Oxidation of p-Methoxytoluene by Manganese(III) and Iron(III) Acetates in the Presence of Strong Acid

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In contrast to the oxidation of various alkylbenzenes with manganese(III) acetate in acetic acid containing strong acid (e.g. $HClO_4$, CF_3SO_3H, or H_2SO_4), where diarylmethanes are almost the only products, a similar treatment of p-methoxytoluene afforded biaryls as the main products. In the presence of less strong acids such as CF_3CO_2H or CCl_3CO_2H, or a low concentration of $HClO_4$, however, diarylmethanes are mainly obtained. On the other hand, with iron(III) acetate diarylmethanes are almost the only products even in the presence of strong acid, as has been observed with other alkylbenzenes. The different behaviour between the metal acetates is explained by assuming a considerable difference in the stability of an oxygen-centred trinuclear species which works as a base to remove a proton from a radical-cation intermediate.

IT has recently been reported that alkylbenzenes are oxidized readily by various metal acetates such as manganese(III), iron(III), cobalt(III), and lead(IV), in acetic acid in the presence of a strong acid such as perchloric or trifluoroacetic, to give diarylmethanes very selectively.[1] When p-methoxytoluene was used as a substrate in these systems, however, it was observed that both biaryls and diarylmethanes were formed, the ratio depending on the kind and/or the concentration of the metal acetates and the acid added. Here we describe these results, focusing on the reactions using manganese(III) and iron(III) acetates. Previously, Norman et al. have reported the formation of both biaryls and diarylmethanes in the reactions of methyl-substituted benzenes with lead(IV) and cerium(IV) salts in trifluoroacetic acid, the product ratio being very dependent on the reaction conditions.[2]

RESULTS AND DISCUSSION

Treatment of p-methoxytoluene with various metal acetates in acetic acid containing perchloric acid (0.4M)
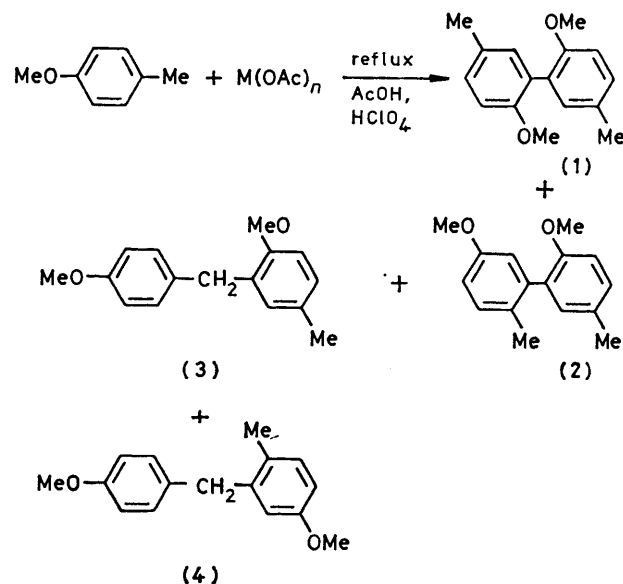
under nitrogen at reflux temperature afforded biaryls [as a mixture of (1) and (2)] and diarylmethanes [as a mixture of (3) and (4)], the ratio depending markedly on the metal salts used. Thus with magnanese(III), cobalt(III), or lead(IV) acetate biaryls are the main products, while with iron(III) or copper(II) acetate diarylmethanes are almost the only products (Table 1). For

TABLE 1

Reaction of p-methoxytoluene with various metal acetates in acetic acid containing perchloric acid (0.4M) [a]

Metal acetate [b]	Products and yields (mmol) [c]		
	(1) + (2)	(3)	(4)
Mn	0.75	0.08	0.04
Fe	Trace	0.88	0.17
Cu	Trace	0.58	0.06
Co	0.28	0.03	0.01 [d]
Pb	0.38	0.05	0.01 [d]
Tl	Trace	0.08	0.09 [e]

