

Diarylmethane Formation in the Reaction of Various Metal Acetates with Alkylbenzenes in the Presence of Perchloric Acid

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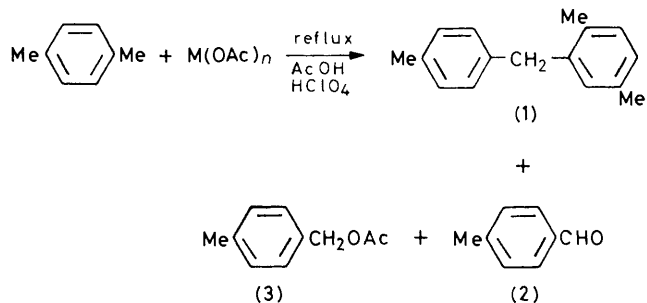
Treatment of alkylbenzenes with various metal acetates (Mn^{III} , Fe^{III} , Co^{III} , Cu^{II} , and Pb^{IV}) in acetic acid containing perchloric acid at reflux temperature affords diarylmethanes as main products; Mn^{III} and Fe^{III} acetates are found to be better reagents than the others, and have comparable activity for diarylmethane formation. Reactions with Mn^{III} acetate-perchloric acid differ from those with Fe^{III} perchlorate (reported previously) in the following ways: the presence of oxygen increases the amount of benzylic aldehyde produced in the former and of diarylmethane produced in the latter reaction; both disproportionation and polymerization, which occur in the latter reaction, are minimized in the former case, making the work-up procedure easier.

RECENTLY we reported¹ that treatment of alkylbenzenes with iron(III) perchlorate or with other iron(III) salt-perchloric acid mixtures in acetic acid affords diarylmethanes selectively through a benzylic cation intermediate. It is known that side-chain oxidation of alkylbenzenes with such metal acetates as those of manganese(III),² cobalt(III),² and lead(IV)³ in acetic acid is greatly enhanced by strong acids, but the products are usually mixtures of several carbonyl compounds, a biaryl, and/or a diarylmethane. When we carried out these reactions at reflux temperature in the presence of perchloric acid under nitrogen, we observed that diarylmethane was the main or in some cases the sole product, and that the efficiency of manganese(III) acetate for diarylmethane formation was comparable to that of iron(III) perchlorate.¹ Here we describe the results of this new finding, focusing on reactivity differences between manganese(III) and iron(III) salts and on the synthetic utility of manganese(III) acetate for diarylmethane formation.

RESULTS AND DISCUSSION

When *p*-xylene was treated with various metal acetates in acetic acid containing perchloric acid at reflux temperature, *o*-(4-methylbenzyl)-*p*-xylene (1), *p*-tolualdehyde (2), and *p*-methylbenzyl acetate (3) were obtained as products, the amount of each depending markedly on the reaction conditions. In no case was the formation of *p*-toluic acid detected. By carrying out the reaction for a longer time in the presence of atmospheric oxygen it was revealed that manganese(III), cobalt(III), lead(IV), and copper(II) acetates were as

effective as iron(III) acetate for the formation of (1) (compare runs 5, 9, 13, and 15 with run 1 in Table 1).[†] In the first three cases the formation of an appreciable amount of (2) was observed, while only a trace of (2)



was detected with iron(III) and copper(II). When the reaction was carried out under nitrogen, (1) was almost the sole product (runs 4, 8, and 12); whereas, under bubbling oxygen, the yield of (2) increased except for the copper(II) case, it being prominent in the cases of manganese(III) and cobalt(III) acetates (runs 2, 6, 10, and 14). This suggests the intermediacy of a benzylic free radical which can be trapped by oxygen to form (2), in the iron(III), manganese(III), and cobalt(III) cases; this has been partially verified.² Another difference was found when the reactions were stopped after very short time (5–10 min). Thus, the formation of (3) was observed in the reaction with manganese(III) or cobalt(III) acetate, especially in the former case (runs 7 and 11), while it was rarely found in the products of the reaction with iron(III) acetate (run 3). In the former cases, prolonged reactions resulted in the disappearance of (3).

