Oxidation by Cobalt(III) Acetate. Part 10.[1] Effects of Ring Substituents on the Product Distributions in the Oxidation of β-Methylstyrenes by Cobalt(III) Acetate in Acetic Acid

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The oxidation of ring-substituted β-methylstyrenes by cobalt(III) acetate in acetic acid has been studied by product analysis and the relative rates were measured by a competition method. Electron-releasing groups (*p*-MeO, *p*-Me, and *p*-Bu^t) accelerated both the reaction rate and the formation of glycol monoacetates, while electron-withdrawing groups (*p*-Cl and *m*-Cl) not only retarded the reaction but also favoured the formation of allylic acetate instead of glycol monoacetate. The good relationship of relative rates with σ^+ in the Hammett plot showed that both products were derived from the same intermediate. The reaction mechanism is discussed in connection with the stabilities of radical cations formed by a one-electron transfer from the olefins to cobalt(III) acetate.

Cobalt(III) acetetate is an important catalyst in the commercial production of terephthalic acid by the autoxidation of *p*-xylene[2] and also a potential oxidant of organic compounds under nitrogen.[2,3]

We described in our previous papers that the oxidation of olefins by cobalt(III) acetate in acetic acid under nitrogen generally gave both glycol monoacetates and allylic acetates and that the ratios of these products depended on the structures of the olefins but not on the reaction conditions. Only allylic acetates were chemoselectively obtained in good yields in the oxidations of aliphatic and alicyclic compounds.[4–6] Glycol monoacetates were the only products in those of aromatic and aliphatic olefins which have no allylic hydrogen.[7–10] Compared with these cases, the oxidation of aromatic olefins bearing an active allylic hydrogen gave both products and the product ratios changed with the structure of olefins;[11] more methyl and/or phenyl groups in the olefin results in more glycol monoacetates and less allylic acetate being obtained. These phenomena were well interpreted in terms of the stabilities of radical cation intermediates which were generated by a one-electron transfer from olefins to cobalt(III) acetate.[12–14]

The stability of a radical cation can be changed by ring substituents in aromatic olefins. Thus, a series of ring-substituted β-methylstyrenes were oxidized with cobalt(III) acetate and the product distributions were examined.

Results

Product Study.—1-(*p*-Methoxyphenyl)prop-1-ene (anethole) (**1a**) was treated with cobalt(III) acetate in acetic acid under nitrogen at room temperature. A mixture of 2-acetoxy-1-(*p*-methoxyphenyl)propan-1-ol (**2a**) and 1-acetoxy-1-(*p*-methoxyphenyl)propan-2-ol (**3a**) was obtained together with a small amount of *p*-anisaldehyde. Elevation of the temperature, prolonged reaction, and an increase in concentration of cobalt(III) acetate resulted in decreasing glycol monoacetates and increasing *p*-anisaldehyde. Similar phenomena were observed for the oxidations of all olefins used in the present study. G.l.c. analysis showed no peaks over 1% of the products except the mixture of (**2a**) and (**3a**), recovered olefin, and *p*-anisaldehyde. Hence, if allylic oxidation occurred during the reaction, it should be < 1% of glycol monoacetates.

Since (**2a**) and (**3a**) could not be separated because of an equilibrium between them as judged from the n.m.r. spectra (see Experimental section),[8,11,15] they are estimated together. The same method of estimation is used for the yields of glycol monoacetates in the oxidation products of every olefin.

