheme 5. Instead it results from further oxidation of (**3**) (Scheme 6) or the analogous anhydride. A check experiment in which manganese(III) was reduced in decanoic anhydride as solvent in the presence of oct-1-ene gave two g.c. peaks one due to the ester of (**19**) (2%) and the second believed, on the basis of its mass spectrum, to be a mixture of the unsaturated esters (**20**) and (**21**).

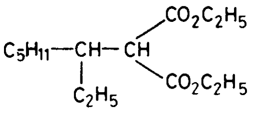
The remaining product in the C_{18} region of the g.c. trace was present in too small an amount for g.c.—m.s. to offer clues as to its identity. Even if it were the dimer methyl 4-hexyldodecanoate (**22**) telomerisation does not appear to be a serious problem.

One other minor product (maximum yield 0.5%) was noted in a number of reactions. This had a retention time similar to methyl 4-acetoxydecanoate. Its yield was greatly boosted in one reaction in which the nitrogen supply failed and, when this oxidation was repeated without nitrogen, the yield reached 20%. This compound was identified as methyl 4-oxodecanoate whose precursor (**23**) probably arises from the trapping of (**7**) or (**16**) by oxygen.

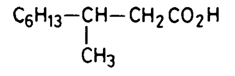
Manganese(III) *as a Catalyst for Converting Oct-*1*-ene into Decanoic Acid.*—The use of one-electron metal oxidants for the generation of carboxy-substituted radicals from acids and anhydrides is not the only way of initiating addition of such species to alkenes. Peroxide initiators have been employed to give good yields of adducts. The nearest comparable study to the one described above is that of Hey *et al.* in which decanoic acid was produced from oct-1-ene in acetic anhydride by the dropwise addition of di-t-butyl peroxide. A comparison of the manganese(III) and the peroxide-initiated processes (Table 7) initially suggests the latter route to be superior. Whilst the efficiency of the initiators is similar, higher conversion of alkene is achieved with peroxide. However, given that unchanged



(24)

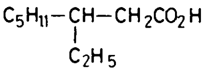


(25)



$C_6H_{13}-\underset{\displaystyle CH_3}{\underset{|}{C}H}-CH_2CO_2H$

(26)



$C_5H_{11}-\underset{\displaystyle C_2H_5}{\underset{|}{C}H}-CH_2CO_2H$

(27)

alkene can be recycled, particularly when reaction is carried out on an industrial scale, the lower conversion with manganese(III) is not an over-riding problem. Moreover with this reagent reaction can be carried out at lower temperatures and over a shorter reaction time.

There is one other advantage to a manganese(III) initiator, that of availability. The usual method employed for synthesising manganese(III) salts, a redox reaction between manganese(II) and permanganate is somewhat expensive.[21] A number of alternative methods are available for the oxidation of manganese(II)[22,23] involving both chemical and electrochemical routes. One simple method would appear to be the aerial oxidation of aqueous manganese(II) in the presence of triethylamine.[23] On stirring the 'manganic hydroxide' precipitated under these basic conditions with acetic acid manganese(III) acetate is said to be obtained in near quantitative yield. We found that this 'hydroxide' is relatively unstable, disproportionating to give a solid from which manganese dioxide precipitates on stirring with acetic acid. The resultant solution will convert oct-1-ene into decanoic acid but in yields which are only about a third of those obtained from manganese(III) acetate produced by conventional means. We found it best to dissolve the basic manganese(III) intermediate immediately in acetic acid without attempting to dry it. Yields of decanoic acid were then just as good as when the oxidant was prepared from permanganate. Given that manganese(II) precipitates from the oxidising system, an effective method of recycling the manganese is available using air as the ultimate oxidant.

The Oxidation of Disubstituted Alkenes by Manganese(III).—Whilst oct-1-ene is a suitable model substrate for investigating most aspects of the manganese(III)-catalysed addition to alkenes a brief study was made of the reaction of a disubstituted olefin, (*Z*)-oct-2-ene, in order to obtain more information about regioselectivity. The reaction of oct-1-ene appears to be completely regiospecific but previous reports of the oxidation of disubstituted substrates have been confined to the symmetrical examples, oct-4-ene and cyclohexene.[1,2] We would expect little selectivity between attack at C-2 and at C-3 in oct-2-ene on electronic grounds though in the peroxide-catalysed addition of diethyl malonate to this alkene the two isomers (**24**) and (**25**) are formed in the ratio 2:1.