² (a) J. Hanotier, M. Hanotier-Bridoux, and P. de Radzitzky, *J.C.S. Perkin II*, 1973, 381; (b) J. Hanotier and M. Hanotier-Bridoux, *ibid.*, p. 1035.

³ R. O. C. Norman, C. B. Thomas, and J. Willson, *J.C.S. Perkin II*, 1973, 325.

[†] The reaction conditions employed here are the same as those reported previously using iron(III) acetate,¹ except the reaction time (24 instead of 5 h).

¹ S. Uemura, S. Tanaka, and M. Okano, *J.C.S. Perkin I*, 1976, 1966.

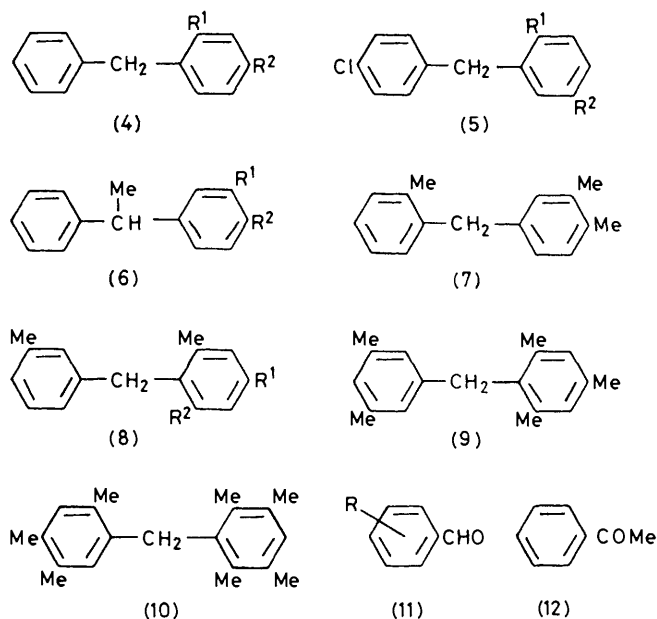
TABLE 1

Reaction of *p*-xylene with various metal acetates in acetic acid containing perchloric acid at reflux temperature (114 °C)

Run	Atmosphere	Metal acetate ^a (mmol)	<i>p</i> -Xylene (mmol)	70% HClO ₄ (mmol)	AcOH (ml)	Time (h)	Yield (mmol) ^b		
							(1)	(2)	
1	Air	Fe	2	32	12	20	24 ^c	0.76	Trace
2	O ₂	Fe	1	40	6	10	3	1.00	0.07
3	N ₂	Fe	1	40	6	10	0.08	0.09	0
4	N ₂	Fe	1	40	6	10	3	0.93	Trace
5	Air	Mn	2	32	12	20	24	1.66	0.40
6	O ₂	Mn	1	40	6	10	3	0.61	0.48
7	N ₂	Mn	1	40	6	10	0.17	0.67	0.04 ^d
8	N ₂	Mn	1	40	6	10	3	1.05	0.06
9	Air	Co	2	32	12	20	24	1.16	0.37
10	O ₂	Co	1	40	6	10	3	0.25	0.31
11	N ₂	Co	1	40	6	10	0.08	0.34	0.08 ^e
12	N ₂	Co	1	40	6	10	3	0.41	0.08
13	Air	Cu	2	32	12	20	24	0.70	0
14	O ₂	Cu	1	40	6	10	3	0.07	Trace
15	Air	Pb	2	32	12	20	24	0.68	0.04
16	Air	Tl	2	32	12	20	24	0.44	Trace