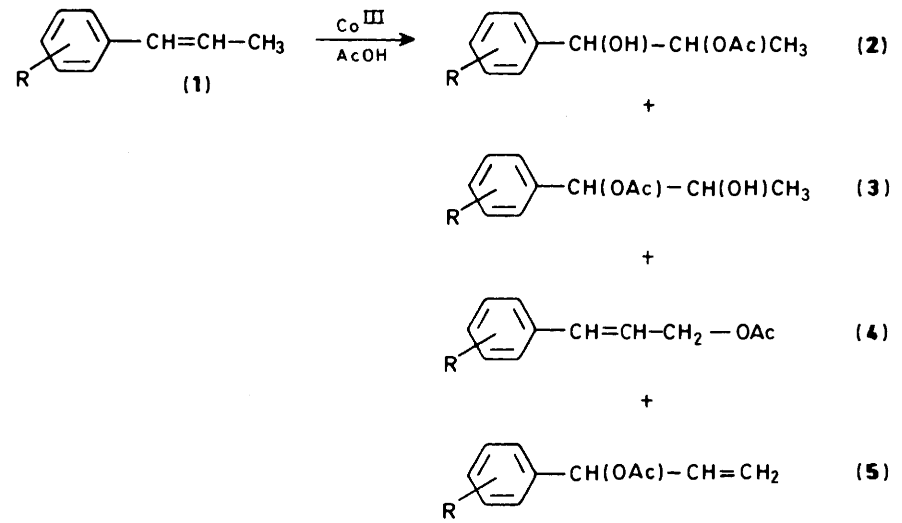
1-(*p*-Methylphenyl)prop-1-ene (**1b**) was oxidized as described above. The reaction gave exclusively a mixture of 2-acetoxy-1-(*p*-methylphenyl)propan-1-ol (**2b**) and 1-acetoxy-2-(*p*-methylphenyl)propan-2-ol (**3b**) with *ca.* 3% of allylic acetate (**4b**) and a trace of *p*-methylbenzaldehyde.

The oxidation of 1-(*p*-t-butylphenyl)prop-1-ene (**1c**) with cobalt(III) acetate in acetic acid gave a mixture of 2-acetoxy-1-(*p*-t-butylphenyl)propan-1-ol (**2c**) and 1-acetoxy-1-(*p*-t-butylphenyl)propan-2-ol (**3c**) with *p*-t-butylcinnamyl acetate (**4c**) and a trace of *p*-t-butylbenzaldehyde. The main product was still the mixture of (**2c**) and (**3c**) but allylic oxidation increased substantially as shown in Table 1.

1-(*p*-Chlorophenyl)prop-1-ene (**1e**) was oxidized as well to give a mixture of 2-acetoxy-1-(*p*-chlorophenyl)propan-1-ol (**2e**) and 1-acetoxy-1-(*p*-chlorophenyl)propan-2-ol (**3e**), *p*-chlorocinnamyl acetate (**4e**), and 1-(*p*-chlorophenyl)allyl acetate (**5e**). Compounds (**4e**) and (**5e**) were isolated from the reaction mixture, but glycol monoacetates [(**2e**) + (**3e**)] were not obtained, perhaps due to the low yield. Hence, the presence of the glycol monoacetates was established by comparison of the g.l.c. retention times of the reaction mixture with those of independently prepared glycol monoacetates. The total yield of (**4e**) and (**5e**) surpassed that of glycol monoacetates in opposition to the results of the oxidation of aromatic olefins bearing electron-donating groups on the aromatic ring.

1-(*m*-Chlorophenyl)prop-1-ene (**1f**) was treated as well to give two products. They were found to be *m*-chlorocinnamyl acetate (**4f**) and 1-(*m*-chlorophenyl)allyl acetate (**5f**) by ^{1}H n.m.r. and i.r. spectra. No glycol monoacetates could be found in the reaction mixture and this was confirmed by comparison of the g.l.c. retention times of the reaction mixture with those of authentic samples prepared by another method. Any attempts to obtain the glycol monoacetate were unsuccessful. These results show that the yield of glycol monoacetate is < 0.5%.