Using conditions under which oxidation of radical adducts is minimised, (*Z*)-oct-2-ene was found to give two products (**26**) and (**27**), the methyl esters of which are readily distinguished by mass spectrometry. Both show *m*/*z* 74 as the base peak but the compound derived from (**26**) has a strong ion at *m*/*z* 101 ($M - C_6H_{13}$) whilst this is shifted to *m*/*z* 115 ($M - C_5H_{11}$) in the case of the ester from (**27**). The combined yield of the two was 17% based on alkene which compares with 29% of (**3**) from oct-1-ene under the same conditions. Given the similar stabilities expected of the two adduct radicals the ratio of the products (3:1) is high, suggesting that there may be a significant amount of steric interaction involved in the addition in line with Tedder's conclusion that steric factors are of greater importance than electronic ones in radical additions to alkenes.[24]

Conclusions.—The product distribution in the oxidation of oct-1-ene by manganese(III) acetate is dependent upon a number of factors. Most critical amongst these is the solvent chosen. A γ-lactone is formed almost exclusively in acetic acid but in acetic anhydride the intermediate adduct radical undergoes hydrogen abstraction rather than oxidation to give predominently a saturated acid. The use of a mixed acid–anhydride solvent results in adduct radicals derived primarily from the anhydride which nevertheless undergo oxidation and, being unable to cyclise, lead to the γ-acetoxy-acid and unsaturated acids. Low temperatures, low concentration of oxidant, and the presence of acetate ions all favour the formation of decanoic acid. In particular, the dropwise addition of the oxidant provides conditions under which yields can be obtained comparable to those resulting from a peroxide-initiated process.

Experimental

G.c. was carried out on a Pye 104 instrument fitted with flame ionization detector and columns (6 ft × $\frac{1}{4}$ in or 12 ft × $\frac{1}{8}$ in) packed with 10% Carbowax 20M, 10% diethylene glycol adipate, or 10% silicone SE30, each coated on acid-washed Celite. 3-Nitrotoluene was employed as internal standard. Preparative-scale g.c. was carried out on a Pye 105, model 15 instrument fitted with similar columns. Mass spectra were recorded on a Kratos MS3076 spectrometer which was coupled *via* a heated capillary and a jet separator to a gas chromatograph: all spectra were recorded at 70 eV and the source temperature was held in the region 150—180 °C. ^1H and ^{13}C n.m.r. spectra were recorded on Varian MH100 or JEOL FX60 instruments, respectively, using deuteriochloroform as solvent. M.p.s were determined on a Kofler microhot-stage and are uncorrected. Elemental analyses were by Butterworth Micro-analytical Services (Teddington).

Acetic acid, acetic anhydride, and potassium acetate were AnalaR reagents. Oct-1-ene and oct-2-ene were laboratory reagents (B.D.H. and Fluka respectively) and were distilled before use.

Manganese(III) *Acetate Dihydrate*.—The method of Christensen[21] was modified as follows. To a suspension of manganese(II) acetate tetrahydrate (85.7 g) in acetic acid (600 cm^3) at 110 °C was added powdered potassium permanganate (13.6 g) in small portions over 20 min. The solution was cooled to room temperature, poured into water (150 cm^3), and left overnight at 3 °C. The resultant brown solid was filtered off, washed with ether, and dried *in vacuo* over sodium hydroxide. The product (95 g, 82%) was a light brown solid, soluble in acetic acid, with a manganese(III) content, by iodometry, of 19.9% [$Mn(OAc)_3 \cdot 2H_2O$ requires 20.5%].

One batch of manganese(III) salt was made by aerial oxidation[23] as follows. Triethylamine (75 cm^3) was added dropwise to a solution of manganese(II) acetate tetrahydrate (63.3 g) in water (250 cm^3), through which was bubbled oxygen. The resulting brown sludge was centrifuged off, washed repeatedly with water, and stirred overnight in acetic acid (500 cm^3). Filtering the brown suspension and drying the solid cake *in vacuo* over potassium hydroxide gave a light brown amorphous powder with a manganese(III) content, by iodometry, of 16.5%.