^a Fe: [Fe₃O(OAc)₆(H₂O)₃]OAc; Mn and Co: [M₃O(OAc)₆(AcOH)₃]OAc; Cu: Cu(OAc)₂; Pb: Pb(OAc)₄; Tl: Tl(OAc)₃. On the structures of Fe^{III}, Mn^{III}, and Co^{III} acetates see ref. 7. ^b Determined by g.l.c. analysis. Since 1 mmol of cluster metal acetate seems to give 3 mmol of Mⁿ⁺ in this acidic condition and 2 Mⁿ⁺ are required to oxidize 2 *p*-xylene to give 1 (1), 1.5 mmol of (1) correspond to 100% yield in the reaction using 1 mmol of metal acetate. In some cases the yield exceeded this because of oxidation of M⁽ⁿ⁻¹⁾⁺ to Mⁿ⁺ by oxygen as has been previously shown.¹ ^c In a 5 h reaction, 0.68 mmol of (1) obtained.¹ ^d Other product (3) (0.42 mmol). ^e Other product (3) (0.07 mmol).

Similar phenomena were also observed in the manganese(III) acetate oxidations of toluene and mesitylene under the conditions of run 7; that is, benzyl acetate (0.78 mmol) and mesityl acetate (0.52 mmol) were



obtained as the main products respectively, together with small amounts of diarylmethanes and benzylic aldehydes.* These results may reflect the differences in Lewis-acid activity amongst the three metal salts, iron(III) being expected to be the strongest. We have confirmed separately that in acidic media benzyl acetate reacts quite readily with toluene to give phenyltolylmethanes in the presence of iron(III) or cobalt(III) acetate as catalyst (see Experimental section).

* It has been reported that the reaction of alkylbenzene with Mn^{III} ^{4a} or Co^{III} ^{4b} acetate in acetic acid (at 80–100 °C under N₂) gives benzylic acetates and acetoxy-methylated compounds in the absence of added strong acid.

In the light of the data summarized in Table 1, the efficiency of manganese(III) acetate seems to be comparable to that of iron(III) acetate for diarylmethane formation, although the reaction should be carried out under nitrogen in order to minimize the formation of aldehyde. When optimum conditions for (1) with manganese(III) acetate were investigated by changing the amounts of *p*-xylene and perchloric acid, keeping the amounts of metal salt and acetic acid constant, no appreciable improvement in the yield of (1) was observed over that in run 8 of Table 1. The effect of strong acids other than perchloric was also investigated. In contrast to the cases of iron(III) salts where many strong acids other than perchloric were inadequate for the formation of (1), both sulphuric and trifluoromethanesulphonic acids were revealed to be as effective as perchloric acid for (1). On the other hand, the addition of trichloro- or trifluoro-acetic acid resulted in high yields of (3). Typical results are shown in Table 2.

TABLE 2

Effect of the kind of acid on the product distribution in the reaction of *p*-xylene with manganese(III) acetate in acetic acid^a

Acid	Products and yields (mmol)		
	(1)	(2)	(3)
HClO ₄ ^b	1.05	0.06	0
CF ₃ SO ₃ H	0.99	0.15	0
H ₂ SO ₄	1.01	0.09	0
CF ₃ CO ₂ H	0.06	0.14	0.75
CCl ₃ CO ₂ H	0.05	0.14	0.66

^a Mn(III) acetate 1 mmol, *p*-xylene 40 mmol, acid 6 mmol. AcOH 10 ml; at 114 °C for 3 h under N₂. ^b Run 8 in Table 1.

Since manganese(III) acetate-perchloric acid was revealed to be a good reagent for formation of (1), we applied this reaction to various other alkylbenzenes under the conditions of run 8 in Table 1 in order to compare the characteristics of this reaction with the

⁴ E. I. Heiba, R. M. Dessau, and W. J. Koehl, jun., *J. Amer. Chem. Soc.*, 1969, **91**, (a) 138; (b) 6830.

iron(III) one. In each case, the products were mostly diarylmethane and benzylic aldehyde, the former being predominant. The isolated and identified products and their yields are summarized in Table 3. Under our oxidation conditions, neither biaryls nor acetoxy-methylated compounds^{4a} were formed in any case. From toluene, *p*-chlorotoluene, ethylbenzene, and *m*-xylene two positional isomers of the corresponding