[a] At reflux temperature for 3 h under N_2; metal acetate 1 mmol, p-methoxytoluene 40 mmol, 70% perchloric acid 6 mmol, AcOH 10 ml. [b] Mn and Co: [{$M_3O(OAc)_6(AcOH)_3$}OAc]; Fe: [{$Fe_3O(OAc)_6(H_2O)_3$}OAc]; Cu: $Cu(OAc)_2$; Pb: $Pb(OAc)_4$; Tl: $Tl(OAc)_3$. [c] Determined by g.l.c. analysis. Since 1 mmol of cluster metal acetate (Mn, Fe, Co) seems to give 3 mmol of M^{n+} in these acidic conditions and 2 M^{n+} are required to oxidize two p-methoxytoluene to give one (1), (2), (3), or (4), 1.5 mmol of each correspond to 100% yield. [d] Small amounts of p-cresol and p-cresyl acetate was formed. [e] Other products; p-cresol 1.64 mmol, p-cresyl acetate 0.26 mmol.

other alkylbenzenes examined the formation of biaryls has rarely been observed under these conditions using any of these metal salts.[1]

In the light of the data shown in Table 1, manganese(III) and iron(III) acetates are the most efficient salts for the formation of biaryls and diarylmethanes, respectively, and the difference in reactivity between both acetates is very distinctive. Therefore, the effects of the concentration of perchloric acid, and of acids other than perchloric, on the product distribution were investigated in the reactions with these two metal salts. Typical results are shown in Table 2. When magnanese(III) acetate was used, the formation of biaryls was predominant in the presence of trifluoromethanesulphonic

TABLE 2

The effect of strong acid on reactions of p-methoxytoluene with manganese(III) and iron(III) acetates in acetic acid [a]

| Metal acetate (1 mmol)	Acid	Amount/ mmol	Time h	Products, yields/ mmol [b]		
				(1) +(2)	(3)	(4)
Mn	$HClO_4$	1 (0.07M)	2	0.10	0.83	Trace
Mn	$HClO_4$	6 (0.4M)	0.17	0.62	0.08	0
Mn	$HClO_4$	6	3	0.75	0.08	0.04
Fe	$HClO_4$	6	3	Trace	0.88	0.17
Mn	$HClO_4$ [c]	6	2	0.04	0.73	Trace
Mn	$HClO_4$	18 (1.2M)	3	0.16	Trace	0.04
Fe	$HClO_4$	18	3	0.03	0.43	0.50
Mn	CF_3SO_3H	6	3	0.63	0.19	Trace
Fe	CF_3SO_3H	6	3	0.01	0.72	0.02
Mn	H_2SO_4	6	3	0.41	0.04	0.01
Fe	H_2SO_4	6	3	0	0.48	0.02
Mn	CF_3CO_2H	6	3	0	0.92	0
Fe	CF_3CO_2H	6	3	0	0	Trace
Mn	CCl_3CO_2H	6	3	0	0.52	0
Fe	CCl_3CO_2H	6	3	0	Trace	0

[a] At reflux temperature under N_2; p-methoxytoluene 40 mmol, AcOH 10 ml. [b] Determined by g.l.c. analysis. [c] Sodium acetate (6 mmol) was added.

or sulphuric acid, while diarylmethanes were the sole products in the presence of less strong acids such as trifluoroacetic or trichloroacetic. It was also observed that diarylmethanes became predominant even in the presence of perchloric acid when its concentration was low (0.07M) or when sodium acetate was added. The use of a high concentration of perchloric acid (1.2M) resulted in a decrease of both biaryls and diarylmethanes, and an increase of polymeric tar. In the oxidation with iron(III) acetate, on the other hand, diarylmethanes were almost the only products in the presence of perchloric (at any concentration), trifluoromethanesulphonic or sulphuric acids, while almost no products were obtained when trifluoroacetic or trichloroacetic acid was used, as has previously been observed in the case of p-xylene as substrate.[1a] Since the amount of polymeric tar was low in all cases (at most, half the total biaryls + diarylmethanes), except with higher concentration of acid, the differences in the ratio of biaryls to diarylmethanes in Table 2 may be discussed in terms of the metal acetate and the acid used.*

In order to explain the results we assume the reaction pathways outlined in the Scheme, similar in part to those reported by Norman et al.[2] in the reactions of methyl-substituted benzenes with lead(IV) or cerium(IV) salts. Thus, first a radical-cation can be formed easily by a one-electron transfer to the metal salt because of the low ionization potential of p-methoxytoluene. Then an electrophilic attack of this cation on another p-methoxytoluene gives (1) + (2) [path (a)], while a route involving the loss of a proton from the cation, affording the benzylic radical, gives (3) + (4) [path (b)]. Here, the abstraction of the proton in path (b) seems to occur by the oxygen

