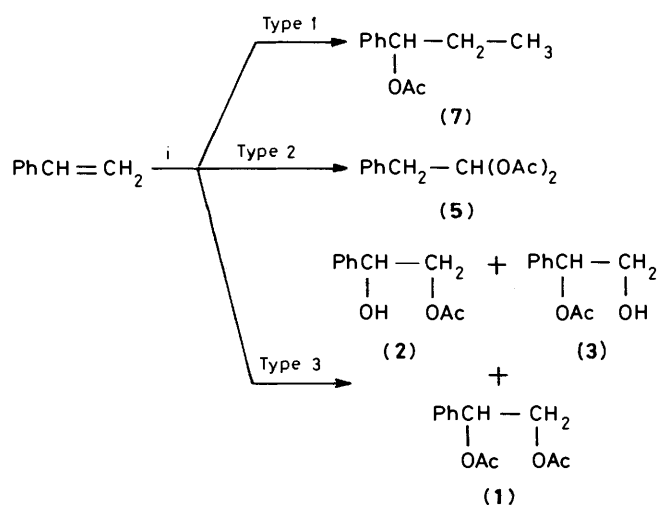


## Radical-Cations as Intermediates in the Oxidation of Alkenes by Metal Ions

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The formation of hydroxy acetates in the reaction of some alkenes with lead(IV), cobalt(III), and manganese(III) in acetic acid is demonstrated to involve the intermediacy of alkene radical-cations. A study employing a range of aryl-substituted alkenes has shown that there is an inverse relationship between the yield of hydroxy acetate and the ionisation potential of the organic substrate. The electron deficiency in the radical-cations derived from these alkenes appears to be localised on the double bond: no evidence could be obtained for reaction at the aromatic ring. The introduction of a chlorine atom into this ring had the effect of repressing electron-transfer in cobalt(III) and manganese(III) oxidations but not in those involving lead(IV).

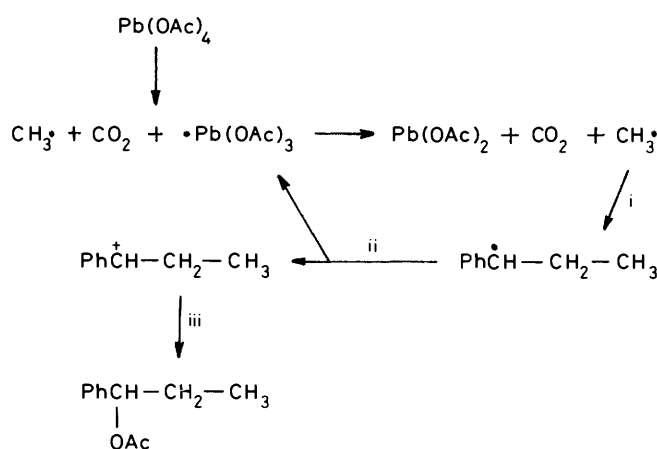
Some years ago we carried out a series of investigations into the oxidation of alkenes by lead(IV) carboxylates.<sup>1-3</sup> When the substrate was an aryl-substituted alkene and the solvent a carboxylic acid three major groups of products were identified. These are typified in Scheme 1 for styrene in acetic acid.



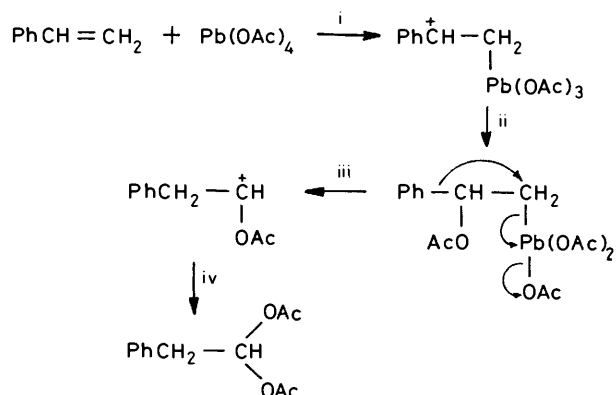
Scheme 1. Reagents: i,  $\text{Pb}(\text{OAc})_4$ ,  $\text{AcOH}$

Compounds of type 1 result from addition of an alkyl radical produced by thermal decomposition of the lead(IV) salt (Scheme 2). The second group of compounds are the products of electrophilic attack on the double bond by the oxidant, the resultant organolead species undergoing rapid decomposition with aryl migration (Scheme 3). The yields of these two groups of products respond as expected to changes in reaction conditions. Thus compounds of type 1 are favoured by the addition of radical initiators and by high temperatures, those of type 2 by the presence of inhibitors and by low temperatures.

The origin of the third group of compounds was less clear. It was shown that most of the diacetate (1) stems from further reaction of the two hydroxy-acetates, (2) and (3) (which are in dynamic equilibrium and are analysed together), but two processes appeared to be involved in the formation of these last compounds. The obvious route is *via* decomposition of the adduct (4) with neighbouring-group participation by the acetoxy function, the resultant acetoxonium ion being known to undergo highly selective ring opening by water<sup>4</sup> (Scheme 4, *cf.* the Prévost reaction<sup>5</sup>).

