

Selective Diarylmethane Formation in the Reaction of Iron(III) Perchlorate with Alkylbenzenes

By Sakae Uemura,* Sakuya Tanaka, and Masaya Okano, Institute for Chemical Research, Kyoto University, Uji, Kyoto, Japan

Treatment of alkylbenzenes with iron(III) perchlorate in acetic acid affords diarylmethanes selectively in good yields; the formation of biaryls reported in previous studies with iron(III) chloride was not observed. Reactions with other iron(III) salts in the presence of perchloric acid proceed similarly. The reaction is interpreted in terms of formation of a benzylic cation, followed by its electrophilic attack on another alkylbenzene molecule.

It has recently been reported¹ that side-chain oxidation of alkylbenzenes with manganese(III) or cobalt(III) acetate in acetic acid is greatly enhanced by strong acids (sulphuric, trichloroacetic, and perchloric). During a study of the oxidation of hydrocarbons with various iron(III) salts we found that diarylmethanes were produced selectively from alkylbenzenes by addition of perchloric acid to the reaction system, or by use of iron(III) perchlorate as the oxidant. It has hitherto been considered² that the reaction of alkylbenzenes with iron(III) chloride involves several competing processes (nuclear chlorination, formation of biaryls and diarylmethanes, disproportionation, and polymerization). Reactions with other Lewis acid metal halides, such as SbCl_5 ,³ CuCl_2 ,⁴ CuBr_2 ,⁵ and TlX_3 ,⁶ have also afforded diarylmethanes, but the yields and selectivities were low and the reactions were limited to particular alkylbenzenes.

RESULTS AND DISCUSSION

First the ability of various iron(III) salts to oxidize alkylbenzenes to diarylmethanes was examined by using *p*-xylene as a substrate in acetic acid in the presence or

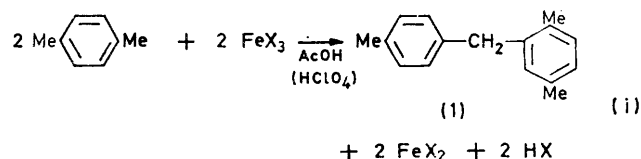
¹ J. Hanotier, M. Hanotier-Bridoux, and P. de Radzitzky, *J.C.S. Perkin II*, 1973, 381.

² P. Kovacic, 'Friedel-Crafts and Related Reactions,' vol. IV, ed. G. A. Olah, Interscience, New York, 1965, pp. 114—117.

³ P. Kovacic and A. K. Sparks, *J. Org. Chem.*, 1963, **28**, 972.

⁴ C. A. Cummings and D. J. Milner, *J. Chem. Soc. (C)*, 1971, 1571.

absence of perchloric acid. The only isolated product was *o*-(4-methylbenzyl)-*p*-xylene (I). The results are shown in Table 1. Addition of perchloric acid greatly increased the yield of (I) (runs 1, 4, 5, and 7), and high



conversions were generally accomplished by iron(III) perchlorate even without added perchloric acid (run 6). It is probable that the addition of perchloric acid results in conversion of iron(III) salts other than the perchlorate into a reactive species such as $\text{Fe}(\text{ClO}_4)_3$ or its dissociated form, and also enhances the oxidizing activity of iron(III) salts. Other strong acids (sulphuric, trichloroacetic, and trifluoroacetic) did not show such a strong effect as perchloric acid. With *p*-xylene itself as solvent, the reaction with iron(III) perchlorate proceeded similarly, and afforded a better yield of (I) (runs 10 and 11), but significant amounts of high boiling resinous products were also formed.

⁵ P. Kovacic and K. E. Davis, *J. Amer. Chem. Soc.*, 1964, **86**, 427.

⁶ (a) K. Ichikawa, S. Uemura, T. Nakano, and E. Uegaki, *Bull. Chem. Soc. Japan*, 1971, **44**, 545; (b) S. Uemura, K. Sohma, M. Okano, and K. Ichikawa, *ibid.*, p. 2490.