The difference in the amount of benzylic aldehyde produced in the two reactions may suggest that iron(III) is a stronger oxidizing agent towards the intermediate benzylic radical than manganese(III).⁵ Since the oxidation to a benzylic cation is slower in the latter case, the amounts of aldehyde are larger. This is consistent with the observation that almost no aldehyde formation was observed in the oxidation with copper(II) acetate even in

TABLE 3
Reaction of alkylbenzenes with manganese(III) acetate-perchloric acid in acetic acid^a
Products and yields (mmol)^b

Alkylbenzene (40 mmol)	Temp. (°C)	Time/h	Products and yields (mmol) ^b	
			Diarylmethane	Aldehyde
Toluene	105	3	(4; R ¹ = H, R ² = Me) + (4; R ¹ = Me, R ² = H)	0.70 ^c (11; R = H) 0.10
Toluene	105	24	(4; R ¹ = H, R ² = Me) + (4; R ¹ = Me, R ² = H)	0.79 (11; R = H) 0.06
Toluene ^d	105	3	(4; R ¹ = H, R ² = Me) + (4; R ¹ = Me, R ² = H)	0.21
<i>p</i> -Chlorotoluene	116	3	(5; R ¹ = Me, R ² = Cl) + (5; R ¹ = Cl, R ² = Me)	0.13 ^e (11; R = 4-Cl) 0.09
<i>p</i> -Chlorotoluene	116	24	(5; R ¹ = Me, R ² = Cl) + (5; R ¹ = Cl, R ² = Me)	0.56 ^f (11; R = 4-Cl) 0.10
Ethylbenzene	114	3	(6; R ¹ = H, R ² = Et) + (6; R ¹ = Et, R ² = H)	0.44 ^g (12) 0.22
<i>o</i> -Xylene	114	3	(7)	0.73 (11; R = 2-Me) 0.32
<i>m</i> -Xylene	114	3	(8; R ¹ = Me, R ² = H) + (8; R ¹ = H, R ² = Me)	0.59 ^h (11; R = 3-Me) 0.05
<i>p</i> -Xylene	114	3	(1)	1.05 (2) 0.05
Mesitylene	118	3	(9)	0.71 (11; R = 3,5-Me ₂) 0.10
Mesitylene	118	24	(9)	0.83 ⁱ (11; R = 3,5-Me ₂) 0.10
Mesitylene	118	3	(9)	0.40 ^j
Durene	116	3	(10)	0.49 (11; R = 2,4,5-Me ₃) 0.17

^a Mn(III) acetate 1 mmol, 70% HClO₄ 6 mmol, AcOH 10 ml; under N₂. ^b Determined by g.l.c. analysis. ^c 53 : 47 (by n.m.r.). ^d Data obtained using iron(III) acetate (1 mmol). ^e 56 : 44 (by g.l.c.); other product *p*-chlorobenzyl acetate (0.52 mmol). ^f 53 : 47 (by g.l.c.). ^g 85 : 15 (by g.l.c.). ^h 77 : 23 (by g.l.c.). ⁱ Other product dimesitylmethane (0.07 mmol). ^j Other product dimesitylmethane (0.32 mmol).

diarylmethane were obtained in each case, the isomer ratio being nearly the same as in the iron(III) case. This suggests that the two reactions proceed through a similar intermediate, *i.e.* a benzylic cation, for diarylmethane formation.

On the other hand, several differences between oxidations with manganese(III) and iron(III) salts were observed, as follows. First, benzylic aldehyde was always formed in the former case, despite the fact that all reactions were carried out under nitrogen, while almost none was formed with the iron(III) salt even in the presence of oxygen; on the contrary, the presence of oxygen improved the yield of diarylmethane in the latter case.¹ Secondly, little or no product arising from disproportionation, such as dixylylmethane and dimesitylmethane, was obtained in the former case, whereas many such products were formed in the latter case,¹ this being consistent with the milder Lewis acidity of manganese(III) than of iron(III). Thirdly, in connection with this difference, the work-up procedure was very easy in all cases with manganese(III) acetate, in sharp contrast to the iron(III) cases where polymerization (affording tars) is inevitable.