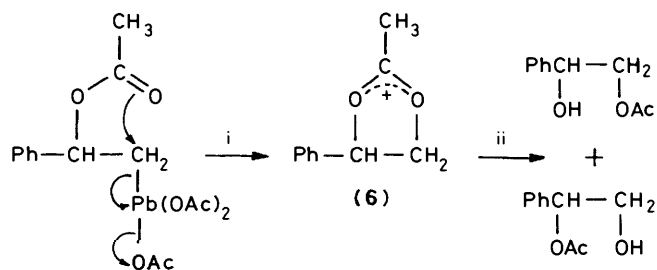


Scheme 2. Reagents: i,  $\text{PhCH}=\text{CH}_2$ ; ii,  $\text{Pb}(\text{OAc})_4$ ,  $-\text{AcO}^-$ ; iii,  $\text{AcOH}$ ,  $-\text{H}^+$



Scheme 3. Reagents: i,  $-\text{AcO}^-$ ; ii,  $\text{AcOH}$ ,  $-\text{H}^+$ ; iii,  $-\text{Pb}(\text{OAc})_2$ ,  $-\text{AcO}$ ; iv,  $\text{AcOH}$ ,  $-\text{H}^+$

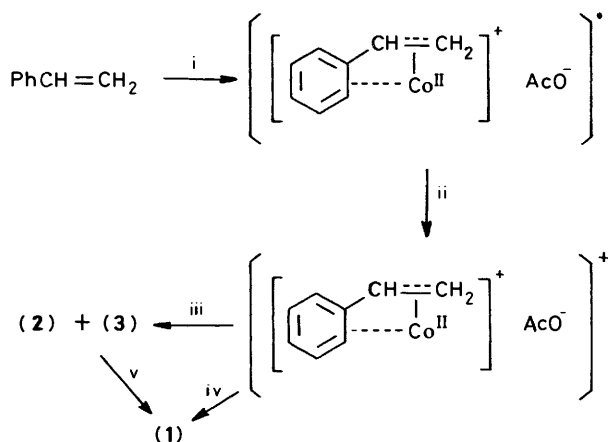
However the fact that the yields of (1), (2) and (3) did not parallel that of (5) as conditions changed, and indeed were much less sensitive to the presence of initiator or inhibitor or to changes in temperature, suggested that this heterolytic route had to be counterbalanced by one involving radicals. A number of possibilities were explored in an attempt to pin down this last process but none was particularly convincing. The only point which could be established with any confidence was that, given that autoxidation of the alkene to an epoxide did not occur to a



Scheme 4. Reagents: i,  $-\text{Pb}(\text{OAc})_2$ ,  $-\text{AcO}^-$ ; ii,  $\text{H}_2\text{O}$ ,  $-\text{H}^+$

significant extent, the incorporation of a hydroxy function under conditions in which water was not deliberately added to the solvent\* implied that the acetoxonium ion (6) must be an intermediate.

Recently Hirano and his co-workers reported that cobalt(III) in acetic acid converts styrene and related compounds to hydroxy acetates in good yield under relatively mild conditions.<sup>6,7</sup> Cobalt(III), unlike lead(IV), can only function as a one-electron oxidant. It seemed likely, therefore, that this conversion and the one-electron route identified in lead(IV) oxidations are one and the same. The mechanism proposed by Hirano (Scheme 5) for oxidation by cobalt involves  $\pi$ -



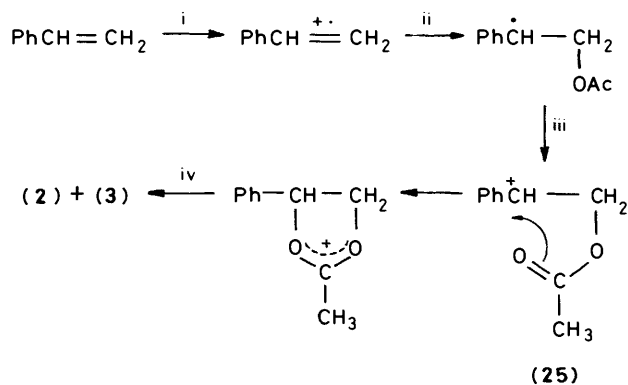
Scheme 5. Reagents: i,  $\text{Co}(\text{OAc})_3$ ; ii,  $\text{Co}(\text{OAc})_3$ ,  $-\text{Co}(\text{OAc})_2$ ,  $-\text{AcO}^-$ ; iii,  $\text{H}_2\text{O}$ ,  $-\text{Co}^{\text{II}}$ ; iv,  $\text{AcOH}$ ,  $-\text{Co}^{\text{II}}$ ; v,  $\text{AcOH}$ ,  $-\text{H}_2\text{O}$

complexation between the alkene and the metal atom followed by internal electron-transfer. However, whilst such complexes have frequently been invoked in the chemistry of cobalt<sup>8</sup> they are unknown in analogous lead systems. It seems unlikely too that competitive attack by water and by acetic acid (or acetate anion) on the complex would lead to the highly selective formation of hydroxy acetates at 70 °C [(2) + (3):(1), 71:0.9] given that the relative amounts of water to acid should not be greater than 1:100.

One property that cobalt(III) and lead(IV) share is that both can effect electron-transfer from aromatic substrates of suitably low ionisation potential with the formation of radical-cations.<sup>9,10</sup> In the case of lead(IV) the process is a chain reaction with lead(III) being the effective transfer agent. Aromatic radical-cations characteristically undergo nucleophilic attack.<sup>10</sup> One might postulate, therefore, that the route from alkenes to hydroxy acetates common to both cobalt(III) and lead(IV)

\* Acetic acid stirred under the reaction conditions for the appropriate time showed a water content of ca. 0.5% mol per mol.

systems involves a direct electron-transfer. The resultant alkene radical-cation would be expected to be attacked by nucleophiles selectively at C-2 to give the benzylic radical, oxidation of which would then lead, *via* the acetoxonium ion, to (2) and (3). The sequence is shown in Scheme 6 for lead(IV) and styrene.