Relative Rates.—The relative rates of oxidation were determined by competition reaction methods. Almost equimolar



a; R = *p*-CH$_3$O, b; R = *p*-CH$_3$, c; R = *p*-(CH$_3$)$_3$C
d; R = H, e; R = *p*-Cl, f; R = *m*-Cl

Table 1. The oxidation of 1-arylpropenes by cobalt(III) acetate in acetic acid

X	[Olefin]$_0$/ mol dm^{-3}	[Co^{III})]$_0$/ mol dm^{-3}	Temp. (°C)	Time (h)	Recovered olefin %	Diol (%)[a]	Allylic acetates (%)[b]	Allylic acetates (%)[c]
p-MeO	0.116	0.232	R.t.	0.5	22	60	0	0
	0.116	0.232	R.t.	4	4	70	0	0
Me	0.121	0.240	60	0.5	38	54	<3	0
	0.063	0.135	60	8	14	68	<3	0
p-Bu^t	0.117	0.230	60	0.7	40	36	12	<1
	0.117	0.230	60	4	13	48	12	<1
cis-H	0.114	0.284	60	4	45	8.5	26	4.5
trans-H	0.116	0.291	60	4	38	11	25	5
p-Cl	0.127	0.254	60	4	45	9	15	9
	0.127	0.254	60	12	35	15	24	11
m-Cl	0.124	0.248	60	1	79	0	8	5
	0.124	0.248	60	48	40	0	24	15

[a] Mixture of glycol monoacetates. [b] Cinnamyl acetate. [c] Allyl acetate.

Table 2. The relative rates of the oxidation of 1-arylpropenes in acetic acid for 30 min[a] at 60 °C

Substituent (X)	log(k_X/k_H)		σ^+
p-MeO	2.024	2.019	−0.764
	2.013		
p-Me	0.606	0.645	−0.306
	0.665		
	0.665		
p-Cl	−0.347	−0.314	0.112
	−0.332		
	−0.282		
m-Cl	−0.608	−0.618	0.391
	−0.554		
	−0.691		

[a] 10 min for the reactions involving *p*-methoxy derivatives.

amounts of two olefins were treated with cobalt(III) acetate in acetic acid under nitrogen for 30 min [or for 10 min for reaction involving (**1a**)]. After work-up, the amounts of each olefin remaining were determined by g.l.c. analysis. On the assumption that the oxidation rates of olefins by cobalt(III) acetate is proportional to the concentration of olefins,[16,17] the relative rates of the oxidation are given by equation (1) where $[S^1]_0$ and

$$k_1/k_2 = \ln[S^1]/[S^1]_0/\ln[S^2]/[S^2]_0 \qquad (1)$$

$[S^1]$ are the initial and final concentrations of olefin 1 and $[S^2]_0$ and $[S^2]$ are the initial and final concentrations of olefin 2, respectively.

The results of the relative rates for the five olefins are presented in Table 2. Here, the relative rate, $k_{(1a)}/k_{(1d)}$, was obtained by multiplying the value of $k_{(1a)}/k_{(1b)}$ by that of $k_{(1b)}/k_{(1d)}$, since the reaction of (**1a**) was too fast to compare with that of (**1d**).

The logarithms of these relative rate constants were plotted against σ^{18} and σ^+ values (Figure).[19] The best Hammett correlation was obtained with the σ^+ values of Brown and Okamoto[19] which gave a ρ −2.34.

Discussion

We have already reported that the oxidation of olefins by cobalt(III) acetate gave allylic acetates and glycol monoacetates and the highly substituted olefins favoured the formation of glycol monoacetate and the less substituted olefins favoured the formation of allylic acetate.[11] In order to explain the facts, we suggested the mechanism illustrated in the Scheme, in which the stabilities of radical cations play an important role in the determination of products.[4b]