Methyl Decanoate.—This ester was prepared from decanoic acid *via* the acid chloride by a standard method in 82% yield and had b.p. 72—74 °C at 1.3 mmHg (lit.,[25] 79 °C at 2 mmHg),

δ_H 3.62 (3 H, s, OCH_3), 2.22 (2 H, t, *J* 6.5 Hz, CH_2CO), and 1.7—0.7 (17 H, aliphatic envelope); *m/z* 186 (3%, $M^{+\cdot}$), 143 (12, $M - 43$), 87 (64, $C_4H_7O_2^+$), 74 (100, $C_3H_6O_2^{+\cdot}$), 44 (25), and 43 (21).

Methyl (E)-*Dec*-4-*enoate*.—To the Grignard reagent from magnesium (3.5 g) and 1-bromopentane (20 g) in dry ether (140 cm^3) was added dropwise a solution of acrolein (7.4 g) in dry ether (35 cm^3) at −20 °C. After warming to room temperature, the solution was poured onto ice (60 g), 15% sulphuric acid (50 cm^3) added, and extracted with ether. The extract was washed, dried ($MgSO_4$), the solvent removed, and the residue distilled to give oct-1-en-3-ol (3 g, 18%) as an oil, b.p. 80—82 °C at 21 mmHg (lit.,[26] 70 °C at 13 mmHg). A mixture of oct-1-en-3-ol (0.5 g), 1,1,1-trimethoxyethane[27] (3.24 g), and propanoic acid (0.025 g) was heated at 105 °C for 4.5 h, the methanol produced being distilled off. Distillation of the residue afforded methyl (*E*)-dec-4-enoate (0.62 g, 87%) as a liquid, b.p. 58—60 °C at 0.25 mmHg (lit.,[28] 107—108 °C at 13 mmHg); δ_H 5.6—5.3 (2 H, m, $-CH{=}CH-$), 3.65 (3 H, s, OCH_3), 2.40—2.22 (4 H, m, $=CHCH_2CH_2CO$), 2.11—1.82 (2 H, m, $CH_2CH=$), and 1.6—0.6 (9 H, aliphatic envelope); *m/z* 184 (5%, $M^{+\cdot}$), 110 (41, $C_8H_{14}^{+\cdot}$), 85 (64, $C_6H_{13}^+$), 74 (100, $C_3H_6O_2^{+\cdot}$), 55 (62, $C_4H_7^+$), and 43 (23, $C_3H_7^+$).

Methyl 4-*Oxodecanoate*.—This keto-ester was prepared using the organocadmium compound from 1-bromohexane and 2-methoxycarbonylpropanoyl chloride[29] by a modification of the method of Cason and Prout.[30] It was obtained in 36% yield as an oil, b.p. 69—71 °C at 0.02 mmHg (lit.,[31] 104—105 °C at 1.2 mmHg); δ_H 3.67 (3 H, s, OCH_3), 2.82—2.55 (4 H, m, $COCH_2CH_2CO$), 2.42 (2 H, t, *J* 8 Hz, CH_2CO), and 1.76—0.74 (11 H, aliphatic envelope); *m/z* 200 (0.5%, $M^{+\cdot}$), 169 (9, $M - CH_3O$), 130 (50, $M - C_5H_{10}$), 115 (68, $M - C_6H_{13}$), 113 (36, $C_6H_{13}CO^+$), 111 (15, $C_6H_7O_2^+$), 98 (75, $M - C_5H_{10} - CH_3OH$), 85 (19, $C_6H_{13}^+$), 59 (29, $CO_2CH_3^+$), 57 (13, $C_4H_9^+$), 56 (14, $C_4H_8^{+\cdot}$), 55 (64, $C_4H_7^+$), 43 (100, $C_3H_7^+$), 42 (9, $C_3H_6^{+\cdot}$), and 41 (50, $C_3H_5^+$).

γ-*Decanolactone*.—A solution of methyl 4-oxodecanoate (4.2 g) in methanol (50 cm^3) was added slowly to a solution of sodium borohydride (1.2 g) in aqueous sodium hydroxide [2.5 g in water (60 cm^3)] at 0 °C. The resulting mixture was stirred for 1 h, and acidified with 2M-sulphuric acid. The solution was extracted with ether, dried, and the solvent removed to give, after distillation, γ-decanolactone (2.5 g, 70%) as an oil, b.p. 120—122 °C at 2.5 mmHg (lit.,[32] 118—120 °C at 3 mmHg); δ_H 4.43 (1 H, quintet, *J* 6 Hz, OCH), 2.65—2.10 (2 H, m, CH_2CO), and 2.0—0.7 (15 H, m, aliphatic envelope); *m/z* 170 (0.1%, $M^{+\cdot}$), 128 (9, $M - 42$), 85 (100, $M - C_6H_{13}$), 55 (8, $C_4H_7^+$ and/or $C_3H_3O^+$), and 43 (10, $C_3H_7^+$).