Scheme 6. Reagents: i,  $^*\text{Pb}(\text{OAc})_3$ ,  $-\text{Pb}(\text{OAc})_2$ ,  $-\text{AcO}^-$ ; ii,  $\text{AcOH}$ ,  $-\text{H}^+$ ; iii,  $\text{Pb}(\text{OAc})_4$ ,  $-\text{Pb}(\text{OAc})_3$ ,  $-\text{AcO}^-$ ; iv,  $\text{H}_2\text{O}$ ,  $-\text{H}^+$

If the reaction does proceed through radical-cation intermediates there should be, as with aromatic substrates, a relationship between the ease of oxidation and the ionisation potential of the alkene. Some evidence in support of this view is provided by the report that aliphatic alkenes of ionisation potentials higher than styrene are not converted into hydroxy acetates on oxidation by cobalt(III).<sup>11</sup>

The possibility that alkene radical-cations might be formed readily under relatively mild homogeneous conditions led us to investigate in more detail these oxidations effected by metal ions. In particular, we wished to obtain evidence confirming the intermediacy of radical-cations. The results of the study are presented in this paper.

## Results and Discussion

Previous studies of the oxidation of aryl-substituted alkenes by metal ions have been carried out by different groups of workers using a variety of conditions. The first task therefore was to make a comparative study under constant conditions. In addition to lead(IV) and cobalt(III), manganese(III) was also employed as an oxidant. We are aware of only a single report of this last reagent converting alkenes into hydroxy acetates and then in a yield of only 1%.<sup>12</sup> In other respects though there is a close similarity between the organic chemistry of manganese(III) and of cobalt(III).

Comparative studies were carried out by oxidising 0.01 mol of alkene dissolved in 12.5 cm<sup>3</sup> of acetic acid with 0.02 mol of oxidant [0.01 mol in the case of lead(IV) which is able to transfer two electrons per mol of reagent] until all the oxidant had been consumed. The results from the oxidation of styrene are set out in Table 1. Reaction with lead(IV) gave the same products [(1)–(3), (5), (7), and benzaldehyde] as we reported earlier together with a small amount of phenacyl acetate (8). The cobalt(III) oxidation resulted in a very similar product distribution to that of Hirano *et al.* with the exception that we did not analyse for benzoic acid, a product which would be removed along with the solvent during work-up.

In comparing the reactions two points deserve comment. The first concerns the much greater yield of (1) relative to (2) + (3) when lead(IV) is the oxidant. Earlier we stated that the diacetate results from further reaction of the hydroxy acetates. Whilst

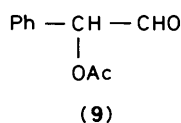
**Table 1.** Products from the oxidation of styrene by metal oxidants in acetic acid.

Oxidant	Temp (°C)	Time (h)	Products (% based on alkene)								
			PhCH=CH <sub>2</sub> (2) + (3)		(1)	(5)	(7)	(8)	PhCHO	PhCH(OAc) <sub>2</sub>	(11)
Pb(OAc) <sub>4</sub>	70	2	6.7	11	5.4	30	19.	2.7	5.1		
Co(OAc) <sub>3</sub>	70	2	0.8	77	1.9		0.7	0.9	4.1	4.7	
Mn(OAc) <sub>3</sub>	70	4	66						2.2		
Mn(OAc) <sub>3</sub>	118	2	0.3	1.4	0.4				11		17
Pb(OAc) <sub>4</sub> <sup>a</sup>	70	2	3.3	15	8.3	15	52	1.1	2.7		
Co(OAc) <sub>3</sub> <sup>a</sup>	70	2	13	79	2.0		0.2	0.4	0.8	0.4	

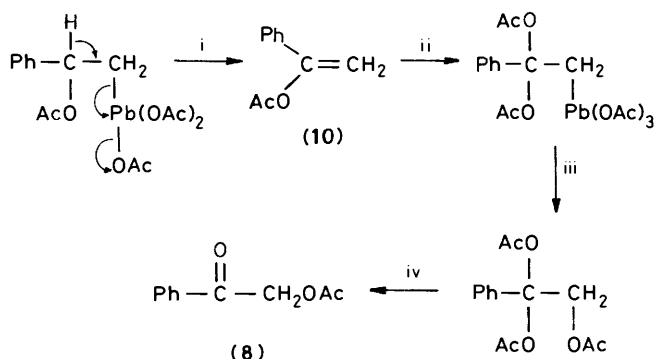
<sup>a</sup> Di-isopropyl peroxydicarbonate added.

reaction with the solvent is an obvious route, lead(IV) acetate is well known to convert alcohols into acetate esters even in the absence of acetic acid.<sup>13</sup> Presumably such a process is operating here.