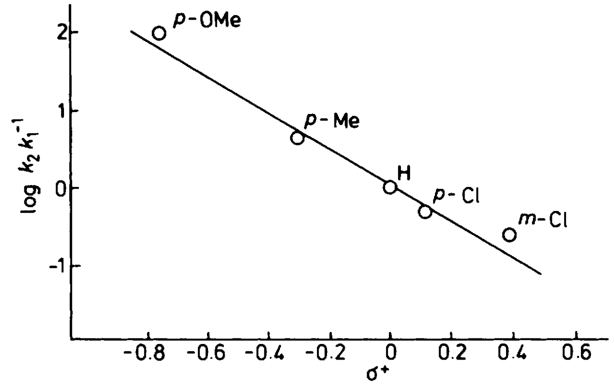
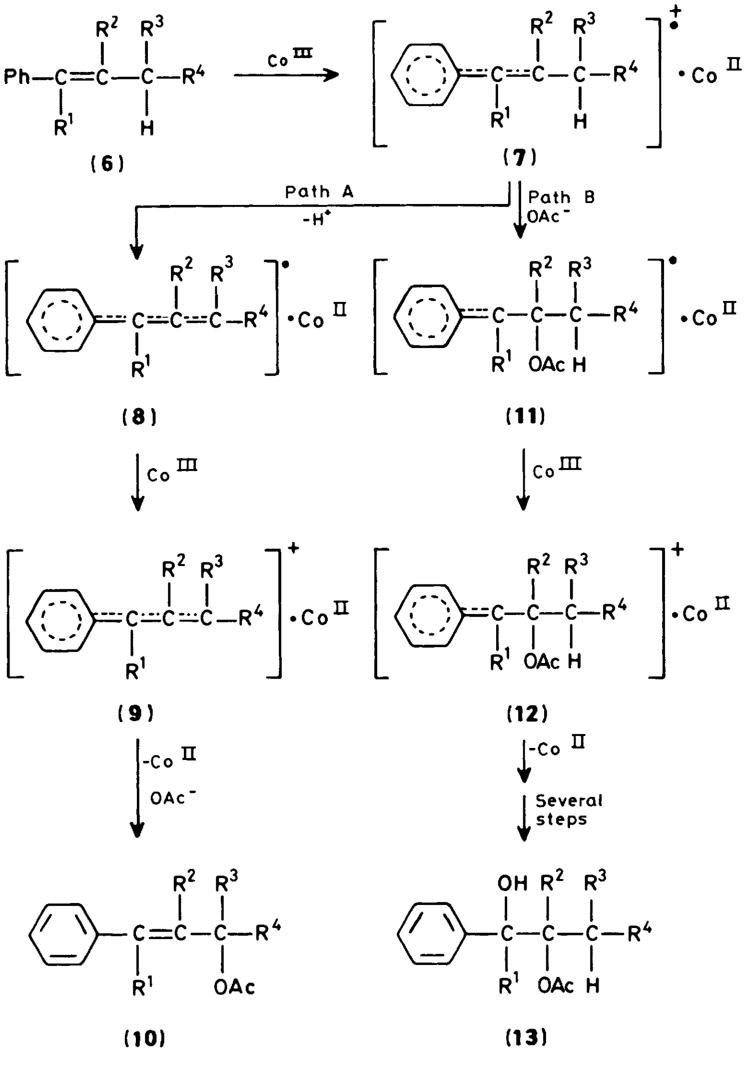


Figure. The Hammett plot of the relative rates with σ^+ at 60 °C

and no allylic acetate was found in the reaction mixture. The oxidation of (**1b**) gave predominantly glycol monoacetates but in this case a small percentage of allylic acetate was found. When the *p*-t-butyl group was introduced into the aromatic ring, considerable amounts of allylic acetate were obtained together with the main product, glycol monoacetates.

On the other hand, non-substituted and electron-withdrawing groups favoured the formation of allylic acetate although the rates of the reaction were much slower. In the oxidations of (**1d** and **e**), allylic acetates were the main product together with a relatively small amount of glycol monoacetates. Furthermore, the introduction of an *m*-chloro group into the benzene ring of β-methylstyrene diminished the formation of glycol monoacetates and only allylic acetates were obtained. These results show that when the electron density at the double bond of the olefins are high, oxidative 1,2-addition is favourable and when it is low, allylic oxidation is favoured, although the order of increasing allylic acetates was reversed between (**1d** and **e**).