TABLE 1

Formation of *o*-(4-methylbenzyl)-*p*-xylene (1) from *p*-xylene under various conditions ^a

Run	Fe ^{III} salt (mmol)	<i>p</i> -Xylene (mmol)	AcOH (ml)	Temp. (°C)	Time (h)	Yield of (1) (mmol) ^b		
						Additive		
						None	70% HClO ₄ (12 mmol)	KClO ₄ (12 mmol)
1	FeCl ₃	32	20	114	5	0.04 ^c	0.70 ^c	0.09 ^c
2	FeCl ₃	80	0	139	5	0.87		
3	Fe ₂ (SO ₄) ₃ ·7H ₂ O	32	20	114	5	0	0.22	
4	Fe(NO ₃) ₃ ·9H ₂ O	32	20	114	5	0	0.58 ^d	
5	[Fe ₃ O(OAc) ₆ (H ₂ O) ₃]OAc	32	20	114	5	Trace	0.68	
6	Fe(ClO ₄) ₃ ·9H ₂ O	80	10	114	5	2.63		
7	Fe(ClO ₄) ₃ ·9H ₂ O	80	10	107	3	1.22 ^e	2.78	
8	Fe(ClO ₄) ₃ ·9H ₂ O	80	10	107	3	1.58 ^f		
9	Fe(ClO ₄) ₃ ·9H ₂ O	80	10	107	3	1.06 ^g		
10	Fe(ClO ₄) ₃ ·9H ₂ O	80	0	114	5	3.96		
11	Fe(ClO ₄) ₃ ·9H ₂ O	80	0	139	5	5.23		

^a In the presence of atmospheric oxygen unless otherwise stated. ^b Determined by g.l.c. analysis. Other product chloro-*p*-xylene (trace). ^c Other products nitro-*p*-xylene (0.30 mmol) and *p*-methylbenzaldehyde (0.30 mmol). ^d Other product *p*-methylbenzaldehyde (0.03 mmol). ^e Under O₂; other product *p*-methylbenzaldehyde (0.10 mmol). ^f Under N₂; other product *p*-methylbenzaldehyde (trace).

Since iron(III) perchlorate was thus the most promising reagent for diarylmethane formation of the salts examined, we applied this reaction to various other alkylbenzenes. In each case, the product was mostly

diarylmethane, obtained together with a small or trace amount of benzylic aldehyde and acetate. The isolated and identified diarylmethanes and their yields are summarized in Table 2. Formation of biaryl was not