The second point concerns the formation of the previously unidentified product (8) in the lead(IV) oxidation. Again, by analogy with the behaviour of alcohols,<sup>13</sup> this could result from the reaction of (2) with lead(IV) but, as the corresponding product (9) from (3) appears not to be formed, it seems unlikely



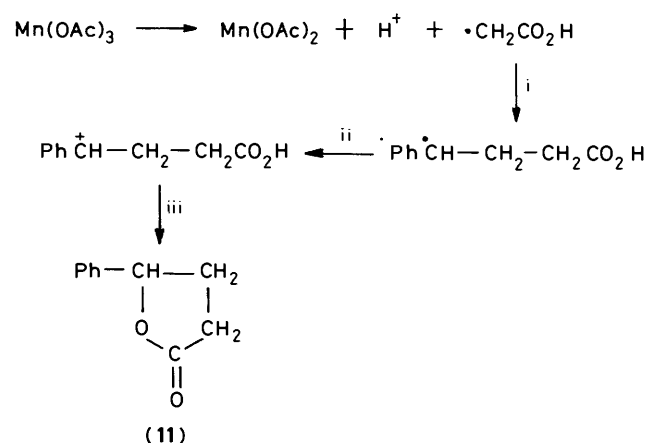
that this is an important process. In addition, a check experiment showed that the rate of conversion of a mixture of (2) and (3) into (8) was too slow to account for all the phenacyl acetate present. The compound seems most likely to arise in the lead(IV) reaction from oxidation of the enol acetate (10). Whilst this compound was not found amongst the products of oxidation of styrene, a competitive reaction showed it to be oxidised much faster than was styrene. There is an obvious route to (10) from the organolead adduct (4) (Scheme 7).



**Scheme 7.** Reagents: i, -Pb(OAc)<sub>2</sub>, -AcOH; ii, Pb(OAc)<sub>4</sub>; iii, -Pb(OAc)<sub>3</sub> iv, H<sub>2</sub>O, -2AcOH

Oxidation of styrene with manganese(III) under the same conditions gave no products other than a minor amount of benzaldehyde. The recovery of unchanged alkene was less than quantitative presumably because styrene slowly polymerises under these conditions. In an attempt to effect reaction a further experiment was carried out at reflux temperature. However, even under these more forcing conditions only traces of (1), (2),

and (3) were found, the major product being the lactone (11) formed as in Scheme 8. The result is perhaps not unexpected



**Scheme 8.** Reagents: i, PhCH=CH<sub>2</sub>; ii, Mn(OAc)<sub>3</sub>, -Mn(OAc)<sub>2</sub>, -AcO<sup>-</sup>; iii, -H<sup>+</sup>

since the reaction of alkenes with manganese(III) in carboxylic acid solvents has been suggested as a useful route to  $\gamma$ -lactones.<sup>12,14</sup> The low apparent conversion in our experiment can be explained partly by polymerisation of the styrene and partly by the fact that lactone formation is accompanied by production of other acidic, and therefore base-soluble, products resulting from addition of the carboxymethyl radical to the double bond.<sup>15</sup>

The results with manganese(III) pose two problems. The first is the different behaviour of manganese(III) and cobalt(III). We return to this point later. The second difficulty concerns the different radicals produced on thermal decomposition of manganese(III) acetate and lead(IV) acetate. In the former case a carboxymethyl radical is trapped by the alkene: in the latter a methyl radical. At the reflux temperature of acetic acid methyl radicals derived from lead(IV) acetate can abstract a hydrogen atom from the solvent to form carboxymethyl radicals<sup>16</sup> but the majority are still trapped by an alkene. Direct thermolysis of manganese(III) acetate to  $\cdot\text{CH}_2\text{CO}_2\text{H}$  would seem to be required<sup>14</sup> though the details are by no means clear.

The addition of a radical initiator, di-isopropyl peroxydicarbonate, to the lead(IV) system altered the balance of products significantly. Type 1 products were boosted at the expense of type 2 compounds whilst the yields of (1), (2), and (3) also rose confirming that they do result, at least in part, from a radical chain process. The mechanism outlined in Scheme 6 is a chain sequence providing lead(III) is the effective electron-transfer agent. In contrast, initiator has a negligible effect on the

course of the cobalt(III) oxidation as is to be expected of a sequence in which cobalt(III) must function as an electron-accepting species from both the alkene and from the benzylic radical.

At first sight manganese(III) behaves inconsistently in that it gives rise to very different products from cobalt(III). However, the former ion is the less efficient of the two at electron-transfer: Heiba and Dessau have estimated the ionisation potential of an aromatic substrate requires to be less than *ca.* 8 eV before radical cations are produced by this oxidant.<sup>17</sup> As the ionisation potential of styrene is 8.47 eV<sup>18</sup> the virtual absence of hydroxy acetate is perhaps not unexpected.

If our view is correct that a one-electron metal oxidant can effect electron-transfer from alkenes then we should find that, as the ionisation potential of the alkene falls, the proportion of product analogues of (1), (2), and (3) increases at the expense of the 'normal' radical product. Accordingly, we oxidised with manganese(III) three further aryl-substituted alkenes with ionisation potentials ranging from 8.35 eV down to 7.94 eV. The neutral products and their yields are presented in reactions (1)–(3). That the expected relationship between lactone and diol derivatives holds is shown clearly in the Figure and, we believe,