Scheme

A similar radical cation mechanism has been suggested for the oxidation of aromatic olefins to diacetates by persulphate ion catalysed by copper(II) ion.[20]

The results of the present study support the mechanism in the Scheme. There is no doubt that the electron-releasing groups on benzene ring accelerated the formation of glycol monoacetate. Only glycol monoacetates were obtained in the oxidation of (**1a**)

Radical cation formed by a one-electron transfer from an olefin to cobalt(III) acetate can be stabilized by electron-donating groups with the reduction of positive charge at the radical cation centre. In this case, the radical cation can be present for a longer time without the departure of allylic hydrogen. Therefore, there is enough time for the radical cation to react with acetate ion [probably, a ligand of cobalt(III) acetate], giving glycol monoacetates (path A).

On the other hand, electron-withdrawing groups make the radical cation unstable by pulling electron out of the centre. In this case, the radical cation tends to split off an allylic proton or to be removed by some basic species (perhaps AcO^- in the oxidant) to form an allylic radical since the latter is more stable than the former because of prolonged conjugation, eventually giving allylic acetate (path **B**).

The same explanation was offered for the oxidations of highly substituted aromatic olefins by cobalt(III) acetate, in which substitution by methyl and/or phenyl at the double bond accelerated the formation of glycol monoacetates.[11] In conclusion, which products, allylic acetate or glycol monoacetates, are obtained depends largely on the stabilities of the intermediate radical cations, in other words, the structure of the parent olefins.

If the reaction proceeds through the mechanism in the Scheme and the rate-determining step is electron abstraction from olefin by cobalt(III) acetate (it may be so), the oxidation rates of olefins by the oxidant should be influenced only by the electron density of the olefinic double bond. There may be no relationship between the rate and the product since the product ratio is determined after the rate-determining step. The electron density at double bond can be changed by the substituents on the aromatic ring and thus the relative rates were measured using a series of substituted β-methylstyrenes. Since Hammett substituent constants are a measure of changes in electron density, the rates of oxidation can be correlated with the constants.

As shown in the Figure, a plot of the logarithms of relative rates *versus* σ^+ gave a good straight line with ρ -2.34. This linear relationship supports the mechanism in which both allylic acetates and glycol monoacetates were obtained from the same intermediate radical cation.

Similar relatively large ρ values were obtained in the oxidation of toluenes by cobalt(III) acetate,[12] in the oxidative decarboxylation of phenylacetic acid by cobalt(III) acetate[21] and by cerium(IV) ammonium nitrate,[22] and in the autoxidation of toluenes catalysed by cobalt(III) acetate.[23] These reactions were considered to proceed through a radical cation intermediate. The similar ρ value for the present reaction strongly suggests the presence of a radical cation intermediate.

Experimental

^{1}H N.m.r. spectra were measured for solutions in CCl_4 or $CDCl_3$ on a JEOL model PMX-60 spectrometer. I.r. spectra were recorded for liquid films on a JASCO DS-403G spectrophotometer. G.l.c. was carried out on Shimadzu GC-6A and GC-4C instruments with a 2 m glass column packed with 5% PEG-20M on Chromosorb W-DMCS or a 2 m glass column packed with 1% Silicone OV-17 on Chromosorb W-DMCS. For the determination of product distributions, appropriate internal standards were used. Preparative g.l.c. was performed on a Shimadzu GC-4A instrument with a 2 m stainless steel column packed with 30% PEG-20M or 30% Silicone SE-30 on Celite 545, attached to a Shimadzu APP-5 fraction collector through a heated glass joint.