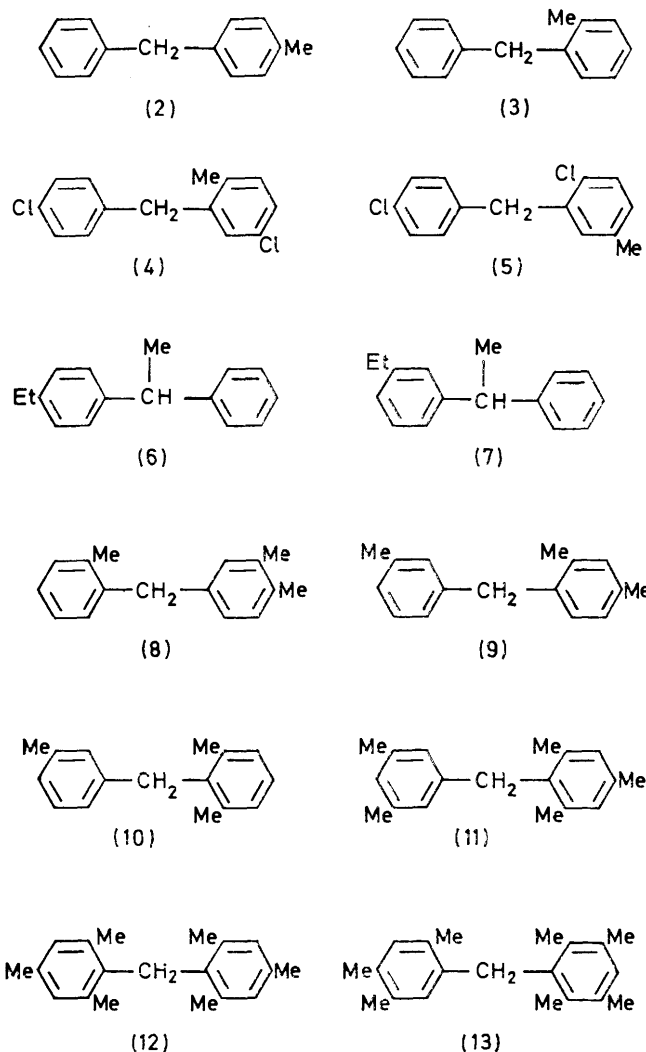


TABLE 2

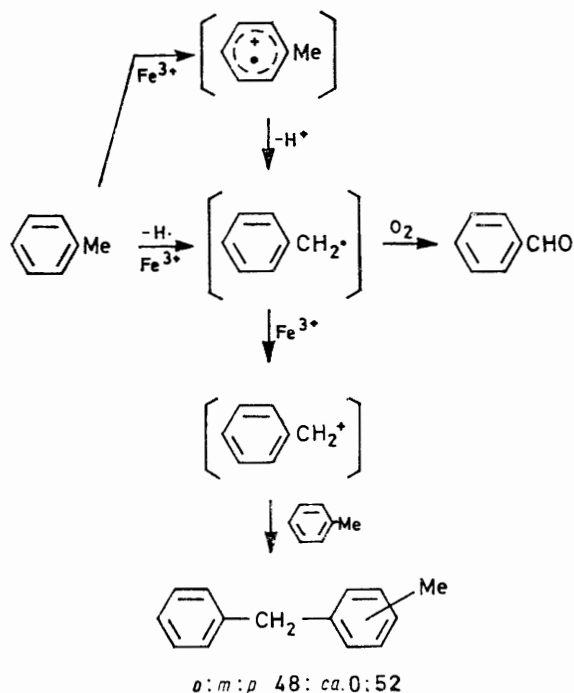
Reaction of alkylbenzene with iron(III) perchlorate (nonahydrate) (5 mmol) in acetic acid (10 ml) ^a

Alkylbenzene (80 mmol)	Temp. (°C)	Time (h)	Products	Yield [mmol ^b (%)] ^c
Toluene	103	24	(2) + (3) ^d	1.06 (42)
<i>p</i> -Chlorotoluene	116	24	(4) + (5) ^e	2.90 (116)
Ethylbenzene	114	3	(6) + (7) ^f	1.12 (45)
Ethylbenzene	114	24	(6) + (7) ^f	1.39 (56)
<i>o</i> -Xylene	114	24	(8)	2.34 (94)
<i>m</i> -Xylene	114	3	(9) + (10) ^g	0.76 (30)
<i>m</i> -Xylene	114	24	(9) + (10) ^h	1.34 (54)
<i>p</i> -Xylene	114	24	(1)	4.38 (175)
Mesitylene	118	3	(11)	1.13 (45)
			(12)	0.32
Mesitylene	115	24	(11)	1.84 (74)
			(12)	1.05
Durene	116	24	(13)	3.48 (139)

^a In the presence of atmospheric oxygen. ^b Determined by g.l.c. analysis. ^c Based on initial Fe^{III} and on the stoichiometry of equation (i). ^d 48:52 (by n.m.r.). ^e 55:45 (by n.m.r.); other products *p*-chlorobenzyl acetate (<0.1 mmol) and *p*-chlorobenzaldehyde (<0.1 mmol). ^f 78:22 (by g.l.c.). ^g 76:24 (by g.l.c.); other product dixylylmethane (0.08 mmol). ^h 73:27 (by g.l.c.); other product dixylylmethane (0.60 mmol).

observed in all cases, and polymerization giving dark brown tars was unavoidable with longer reaction times. From toluene, *p*-chlorotoluene, ethylbenzene, and *m*-xylene two positional isomers of the corresponding diarylmethane were obtained in each case, whereas *o*- and *p*-xylene and durene afforded essentially one diarylmethane only. In the cases of *m*-xylene and mesitylene other kinds of diarylmethanes [dixylylmethane and dimesitylmethane (12), respectively] were also produced. The formation of these compounds seems to be a result of disproportionation of a methyl group in the alkylbenzenes. In several cases the yield of products exceeded 100%, showing that reoxidation of iron(II) to iron(III) by atmospheric oxygen occurred during the reaction.