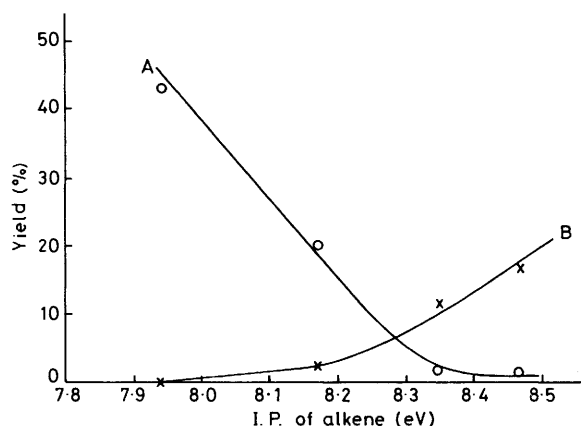
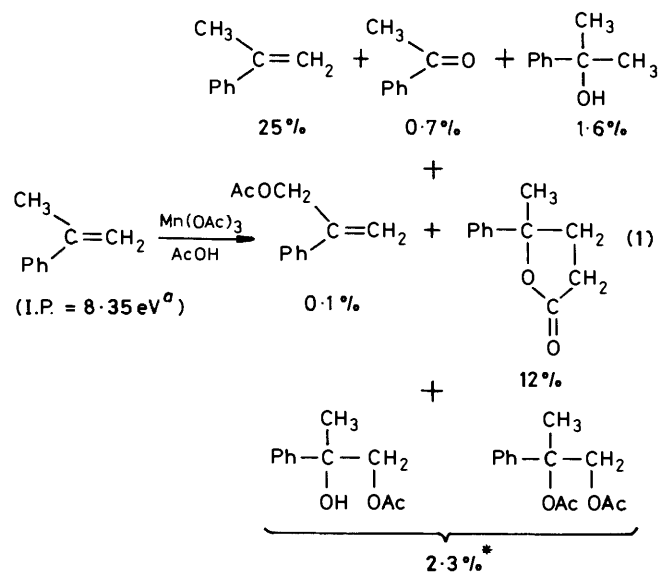


Figure. Yields of products from the oxidation of alkenes by manganese(III) as a function of ionisation potential: A, radical-cation product; B, lactone

provides convincing evidence that the hydroxy acetate adducts do stem from a radical-cation intermediate.

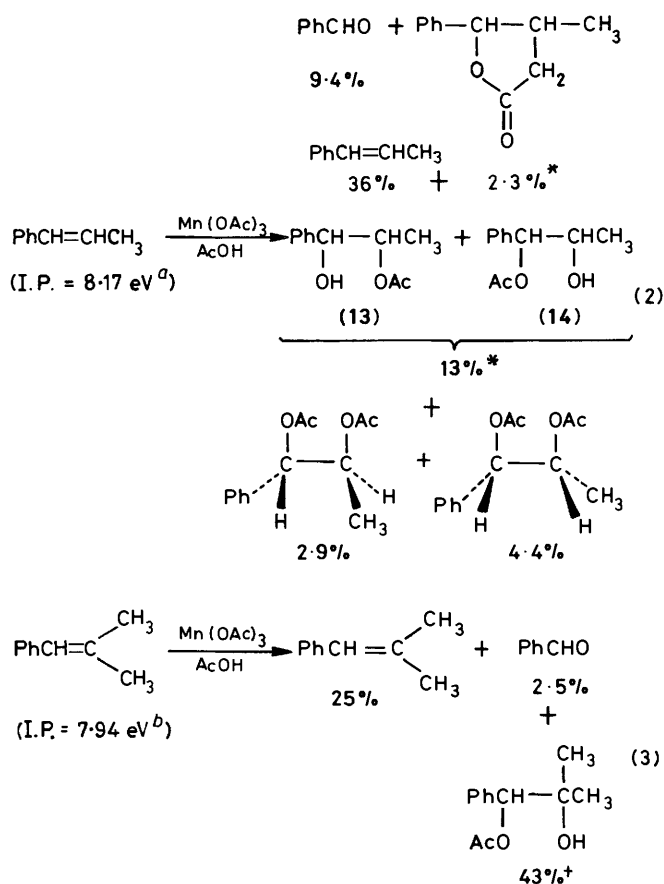
The yields cited in reactions (1)–(3) are not quantitative. This is particularly the case when  $\alpha$ -methylstyrene is the substrate. Part of the answer in reactions (1) and (2) is that a  $\gamma$ -lactone is not the only product of addition of the carboxymethyl radical to the double bond. Saturated, unsaturated, and acetoxy-substituted acids can be produced<sup>15</sup> and these would be lost on work-up. Another factor is likely to be telomerisation. Reaction required 2–2.5 h at 118 °C: certainly with  $\beta$ -methylstyrene there was evidence of polymeric material in the product.

That there is a value of the ionisation potential of an organic substrate above which are observed 'normal' radical products as opposed to those derived from a radical-cation, may explain the reports that simple alkenes, when oxidised with cobalt(III), do not give hydroxy acetates. Instead allylic acetates are formed.<sup>11,19</sup> These alkenes have all had ionisation potentials of 8.65 eV or greater.<sup>18,20</sup> This value may be too high for cobalt(III) to effect electron-transfer. The exception to this generalisation is  $\beta$ -methylstyrene for which both *E*- and *Z*-isomers are claimed to give cinnamyl acetate (12).<sup>6</sup> Since the mild oxidant, manganese(III) gives 1,2-adducts in reasonable yield with no more than a trace of cinnamyl acetate we repeated this



<sup>a</sup> Ref. 18.

\* The hydroxy acetate and diacetate were incompletely resolved by g.c. They were analysed together after conversion of the former into the latter using acetic anhydride. Only one regioisomer of the hydroxy acetate was present.



<sup>a</sup> Ref. 22. <sup>b</sup> I. Benito, H. Seidl, and H. Boch, *Rev. Fac. Cienc., Univ. Oviedo*, 1973, 14, 95.

\* The pairs of stereoisomers were unresolved by g.c.