Starting Materials.—Cobalt(III) acetate was prepared by the method described previously.[1] Anethole [1-(*p*-methoxyphenyl)-prop-1-ene] (**1a**) was commercially available. Ring-substituted olefins were prepared by the dehydrations of the corresponding 1-arylpropanols obtained by reduction of propiophenones over potassium hydrogensulphate under reduced pressure.[24] 1-(*p*-Methylphenyl)prop-1-ene (**1b**) had b.p. 97—98 °C at 30 mmHg; $\delta(CCl_4)$ 1.8 (d, 3 H), 2.3 (s, 3 H), 5.6—6.7 (m, 2 H), and 7.2 (s, 4 H). 1-(*p*-t-Butylphenyl)prop-1-ene (**1c**) had b.p. 123—125 °C at 18 mmHg; $\delta(CCl_4)$ 1.2 (s, 9 H), 1.9 (d, 3 H), 5.6—6.8 (m, 2 H), and 7.2 (s, 4 H). 1-Phenylprop-1-ene (**1d**) had b.p. 97 °C at 30 mmHg. 1-(*p*-Chlorophenyl)prop-1-ene (**1e**) had b.p. 105—107 °C at 25 mmHg; $\delta(CCl_4)$ 1.8 (d, 3 H), 5.6—6.7 (m, 2 H), and 7.1 (s, 4 H). 1-(*m*-Chlorophenyl)prop-1-ene (**1f**) had 104—105 °C at 23 mmHg; $\delta(CCl_4)$ 1.8 (d, 2 H), 5.6—6.7 (m, 2 H), and 7.0 (s, 4 H).

Reference Compounds.—All the products, except for mixtures of (**2e**) and (**3e**) and (**2f**) and (**3f**), were obtained by the reaction of parent olefins with cobalt(III) acetate as follows.

Olefins were treated with cobalt(III) acetate ($[\text{olefin}]_0/[\text{Co}^{\text{III}}]_0 = 1/2.4 - 1/4$) in acetic acid under nitrogen. The mixture was poured into water and extracted with ether. The ethereal solution was washed successively with water, 10% aqueous sodium carbonate, and water, and then dried (Na_2SO_4). After filtration, the ether was evaporated on a rotary evaporator to leave an oil which was chromatographed on silica gel (a 7:3 mixture of n-hexane and ethyl acetate).

A mixture of 2-acetoxy-1-(*p*-methoxyphenyl)propan-1-ol (**2a**) and 1-acetoxy-1-(*p*-methoxyphenyl)propan-2-ol (**3a**):[25] $\delta(CDCl_3)$ 1.0 (d, 3 H), 2.1 (s, 3 H), 3.2 (s, 1 H), 3.8 (s, 3 H), 4.0—5.6 (m, 2 H), and 7.1 (s, 3 H); $\nu_{max.}$ (liquid film, cm^{-1}) 3 450 (OH) and 1730 cm^{-1} (C=O). Several peaks assignable to two hydrogens at C-1 and -2 were observed in the range δ 4.0—5.6, showing the presence of an equilibrium between (**2a**) and (**3a**). Similar spectra were obtained in the case of other glycol monoacetates (**2b**—**e**) and (**3b**—**e**). Complex n.m.r. spectra at δ 4—6 were observed in the case of glycol monoacetates derived from 1-phenylbut-1-ene, 3-methyl-1-phenylbut-1-ene, and 2-methyl-3-phenylbut-2-ene.[11]