In the reaction of alkylbenzenes with iron(III) chloride it has been reported² that diarylmethane formation is always accompanied by nuclear chlorination and biaryl formation; sometimes the latter reactions occurred predominantly or exclusively. For example, diarylmethanes were not obtained from *o*- and *m*-xylene and mesitylene.^{2,7} Another discrepancy between the reactions with iron(III) chloride and those with the perchlorate is the fact that the yield of diarylmethanes increased in the order of $\text{PhMe} < p\text{-ClC}_6\text{H}_4\text{Me} < \text{PhEt} < \text{PhPr}^i$ in the chloride case, whereas the reverse order was observed with the perchlorate, $\text{PhPr}^i \ll \text{PhEt} < p\text{-ClC}_6\text{H}_4\text{Me}$. Very little diarylmethane was obtained from the reaction of cumene with the perchlorate under the present conditions; instead dark brown polymer-like tars were produced. On the other hand only a small amount of tarry compound was formed in the case of *p*-chlorotoluene.



SCHEME

The apparent absence of *m*-substituted product (*m*-benzyltoluene) in the reaction with toluene (i.r. spectrum in the range 700–800 cm^{-1}) shows that the reaction may involve electrophilic attack. In order to obtain more information on the reaction path we carried out the reaction of *p*-xylene with iron(III) perchlorate under oxygen and under nitrogen, and compared the products with those obtained in air. The amount of *p*-methylbenzaldehyde produced was increased in the presence of oxygen (*cf.* runs 7 and 9 with run 8 in Table I). These results indicate that a benzylic free radical is produced from the substrate, as proposed for the cobalt(III) acetate oxidation of alkylbenzenes.¹ Therefore we tentatively propose the mechanism shown in the Scheme

for diarylmethane formation. The high reaction temperature and the strong oxidizing activity of iron(III) perchlorate probably results in very rapid oxidation of the benzylic radical to the carbocation, and this may be the reason why diarylmethane is formed selectively. In contrast to the report¹ that benzylic acetate is the main product in the cobalt(III) acetate oxidation, appreciable amounts of benzylic acetate were not formed under our conditions. We confirmed in separate experiments, however, that benzylic acetates reacted quite readily with alkylbenzenes in the presence of iron(III) perchlorate to give diarylmethanes almost quantitatively at 100 °C in 3 h, showing that iron(III) perchlorate also acts as a Lewis acid catalyst.

EXPERIMENTAL

N.m.r. spectra were taken with a Varian EM-360 spectrometer (CCl_4 as solvent), and i.r. spectra with Hitachi EPI-S2 and Perkin-Elmer 521 spectrometers. G.l.c. analyses were carried out with a Shimadzu 5APTF 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.

Reaction of p-Xylene with Fe^{III} Salts in Acetic Acid in the Presence of Perchloric Acid.—A typical procedure is given. To a stirred solution of iron(III) acetate $\{[\text{Fe}_3\text{O}(\text{OAc})_6(\text{H}_2\text{O})_3]\text{OAc}^8\}$ (3.3 g, 5 mmol) in acetic acid (50 ml) and 70% perchloric acid (4.3 g, 30 mmol) was added *p*-xylene (8.5 g, 80 mmol). The mixture was stirred for 5 h at 114 °C, then cooled; benzene (100 ml) was added and the solution was decanted from ca. 0.4 g of insoluble black tarry product. The benzene solution was washed with aqueous sodium hydrogen carbonate and water, dried (Na_2SO_4), and evaporated. The residue (ca. 8 g) contained *o*-(4-methylbenzyl)-*p*-xylene (1) (1.80 mmol) and *p*-xylene (g.l.c.; benzophenone as internal standard). Distillation gave the pure product (1) (0.38 g), leaving ca. 0.5 g of dark brown tar; b.p. 123–125° at 3.5 Torr (lit.,^{6a} 128–131° at 2.5 Torr). The n.m.r. spectrum was in accord with that reported.^{6a}

Similar treatment of toluene on a five times larger scale afforded 0.68 g of distillate (0.9 g of residue), b.p. 93–97° at 5.5 Torr [lit.,⁹ for (2), b.p. 138–139° at 14 Torr; for (3), b.p. 138° at 13 Torr]. The distillate was shown to be a mixture of diarylmethanes (2) and (3) (48 : 52) by its n.m.r. spectrum [δ (2) 2.30 (Me) and 3.90 (CH_2); δ (3) 2.20 (Me) and 3.95 (CH_2)]. Compound (3) was also prepared by the reported method.⁹ No *m*-benzyltoluene was detected (g.l.c. and i.r. spectrum).