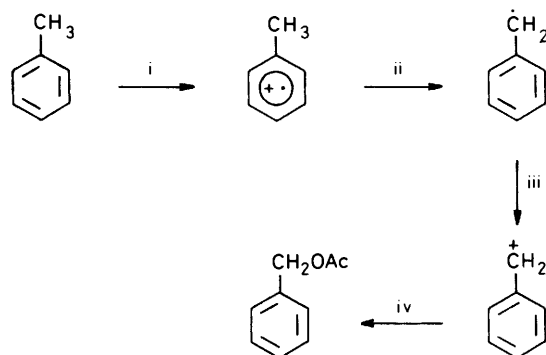
† Only one regioisomer was detected.

**Table 2.** Products from the oxidation of 2- and 4-methylstyrenes in acetic acid.

Alkene	Oxidant	Temp (°C)	Time (h)	Products (%)						
				(16 + (17))	(18)	(19)	(20)	(21)	(22)	(23)
4-Methylstyrene	Co(OAc) <sub>3</sub>	70	2	49	10	3.2	13	10	2.1	0.8
2-Methylstyrene	Co(OAc) <sub>3</sub>	70	2	63	4.5	0.3		8.2	0.4	
4-Methylstyrene	Mn(OAc) <sub>3</sub>	118	2	18	4.5	0.3		12		
2-Methylstyrene	Mn(OAc) <sub>3</sub>	118	2	19	14	0.2	1.9	10		

cobalt(III) oxidation. At 70 °C no reaction occurred over 5 days but at 95 °C cinnamyl acetate was indeed formed together with (13) and (14) and lesser amounts of the stereoisomeric diacetates. The only other significant product was benzaldehyde. It seems most unlikely that an alkene radical-cation would behave differently in two systems which are so similar. We suspect, therefore, that cinnamyl acetate is not derived from the radical-cation: a more prosaic origin could be hydrogen abstraction from the alkene by some radical in the system.<sup>21</sup>

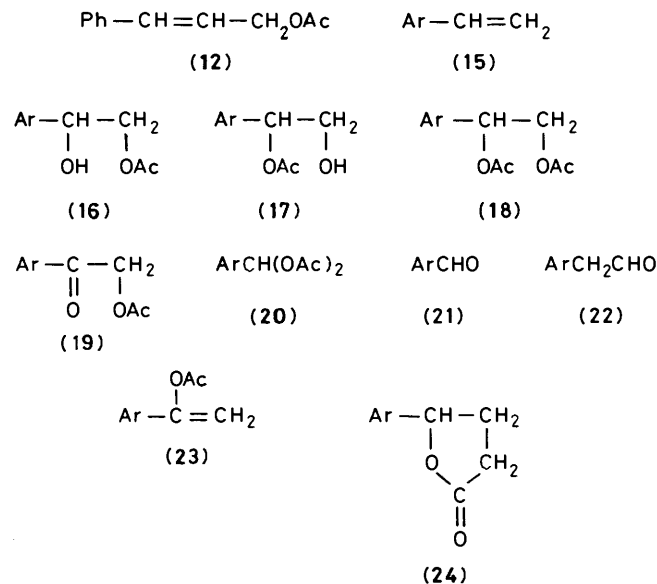
An aryl-conjugated alkene could, in theory, produce a radical-cation in which the electron-deficiency is delocalised over the aromatic ring as well as the double bond. Now radical-cations of benzene derivatives possessing alkyl groups on the ring characteristically lose a proton from the  $\alpha$ -position of the substituent leading to benzylic products (e.g. Scheme 9).<sup>9,10</sup> If

**Scheme 9.** Reagents: i, -e; ii, -H<sup>+</sup>; iii, -e; iv, AcOH, -H<sup>+</sup>

delocalisation occurs we might, therefore, expect an alkene such as 4-methylstyrene to form products substituted in the methyl group as well as hydroxy acetates from addition to the double bond.

Oxidation of (15; Ar = 4-MeC<sub>6</sub>H<sub>4</sub>) by cobalt(III) under the same conditions as styrene gave analogous products, viz. (16)—(23) (Ar = 4-MeC<sub>6</sub>H<sub>4</sub>). Their identities were confirmed by comparison of <sup>1</sup>H and <sup>13</sup>C n.m.r. and g.c.-mass spectrometric results with those of the products of styrene oxidation since authentic samples of the compounds were not all available. The yields set out in Table 2 have similarly been arrived at by extrapolation from those obtained with styrene. No trace was found of any product stemming from attack on the methyl group. Oxidation of (15; Ar = 2-MeC<sub>6</sub>H<sub>4</sub>) gave similar results: there was no evidence for benzylic substitution.

2- and 4-Methylstyrenes were also treated with manganese(III) at 118 °C. Both, unlike styrene itself, gave substantial amounts of hydroxy acetates and diacetates together with the lactone (24). Now, the ionisation potential of the 4-isomer is 8.12 eV,<sup>22</sup> below what appears to be the threshold value for radical-cation formation by this oxidant. The value for the 2-compound appears not to have been determined but would be expected to



be similar. It is very doubtful if the introduction into the aromatic ring of a substituent with such a weak electronic effect as a methyl group could cause a switch from one type of product to another if formation of the hydroxy acetate involved initial attack on the alkene by a short-lived reactive intermediate. However, the result can be explained well by invoking an electron-transfer mechanism.