The mixture of 2-acetoxy-1-(*p*-methylphenyl)propan-1-ol (**2b**) and 1-acetoxy-1-(*p*-methylphenyl)-propan-2-ol (**3b**) showed $\delta(CDCl_3)$ 1.1 (d, 3 H), 2.0 (s, 3 H), 2.4 (s, 3 H), 3.9 (s, 1 H), 4.4—5.5 (m, 2 H), and 7.2 (s, 4 H); $\nu_{max.}$ (liquid film) 3 450 (OH) and 1 720 cm^{-1} (C=O). The mixture of 2-acetoxy-1-(*p*-t-butylphenyl)propan-1-ol (**2c**) and 1-acetoxy-1-(*p*-t-butylphenyl)propan-2-ol (**3c**) showed $\delta(CDCl_3)$ 1.2 (d, 3 H), 1.4 (s, 9 H), 2.1 (s, 3 H), 4.3 (s, 1 H), 4.5—5.5 (m, 2 H), and 7.2 (s, 4 H); $\nu_{max.}$ (liquid film) 3 450 (OH) and 1 730 cm^{-1} (C=O). *p*-t-butylcinnamyl acetate (**4c**) gave $\delta(CCl_4)$ 1.4 (s, 9 H), 2.1 (s, 3 H), 4.8 (d, 2 H), 6.2—6.9 (m, 2 H), and 7.2 (s, 4 H); $\nu_{max.}$ (liquid film) 1 730 cm^{-1} (C=O). *p*-Chlorocinnamyl acetate (**4e**) had $\delta(CCl_4)$ 2.0 (s, 3 H), 4.6 (d, 2 H), 6.1—6.8 (m, 2 H), and 7.1 (s, 4 H). 1-(*p*-Chlorophenyl)allyl acetate (**5e**) had $\delta(CCl_4)$ 2.3 (s, 3 H), 5.35 (d, 2 H), 6.0 (m, 2 H), and 7.1 (s, 4 H). *m*-Chlorocinnamyl acetate (**4f**) afforded $\delta(CCl_4)$ 2.1 (s, 3 H), 4.7 (d, 2 H), 6.4 (m, 2 H), and 7.1 (s, 4 H). 1-(*m*-Chlorophenyl)allyl acetate (**5f**) had $\delta(CCl_4)$ 2.1 (s, 3 H), 5.2 (m, 2 H), 5.9 (m, 2 H), and 7.1 (s, 4 H).

Mixtures of (**2e**) and (**3e**)[15] and (**2f**) and (**3f**)[26] were prepared by known methods. The mixture of 2-acetoxy-1-(*p*-chlorophenyl)propan-1-ol (**2e**) and 1-acetoxy-1-(*p*-chlorophenyl)-propan-2-ol (**3e**) showed $\delta(CDCl_3)$ 1.0 and 1.2 (d, total 3 H), 2.1 (s, 3 H), 2.8 (s, 1 H), 4.0—5.7 (m, 2 H), and 7.1 (s, 4 H). The mixture of (**2f**) and (**3f**) and their acetates had retention times on g.l.c. which did not agree with those of the reaction mixture of (**1f**) with cobalt(III) acetate. Thus, they were not further purified.

Product Distributions.—A typical procedure was as follows. Weighed β-methylstyrene was mixed with cobalt(III) acetate in acetic acid (5 cm^3) in a flask. After flushing with nitrogen, the flask was kept at constant temperature for a given time in a thermostat. An internal standard was added and the mixture was poured into water (30 cm^3) and the product was extracted with ether (10 cm^3 × 3). The combined ethereal solution was washed with brine, aqueous sodium carbonate, and brine and then dried (Na_2SO_4). After filtration, the solution was condensed on a rotary evaporator to leave a pale yellow oil, which was analysed by g.l.c.

Glycol monoacetates could not be well separated from cinnamyl acetate by g.l.c. analysis of the sample obtained above, and the quantitative analysis was performed by acetylation of the original sample. The sample was mixed with acetic anhydride and sodium acetate in a flask and was refluxed for 12 h. The same procedure was employed as described above to give the acetylated sample, which was analysed by g.l.c.

Competition Reactions.—Combinations of *p*-methoxy and *p*-methyl, *p*-methyl and unsubstituted, unsubstituted and *p*-chloro, and unsubstituted and *m*-chloro derivatives were used for the determination of relative rates. Typical procedures are as follows. 1-Phenylprop-1-ene in acetic acid (0.0263 mol dm^{-3}, 2 cm^3) and 1-*p*-methylphenyl)prop-1-ene (0.0263 mol dm^{-3}, 2 cm^3) were mixed with cobalt(III) acetate (0.2043 mol dm^{-3}, 1 cm^3) in acetic acid in a flask. After flushing with nitrogen, the flask was maintained at 60 °C for 30 min (10 min for the reaction of the *p*-methoxy derivative). After an internal standard was added, the same procedures for the determination of product distributions were employed.

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