⁵ Oxidation of benzylic radicals with Fe^{III} is well documented: see, *e.g.*, C. Walling, *Accounts Chem. Res.*, 1975, **8**, 125.

⁶ See, *e.g.*, 'Free Radicals,' ed. J. K. Kochi, Wiley, New York, 1973, ch. 11.

⁷ S. Uemura, A. Spencer, and G. Wilkinson, *J.C.S. Dalton*, 1973, 2565.

the presence of oxygen (for example, runs 13 and 14 in Table 1) because of its strong oxidizing ability towards alkyl radicals to give cations.^{5,6}

EXPERIMENTAL

N.m.r. spectra were recorded on a Varian EM-360 spectrometer (CCl₄ 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 (N₂ as carrier gas)]. Organic materials were used after distillation; commercial inorganic materials were used without further purification. Iron(III),^{7,8} manganese(III),⁹ and cobalt(III)^{2a,10} (50% Co^{III} vs. total cobalt) acetates were prepared by the reported methods. In the case of Co^{III} acetate two-fold amounts of it were used because of its 50% purity. Identification of all diarylmethanes was reported in a previous paper.¹ Other products were identified by comparison with commercial products.

Reaction of p-Xylene with Manganese(III) Acetate in Acetic Acid in the Presence of Perchloric Acid.—A typical procedure is given. To a stirred suspension of manganese(III) acetate {[Mn₃O(OAc)₆(AcOH)₃]OAc}⁷ (0.774 g, 1 mmol) and *p*-xylene (4.25 g, 40 mmol) in acetic acid (10 ml) was added 70% perchloric acid (0.85 g, 6 mmol) under N₂. The

⁸ A. E. Earnshaw, B. N. Figgis, and J. Lewis, *J. Chem. Soc. (A)*, 1966, 1656.

⁹ J. M. Vaerman and J. N. M. Bertrand, *Ger. Offen.* 2124876 (*Chem. Abs.*, 1972, **77**, 100812z).

¹⁰ W. O. Walker and U. Kopsch, U.S.P. 1976757 (*Chem. Abs.*, 1934, **28**, 7264⁹).

mixture was stirred for 3 h at 114 °C then cooled, and benzene was added (50 ml). The benzene solution was washed with aqueous sodium hydrogencarbonate and water, dried (Na_2SO_4), and evaporated. The residue (*ca.* 8 g) contained *o*-(4-methylbenzyl)-*p*-xylene (1) (1.05 mmol), *p*-tolualdehyde (2) (0.06 mmol), and *p*-xylene (g.l.c.; benzophenone as internal standard). *p*-Toluic acid was not detected in the acidified water solution.

Reaction of Benzyl Acetate with Toluene in Acetic Acid in the Presence of Perchloric Acid and a Catalytic Amount of Metal Acetate.—To a stirred suspension of benzyl acetate (0.161 g, 1.07 mmol), toluene (3.69 g, 40 mmol), and manganese(III) acetate (0.078 g, 0.10 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 then rapidly heated to reflux temperature (105 °C) and stirred for 15 min, and then water (50 ml) and benzene (50 ml) were added. The benzene layer was separated and washed with aqueous sodium hydrogencarbonate, dried (Na_2SO_4), and evaporated. The residue contained phenyltolylmethane (0.73 mmol), benzyl acetate (0.49 mmol), and benzaldehyde (0.09 mmol) (g.l.c.; benzophenone as internal standard). Using iron(III) acetate as catalyst, 1.08 mmol of phenyltolylmethane and 0.06 mmol of benzyl acetate were obtained, whereas with cobalt(III) acetate as catalyst phenyltolylmethane (1.09 mmol), benzyl acetate (0.05 mmol), and benzaldehyde (0.05 mmol) were formed.

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