Two other ring-substituted styrenes were oxidised. Both gave somewhat unexpected results. A chlorine atom on an aromatic ring, like a methyl group, has only a limited electronic effect on typical radical and ionic reactions. Nor does it alter much the ionisation potential of a substrate: 4-chlorostyrene has an ionisation potential of 8.45 eV compared with 8.47 eV for styrene itself.<sup>22</sup> The two alkenes might, therefore, be expected to behave similarly. This is indeed the case when lead(IV) is the oxidant: analogous products were obtained in broadly similar amounts. However, when oxidised with cobalt(III) the alkenes behaved very differently. 4-Chlorostyrene gave no (16), (17), or (18) (Ar = 4-ClC<sub>6</sub>H<sub>4</sub>). Instead a poor yield (15%) of (24; Ar = 4-ClC<sub>6</sub>H<sub>4</sub>) was obtained. This suggests that the radical-cation pathway has been completely repressed. Oxidation by manganese(III) gave no products detectable by g.c., the substrate being recovered in 91% yield.

We can offer no explanation for this failure of 4-chlorostyrene to behave as predicted with cobalt(III) and manganese(III). We speculated initially that co-ordination of the oxidant to the chlorine atom might be altering the electron-transfer ability of the metal ions but the addition of an equimolar amount of chlorobenzene to a styrene oxidation with cobalt(III) and with manganese(III) had a negligible effect upon product yields.

4-Methoxystyrene also behaved anomalously with manganese(III) but for a different reason. The ionisation potential of

this alkene (7.92 eV<sup>22</sup>) is sufficiently low for one to predict that little if any lactone would be formed. Rather, hydroxy acetates and diacetates are to be expected from the radical-cation route. Reaction with manganese(III) at 118 °C led to rapid reduction of the metal ion and the formation of 4-methoxybenzaldehyde (1%) and (**18**; Ar = 4-MeOC<sub>6</sub>H<sub>4</sub>) (29%); hydroxy acetates were absent. We do not believe that the rate of esterification of these last compounds differs greatly from (2) and (3). Rather we suspect that in this system an acetoxonium ion is not formed. The powerful electron donating mesomeric effect of a 4-methoxy group renders cyclization in the carbonium ion analogous to (**25**) (Scheme 6) energetically unfavourable. Instead nucleophilic attack by the solvent occurs directly on this species.

The relatively low yield of (**18**; Ar = 4-MeOC<sub>6</sub>H<sub>4</sub>) can be accounted for by the formation of polymer under the reaction conditions. The yield was enhanced when a solution of the alkene was added dropwise to ensure a minimal concentration of alkene at any one moment. We suspect that an alkene radical-cation may react readily with the very nucleophilic alkene to initiate telomerisation since similar problems arise in the lead(IV) oxidations by electron-transfer of benzene derivatives of low ionisation potentials.<sup>10,23</sup>

### Experimental

Gas chromatography was carried out on a Pye 104 instrument fitted with flame ionisation detector and columns (6 ft ×  $\frac{1}{8}$  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 or 4-ethylnitrobenzene were employed as internal standards. Preparative-scale gas chromatography 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. <sup>1</sup>H and <sup>13</sup>C N.m.r. spectra were recorded on a Varian EM360 or Jeol FX90 instrument, respectively, using deuteriochloroform as solvent. Melting points were determined on a Kofler micro-hot-stage and are uncorrected. Elemental analyses were by Butterworth Microanalytical Services (Teddington).

Lead(IV) acetate<sup>1</sup> and manganese(III) acetate dihydrate<sup>15</sup> were prepared for use as we have described previously. Cobalt(III) acetate was prepared by passing ozone (*ca.* 0.5 mmol min<sup>-1</sup>) through a solution of anhydrous cobalt(II) acetate (55 g) dispersed in acetic acid (350 cm<sup>3</sup>) containing acetic anhydride (25 cm<sup>3</sup>) for 24 h at a temperature of 40–50 °C. The dark green solution was cooled to room temperature and evaporated to dryness under reduced pressure. The green-black solid, cobalt(III) acetate (59 g, 80.5%) [cobalt(III) content estimated at 92%] was stored *in vacuo* over sodium hydroxide.<sup>24</sup>

The alkenes, styrene,  $\alpha$ -methylstyrene,  $\beta$ -methylstyrene,  $\beta$ , $\beta$ -dimethylstyrene, 2-methylstyrene, 4-methylstyrene, 4-chlorostyrene, and 4-methoxystyrene, were commercial samples (Aldrich and Koch-Light) distilled under reduced pressure before use. 4-Chlorostyrene could not be distilled without polymerisation and so was freed of inhibitor by washing an ethereal solution with dilute aqueous sodium hydroxide followed by removal of the solvent. The preparation of many of the products of oxidation has been described previously.<sup>1,2</sup> Others were obtained as follows.