2-*Octyldecanoic Acid*.—This was prepared by a modification of the method of Kaiser *et al.*[33] Diethyl malonate (5 g) in dry tetrahydrofuran (5 cm^3) was slowly added to a stirred suspension of sodium hydride (1.5 g) in tetrahydrofuran (10 cm^3). When effervescence had subsided, further solvent (15 cm^3) was added, the mixture refluxed for 10 min, 1-bromooctane (12 g) in tetrahydrofuran (10 cm^3) added over a period of 30 min to the hot solution, and refluxing resumed for a further 12 h. After removal of the solvent, the product was poured into water (50 cm^3) and extracted with ether. The oil obtained after drying and evaporating the ethereal extracts gave, on distillation, diethyl octylmalonate (4.2 g), b.p. 109—110 °C at 0.05 mmHg (lit.,[34] 186—187 °C at 24 mmHg); *m/z* 272 (0.13%, $M^{+\cdot}$), 173 [31, $CH_2CH(CO_2Et)_2^+$], 160 (100, $M - C_8H_{16}$), 133 (21, $C_5H_9O_4^+$), 88 (20, $C_4H_8O_2^{+\cdot}$), 73 (30, CO_2Et^+), 55 (28, $C_4H_7^+$), 43 (29, $C_3H_7^+$), and 41 (38, $C_3H_5^+$); and a residue of diethyl dioctylmalonate (2.2 g, 18%) which gave a single peak on g.c., δ_H 4.14 (4 H, *J* 7 Hz, OCH_2CH_3), 2.0—0.7 (40 H, aliphatic envelope and CH_3CH_2O); *m/z* 340 (1%, $M - 44$), 311 (2, $M - CO_2Et$), 272 (22, $M - C_8H_{16}$), 173 (55, $C_8H_{13}O_4^+$), 57 (12, $C_4H_9^+$), 55 (29, $C_4H_7^+$), 44 (100), 43 (27, $C_3H_7^+$), and 41 (29, $C_3H_5^+$).

The crude diethyl dioctylmalonate was refluxed with potassium hydroxide (1.5 g) in aqueous ethanol (40% v/v) for 5 h. The solvent was removed, water (75 cm^3) added, and the solution extracted with ether. The aqueous layer was acidified with 12M-hydrochloric acid (10 cm^3), refluxed for 1.5 h, and the mixture again extracted with ether, the extracts washed with water, and dried ($MgSO_4$). Evaporation of the solvent gave crude dioctylmalonic acid which was heated at 200 °C for 3 h. When *ca.* 100 cm^3 of carbon dioxide had been evolved, the dark residue (1.27 g) was cooled and dissolved in light petroleum (b.p. 40—60 °C). On standing at 0 °C, 2-octyldecanoic acid (0.83, 51%) was obtained as crystals, m.p. 36—37 °C (lit.,[34] 38 °C).

Decanoic Anhydride.—Decanoic acid (30 g) was refluxed with acetic anhydride (50 cm^3) for 7 h, excess of acetic anhydride, and any acetic acid removed under vacuum, and the residue distilled to give decanoic anhydride (15 g, 53%) as a viscous oil, b.p. 154—156 °C at 0.2 mmHg (lit.,[20] 135—145 °C at 0.05 mmHg).

Oxidation of Alkenes by Manganese(III) *Acetate Dihydrate*.—Manganese(III) acetate dihydrate (3.35 g) was added to the solvent [acetic acid and/or acetic anhydride in the desired ratio (25 cm^3)] at room temperature. The apparatus was flushed with nitrogen, immersed in an oil-bath at the required temperature, and stirred for a few seconds to bring about complete dissolution of the oxidant. Oct-1-ene (0.7 g) was added, and stirring continued until the dark brown colour of manganese(III) had disappeared to leave a white precipitate of manganese(II) acetate. The mixture was cooled, excess of solvent removed on a rotary evaporator, and a 10% solution of acetic acid in water (35 cm^3) added. After stirring the mixture at 100 °C for 45 min to hydrolyse any residual anhydride, the solution was extracted with ether, the ether layer washed with water and dried. For those oxidations which required the presence of dissolved potassium acetate, both this salt and the oxidant were added to the solvent prior to alkene addition. In cases where the manganese(III) was added in a dropwise manner the oxidant was dissolved in acetic acid at 80 °C, the solution cooled, and an equal volume of acetic anhydride added. This mixture was then added from a dropping funnel over 2 h to a solution of the alkene in acetic acid and/or acetic anhydride held at the desired temperature of reaction.