* Control experiments showed that both biaryls and diarylmethanes are oxidized at a similar rate to form polymeric tars by heating them in acetic acid containing perchloric acid, in the presence of manganese(III) or iron(III) acetate.

of the bridging acetate group and/or the central oxygen of the metal acetate, which has a trinuclear oxygen-centred acetato-bridged structure;[3] thus the metal acetate acts as a base. The oxygen-centred trimer of manganese(III) acetate may be decomposed to the monomer by the presence of strong acids such as perchloric, trifluoromethanesulphonic, or sulphuric, and thus lose the basic site for proton abstraction, resulting in preferential formation of biaryls via path (a). The strong nucleophilicity of p-methoxytoluene compared with other alkylbenzenes may also help the reaction occur via this path. At low concentrations of perchloric acid, or in the presence of less strong acids such as trifluoroacetic
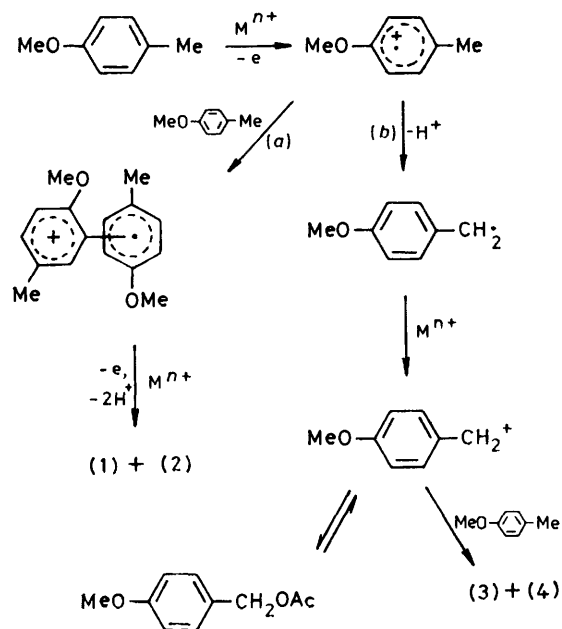
SCHEME

or trichloroacetic, manganese(III) acetate may retain the oxygen-centred structure, making path (b) favourable.† With iron(III) acetate, on the other hand, the products were almost always diarylmethanes. This cannot be explained unless the iron(III) acetate trimer is more stable than the manganese(III) one, assuming that each metal acetate functions as a base. Although there is no direct experimental evidence as to the stability of the acetates to acid, the following facts are suggestive. In the oxidation of p-xylene with iron(III) acetate, the amount of product [only o-(4-methylbenzyl)-p-xylene] was increased successively by increasing the concentration of perchloric acid, while with manganese(III) acetate the yield of the products [o-(4-methylbenzyl)-p-xylene, p-methylbenzyl acetate, and p-methylbenzaldehyde] was almost constant, irrespective of the acid concentration,

† Actually it has been reported that the reaction of p-methoxytoluene with manganese(III) acetate in acetic acid at 130 °C under N_2 (without any acid added) gives mainly p-methoxybenzyl acetate, the precursor of (3) and (4), and no (1) or (2) (E. I. Heiba, R. M. Dessau, and W. J. Koehl, jun., *J. Amer. Chem. Soc.*, 1969, **91**, 138).

and rather high even in low acid concentration.* This may indicate a more facile decomposition of the manganese(III) acetate trimer than the iron(III) one, to give the reactive monomeric species.

Similar results on the effects of acid and metal salt were also obtained by using o- or m-methoxytoluene as a substrate instead of p-methoxytoluene, but detailed studies were not carried out because of the formation of large amounts of polymeric tar, and thus low yields of biaryls and/or diarylmethanes.

EXPERIMENTAL

N.m.r. spectra were recorded on a Varian EM-360 spectrometer (CCl_4 as solvent, with internal lock). G.l.c. analyses were carried out with a Shimadzu 4BMPF apparatus [EGSS-X (30%)–Chromosorb W (1 m) and Apiezon L (1 m) columns (N_2 as carrier gas)]. Organic materials were used after distillation; commercial inorganic materials were used without further purification. Iron(III),[3,4] manganese(III),[5] and cobalt(III) [6,7] (50% Co^{III} vs. total cobalt) acetates were prepared by the reported methods. In the case of cobalt(III) acetate two-fold amounts of it were used because of its 50% purity.