**2-Hydroxy-2-methyl-1-phenylpropyl Acetate.**— $\beta$ , $\beta$ -Dimethylstyrene (4 g) and silver acetate (16.2 g) were vigorously stirred in acetic acid (115 cm<sup>3</sup>) containing water (1.2 cm<sup>3</sup>) and finely ground iodine (10.0 g) was added slowly. After 1 h at room temperature the mixture was heated at 100 °C for 4 h, cooled,

the silver iodide filtered off, and the solution reduced to *ca.* 10 cm<sup>3</sup> under reduced pressure. Water was added, and the product extracted with ether, the extracts washed with aqueous sodium carbonate and dried (MgSO<sub>4</sub>). After removal of the solvent the oil was distilled under reduced pressure to give 2-hydroxy-2-methyl-1-phenylpropyl acetate (3.2 g, 45%) as a colourless liquid, b.p. 115–117 °C at 1 mmHg (lit.,<sup>25</sup> b.p. 146–148 °C at 9 mmHg);  $\delta_{\text{H}}$  1.15 and 1.25 (6 H, 2 s, 2 × Me), 2.05 (3 H, s, OAc), 4.55 (1 H, s, removed by D<sub>2</sub>O, OH), 5.51 (1 H, s, CH), and 7.27 (5 H, s, ArH); *m/z* 165 (8%, *M* – MeCO), 148 (15, *M* – MeCO<sub>2</sub>H), 119 (70), 105 (100, PhCO<sup>+</sup>), 91 (67, C<sub>7</sub>H<sub>7</sub><sup>+</sup>), 77 (60, C<sub>6</sub>H<sub>5</sub><sup>+</sup>), and 43 (67, MeCO<sup>+</sup>).

**1-Phenylethenyl Acetate.**—This compound was prepared by the method of Hagemeyer and Hull.<sup>26</sup> Isopropenyl acetate (4.57 g) was refluxed with acetophenone (5.52 g) in the presence of 2 drops of concentrated sulphuric acid. The acetone formed was distilled off continuously and the residue distilled to give 1-phenylethenyl acetate (6.2 g, 83%) as a colourless liquid b.p. 83–84 °C at 2 mmHg (lit.,<sup>27</sup> 85 °C at 2 mmHg);  $\delta_{\text{H}}$  1.95 (3 H, s, OAc), 5.30 (1 H, m), and 5.02 (1 H, m) (=CH<sub>2</sub>), and 7.2 (5 H, s, ArH).

**1-Methyl-1-phenyl- $\gamma$ -butyrolactone.**— $\alpha$ -Methylstyrene (1.2 g), manganese(III) acetate (2.5 g), acetic acid (250 cm<sup>3</sup>), and acetic anhydride (12.5 cm<sup>3</sup>) were refluxed together for 45 min. The solvent was removed under reduced pressure and the resultant oil distilled to give 1-methyl-1-phenyl- $\gamma$ -butyrolactone (12.1 g, 69%) as a colourless liquid, b.p. 105 °C at 0.1 mmHg (lit.,<sup>28</sup> 89–92 °C at 0.04 mmHg);  $\delta_{\text{H}}$  1.70 (3 H, s, Me), 2.10–2.20 (2 H, m, COCH<sub>2</sub>CH<sub>2</sub>), 2.40–2.55 (2 H, m, CH<sub>2</sub>CO), and 7.25 (5 H, s, ArH).

**Cinnamyl Acetate.**—Cinnamyl alcohol (1.8 g) was heated at 80 °C in acetic anhydride (10 ml) for 2 h, acetic acid and anhydride were removed under reduced pressure, and the residue distilled to give cinnamyl acetate (1.8 g, 81%) as a colourless liquid, b.p. 114–116 °C at 2 mmHg (lit.,<sup>29</sup> 141 °C at 18 mmHg),  $\delta_{\text{H}}$  2.12 (3 H, s, OAc), 4.63 (2 H, d, *J* 6 Hz, CH<sub>2</sub>), 6.27 (1 H, d of d, *J* 6 Hz, *J'* 16 Hz, =CHCH<sub>2</sub>), and 6.64 (1 H, d, *J* 16 Hz, PhCH=), and 7.33 (5 H, br s, ArH).

**Oxidations.**—A typical oxidation was carried out as follows. To a solution of the oxidant [0.02 mol for cobalt(III) and manganese(III) acetate, 0.01 mol for lead(IV) acetate] in acetic acid (6.5 cm<sup>3</sup>) held at the appropriate temperature under nitrogen was added a solution of the alkene (0.01 mol) in acetic acid (6.5 cm<sup>3</sup>). Heating was continued until no oxidant remained when the solution was cooled, poured into water, extracted with ether, and the extracts were washed firstly with aqueous sodium carbonate and then with water. After drying (MgSO<sub>4</sub>) the solvent was removed and the residue analysed by n.m.r. and g.c.–mass spectroscopy.

Some lactones were isolated by preparative g.c. from the appropriate reaction product. These had the following spectral parameters: **1-phenyl- $\gamma$ -butyrolactone.**  $\delta_{\text{H}}$  0.8–1.4 (2 H, m, CH<sub>2</sub>CH<sub>2</sub>CH), 1.8–2.7 (2 H, m, CH<sub>2</sub>-CO), 5.23 (1 H, d of d, *J* = *J'* = 7 Hz, CH), and 7.19 (5 H, s, ArH); *m/z* 162 (13%, *M*<sup>+</sup>), 161 (42, *M* – H), and 85 (100, *M* – Ph); **2-methyl-1-phenyl- $\gamma$ -butyrolactone.**  $\delta_{\text{H}}$  0.61 (d, *J* 7 Hz) and 1.11 (d, *J* 6 Hz) (3 H, CH<sub>3</sub> of *cis*- and *trans*-isomers respectively), 1.88–2.93 (3 H, m, CHCH<sub>2</sub>), 4.78 (d, *J* 8 Hz), and 5.43 (d, *J* 6 Hz) (1 H, PhCH of *trans*- and *cis*-isomers respectively); *m/z* 176 (11%, *M*<sup>+</sup>), 175 (20, *M* – H), 99 (100, *M* – Ph).

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