The crude product obtained on removal of the ether solvent was analysed as follows. To a known weight of the product was added 3-nitrotoluene as internal standard, and *ca.* 50 mg of the resultant mixture dissolved in 'methyl-8' (2 cm^3) (Pierce Chemicals) to which a few drops of pyridine had been added. After heating the solution for 1 h at 65—70 °C, a sample was injected directly into the gas chromatograph. Based on tests with authentic decanoic acid, *ca.* 98% methylation could be achieved by this method.

From one oxidation *methyl* 4-*acetoxydecanoate* was isolated by preparative g.c. This had δ_H 4.84 (1 H, quintet, *J* 6 Hz, CH), 3.64 (3 H, s, OCH_3), 2.25 (2 H, t, *J* 9 Hz, CH_2CO), 1.98 (3 H, s, CH_3CO), 1.9—1.7 (2 H, m, CH_2CH_2CO), and 1.7—0.7 (13 H, aliphatic envelope); δ_C 173.6 (CO), 170.8 (CO), 73.3 ($CHO{-}CO$), 51.7 ($CH_3O{-}CO$), 34.0 (CH_2CO), 31.7, 30.1, 29.1, 25.2, 22.6, and 21.1 (CH_3CO and aliphatic CH_2), and 14.1 p.p.m. (CH_3CH_2); *m/z* 201 (7% $M - CH_3CO$), 159 (8, $M - C_6H_{13}$), 117 (31, $M - C_6H_{13} - CH_2CO$), 110 (7, $C_8H_{14}^{+\cdot}$), 85 (15, $C_4H_5O_2^+$

and $C_6H_{13}^+$), 74 (13, $C_3H_6O_2^{+\cdot}$), 55 (13, $C_4H_7^+$), 44 (25), and 43 (100, CH_3CO^+) (Found: C, 63.7; H, 9.8%; *m/z* 201.151. $C_{13}H_{24}O_4$ requires C, 63.9; H, 9.9%; *M*, 201.149).

Determination of the Ratio of Decenoic Acids in the Reaction Product by Reductive Ozonolysis.—A solution of the reaction product in ether was extracted with sodium carbonate solution, the aqueous layer separated, and dilute sulphuric acid added to it to liberate the free acids. These were isolated by ether extraction, and after removal of solvent from the dried extracts, a portion of the product (100 mg) was dissolved in chloroethane (20 cm^3) cooled in an ice–salt bath. Ozone from a Gallenkamp ozoniser was passed into the solution at −30 °C for 30 min after which the solvent was allowed to evaporate at room temperature. The oil remaining was steam distilled from 30% aqueous acetic acid (50 cm^3) containing zinc dust (5 g) and the distillate extracted with ether. The extract gave two peaks on g.c. which were identified by comparison of their mass spectra and their retention times as hexanal and heptanal and then quantified.

Determination of Residual Alkene in an Oxidation Mixture.—The amount of oct-1-ene remaining at the end of an oxidation was determined as follows. Prior to solvent removal and hydrolysis, enough ether was added to the product mixture to bring the final volume to 150 cm^3. A portion (10 cm^3) of the resultant solution was then added to bromine in acetic acid (25 g dm^{-3}) and stirred for 15 min. The iodine liberated on adding aqueous potassium iodide (35 g dm^{-3}) to the mixture was titrated in the usual manner with standard sodium thiosulphate (0.1 mol dm^{-3}). A 'blank' run in which oct-1-ene was omitted was then performed, and the quantity of alkene in the original mixture estimated from the two titres. Based on results from standard solutions of oct-1-ene in acetic anhydride, the quantity of alkene could be estimated to within ±3% by this method. In cases where alkenic products are known to be present, appropriate allowances are made.

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