Reaction of p-*Methoxytoluene with Manganese*(III) *Acetate in Acetic Acid in the Presence of Perchloric Acid.*—To a stirred suspension of manganese(III) acetate [{$Mn_3O(OAc)_6$-$(AcOH)_3$}OAc][3] (0.774 g, 1 mmol) and p-methoxytoluene (4.88 g, 40 mmol) in acetic acid (10 ml) was added 70% perchloric acid (0.85 g, 6 mmol) under N_2 at room temperature. The mixture was stirred for 3 h at 114 °C, cooled, and benzene added (50 ml). The benzene solution was washed with water, aqueous sodium hydrogencarbonate, and water, dried (Na_2SO_4), and evaporated. The residue was then passed through a short column (2.5 × 15 cm) of silica gel to remove brown polymer-like products and analysed by g.l.c. with benzophenone as internal standard; biaryls [(1) + (2)] (0.75 mmol), (3) (0.08 mmol), (4) (0.04 mmol), and p-methoxytoluene. Carboxylic acid was not detected in the acidified water solution. Repeating the experiment on a three-fold scale and distilling the residue afforded 0.24 g distillate (b.p. 147—151 °C at 5 Torr) which

* In the oxidation of p-xylene (40 mmol) with iron(III) or manganese(III) acetate (1 mmol) in acetic acid (10 ml) containing perchloric acid, at reflux for 3 h under N_2, the yields (mmol) of the sum of o-(4-methylbenzyl)-p-xylene, p-methylbenzyl acetate, and p-methylbenzaldehyde were as follows with the amount (mmol) of perchloric acid in parentheses. Fe^{III}; 0(1), 0.27(3), 0.93(6), 1.31(12), and 1.94(18). Mn^{III}; 0.58(1), 1.15(3), 1.14(6), 1.05(12), 0.98(18).

was a mixture of (1) and (2); δ 2.03 and 2.29 (6 H, s, Me), 3.67 and 3.70 (6 H, s, MeO), and 6.70—7.20 (6 H, m, aromatic) (Found: C, 79.3; H, 7.5. Calc. for $C_{16}H_{18}O_2$: C, 79.3; H, 7.5%). An authentic sample of (1) was prepared from 2-methoxy-5-methylphenylmagnesium bromide with cobalt(II) chloride as a catalyst;[8] b.p. 145—155 °C at 7 Torr (lit.,[9] b.p. 188 °C at 12 Torr); δ 2.29 and 3.67.

Reaction of p-*Methoxytoluene with Iron*(III) *Acetate in Acetic Acid in the Presence of Perchloric Acid.*—A similar reaction to the one above using iron(III) acetate [{Fe_3O-$(OAc)_6(H_2O)_3$}OAc] (0.651 g, 1 mmol) instead afforded (3) (0.88 mmol), (4) (0.17 mmol), and a trace amount of (1) + (2) (g.l.c.; benzophenone as internal standard). The authentic samples of (3) and (4) [(3) : (4) = ca. 3 : 4 by g.l.c.] were prepared from p-methoxybenzyl alcohol (0.1 mol) and p-methoxytoluene (0.2 mol) in acetic acid (25 ml) in the presence of perchloric acid (0.1 mol, ca. 1.6M) at reflux temperature for 2.5 h, yield 7.8 g, b.p. 181—184 °C at 7 Torr; δ 2.13 and 2.20 (3 H, s, Me), 3.60 and 3.77 (6 H, s, MeO), 3.83 (2 H, s, CH_2), and 6.6—7.3 (7 H, m, aromatic). A similar reaction with a lower concentration of perchloric acid (ca. 0.2—0.5M) afforded almost only (3); δ 2.20 and 3.77; m.p. 70—73 °C (lit.,[10] m.p. 74 °C).

Treatment of p-methoxytoluene (80 mmol) with iron(III) perchlorate (5 mmol) [1a] in acetic acid (20 ml) under N_2 at 116 °C for 3 h afforded a mixture of (3) and (4) (0.52 g) [(3) : (4) = 4 : 1 by g.l.c.] as a distillate (Found: C, 79.3; H, 7.4. Calc. for $C_{16}H_{18}O_2$: C, 79.3; H, 7.5%).

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