Reaction of Alkylbenzenes with Iron(III) Perchlorate in Acetic Acid.—The reaction was carried out under the conditions shown in Table 2; the work-up procedure was as described above. From *p*-chlorotoluene (24 h) a mixture (0.66 g) of diarylmethanes (4) and (5) (55 : 45; tentatively assigned by n.m.r.) was obtained, b.p. 135–143° at 2 Torr; δ (4) 2.25 (Me) and 3.98 (CH_2); δ (5) 2.15 (Me) and 3.87 (CH_2). From ethylbenzene (3 h) a mixture (0.1 g) of diarylmethanes (6) and (7) (78 : 22 by g.l.c.) was obtained, b.p. 123° at 3 Torr; δ (6) 1.18 (3 H, t, $\text{CH}_2\text{-CH}_3$), 1.55 (3 H,

⁷ P. Kovacic and C. Wu, *J. Org. Chem.*, 1961, **26**, 759, 762.

⁸ S. Uemura, A. Spencer, and G. Wilkinson, *J.C.S. Dalton*, 1973, 2565.

⁹ G. A. Olah and J. A. Olah, *J. Org. Chem.*, 1967, **32**, 1612.

d, $\text{CH}\cdot\text{CH}_3$), 2.53 (2 H, d, $\text{CH}_2\cdot\text{CH}_3$), 4.00 (1 H, q, CHCH_3), and 6.80—7.20 (9 H, m, aromatic). The i.r. spectrum showed the presence of compound (7) (*m*-substituted). The formation of (7) has also been noted in the reaction with iron(III) chloride.¹⁰ From *o*-xylene (24 h) the diarylmethane (8) (0.41 g) was obtained, b.p. 122—128° at 3.5 Torr (lit.,¹¹ b.p. 173° at 21 Torr); δ 2.15—2.35 (9 H, m), 3.85 (2 H, s), and 6.70—7.15 (5 H, m). From *m*-xylene (24 h) a mixture (0.18 g) of diarylmethanes (9) and (10) and an unidentified compound was obtained, b.p. 118—123° at 3.5 Torr. An authentic mixture of (9) and (10) (76:24 by g.l.c.) was prepared by the reaction of *m*-xylene with 3-methylbenzyl chloride in the presence of thallium(III) chloride; b.p. 135° at 5 Torr; δ (9) 3.83 (s, CH_2); δ (10) 3.96 (s, CH_2). G.l.c. analysis and the n.m.r. spectrum of the mixture showed that the unidentified compound was not bi-*m*-xylyl but dixylylmethane. Bi-*m*-

¹⁰ P. Kovacic, C. Wu, and R. W. Stewart, *J. Amer. Chem. Soc.*, 1960, **82**, 1917.

¹¹ W. Baker, R. Banks, D. R. Lyon, and F. G. Mann, *J. Chem. Soc.*, 1945, 27.

xylyl was produced by the reported method.⁷ From mesitylene (24 h) a mixture (0.68 g) of diarylmethanes (11) and (12) was obtained, b.p. 133—148° at 2 Torr. Compound (12) crystallized out when the mixture was set aside overnight; yield 0.2 g, m.p. 136—137° (from EtOH) (lit.,¹² m.p. 133—135°); δ 2.03 (12 H, s), 2.20 (6 H, s), 3.90 (2 H, s), and 6.67 (4 H, s) (Found: C, 90.3; H, 9.7. Calc. for $\text{C}_{19}\text{H}_{24}$: C, 90.4; H, 9.6%). Compound (11) was isolated as white needles from a 3 h reaction, m.p. 64—65° (from EtOH) (lit.,¹³ m.p. 65—67°); δ 2.15 and 2.20 (15 H, s), 3.85 (2 H, s), and 6.50, 6.67, and 6.78 (5 H, each s). From durene (24 h) the diarylmethane (13) (0.67 g) was obtained by distillation; m.p. 154—155° (from EtOH) (lit.,¹⁴ m.p. 144.6—145.2°). The n.m.r. spectrum was in accord with that reported.¹⁴

[6/406 Received, 1st March, 1976]

¹² J. H. Cornell, jun., and M. H. Gollis, *Org. Synth.*, Coll. Vol. V, 1973, 422.

¹³ M. Weiler, *Ber.*, 1900, **33**, 470.

¹⁴ S. B. Hanna, E. Hunziker, T. Saito, and H. Zollinger, *Helv. Chim. Acta*, 1969, **52**, 1537.