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TRANSITION METAL-PROMOTED REACTIONS

VII *. NOVEL REACTIONS OF ACID CHLORIDES WITH PENTACARBONYLIRON IN AROMATIC SOLVENTS

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Summary

Upon treatment with $Fe(CO)_5$ in an aromatic hydrocarbon solvent aromatic acid chlorides gave a mixture of triarylmethane and tetraarylethane. The reaction may proceed via benzaldehyde and diarylmethanol intermediates. A free radical mechanism is proposed.

Introduction

We recently reported that α-bromoketones are readily reduced by pentacarbonyliron in a free radical process [2]. Reactions of acid halides with pentacarbonyliron have been reported. Thus acetyl chloride was shown to be converted into biacetyl on treatment with pentacarbonyliron in a sealed tube [3]. Butyl ether was reported to be cleaved by acid chloride in the presence of pentacarbonyliron, to give the corresponding ester [4]. More recently, octanal and 8-pentadecanone were isolated from a reaction of octanoyl chloride and enneacarbonyldiiron in diethyl ether [5]. We now describe an investigation of the reactions of pentacarbonyliron with aromatic acid chlorides in aromatic solvents.

Results and discussion

Reactions of aromatic acid chlorides (I) with *m*-xylene (or other aromatic hydrocarbon solvents) in the presence of pentacarbonyliron gave the corresponding triarylmethane (II) and a diastereomeric mixture of tetraarylethanes (III). The results are summarized in Table 1. Reactions in toluene or benzene were

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* For part VI see ref. 1.

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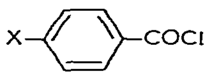
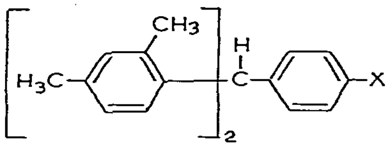
TABLE 1

REACTION OF AROMATIC ACID CHLORIDES WITH $Fe(CO)_5$ IN AROMATIC HYDROCARBON SOLVENTS

Substrate	Solvent	Product (% Yield)
Ia	*m*-xylene	IIa (16); IIIa (17)
Ib	*m*-xylene	IIb (18); IIIb (19)
Ic	*m*-xylene	IIc (13); IIIc (14)
Id	*m*-xylebe	IIId (11)
Ia	*o*-xylene	IV (14), V (12)
Ia	mesitylene	VI (7)

not successful, and aliphatic acid chlorides gave very poor results. Thus, phenylacetyl chloride yielded only a trace amount of triarylethane (VII) on treatment with pentacarbonyliron in *m*-xylene. No reaction was detected when n-hexanoyl chloride was treated with pentacarbonyliron in *m*-xylene.


(Ia, X = H;
Ib, X = Br;
Ic, X = CH_3;
Id, X = CH_3O;
Ie, X = Cl)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IIb, X = Br;
IIc, X = CH_3;
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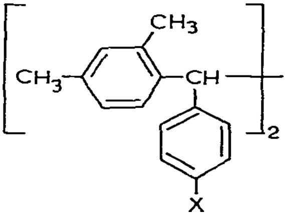
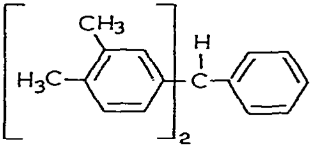

(IIIa, X = H;
IIIb, X = Br;
IIIc, X = CH_3;
IIId, X = CH_3O;
IIIe, X = Cl)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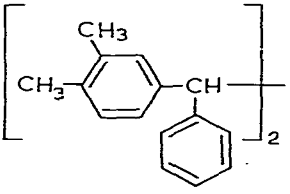
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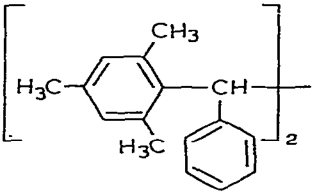
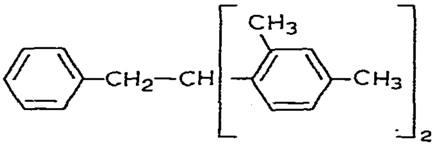

(VI)


(VII)

Interestingly, the yields of II and III were greatly improved when one equivalent of benzaldehyde was present in the reactant mixture. Thus, benzoyl chloride and benzaldehyde reacted with pentacarbonyliron in *m*-xylene to afford IIa and the diastereomeric mixture IIIa in 30 and 40% yield, respectively, although benzaldehyde alone did not react with pentacarbonyliron in *m*-xylene under similar conditions. Moreover, the reaction of benzaldehyde and *p*-bromobenzoyl chloride with pentacarbonyliron in *m*-xylene yielded IIa (28%) and IIIa (42%) as the sole products. No corresponding IIb and IIIb were detected. In a similar manner, *p*-chlorobenzaldehyde reacted with pentacarbonyliron in *m*-xylene in the presence of benzoyl chloride to give IIe (11%) and IIIe (32%) only. Again, IIa and IIIa were not formed in this reaction. It is known that acid can catalyze the Friedel-Crafts reaction of benzaldehyde with aromatic compounds, bearing electron-donating groups [6], and benzaldehyde was found to react with *m*-xylene in the presence of benzoyl chloride to give IIa in 72% yield. This suggests that the triarylmethanes (II) in Table 1 may be formed by a Friedel-Crafts reaction of benzaldehyde with the aromatic solvent catalyzed by acid chloride. Pentacarbonyliron may not be involved in this step. It is noteworthy that the Friedel-Crafts reaction with benzaldehyde may be faster than that with benzoyl chloride as indicated by the experiment just described. The mechanism for the formation of benzaldehyde is of interest. The solvents employed are generally good hydrogen donors for radical abstraction reactions. It seems plausible that, as we suggested previously [2], homolytic cleavage of the carbon—chlorine bond in the acid chloride, leading to acyl radical, is promoted by pentacarbonyliron. The acyl radical would then abstract hydrogen from the solvent molecule to give the aldehyde.

The tetraarylethanes (III) might be formed by dimerization of diarylmethyl species. The possible intermediate could be diarylmethanol formed in a Friedel-Crafts reaction between benzaldehyde and the aromatic solvent. Thus, on treatment with pentacarbonyliron and benzoyl chloride in *m*-xylene, diphenylmethanol was transformed into tetraphenylethane and 2,4-dimethyltriphenylmethane, in 45 and 32% yield, respectively. The formation of the latter product is of no significance, but the reductive coupling of diphenylmethanol to give tetraarylethane is highly interesting. The reaction may proceed by a free radical mechanism. In fact, the diarylmethyl radical which may be formed from diarylmethanol and pentacarbonyliron in the presence of acid chloride has been trapped as diarylmethane in a medium providing a better hydrogen donor [7]. The mechanism for the overall reaction is outlined in Scheme 1. The reaction of benzoyl chlorides or benzaldehyde with pentacarbonyliron in aromatic hydrocarbon solvent provide a convenient synthesis of tetraarylethane and triarylmethane, and represents an additional example of the use of pentacarbonyliron as a powerful reducing agent [8].

SCHEME 1

$$\begin{tikzcd}
\mathrm{ArCOCl} \arrow[r, "\mathrm{Fe(CO)_5}"] & \mathrm{Ar\dot{C}O} \arrow[r, "\mathrm{Ar'H}"] & \mathrm{ArCHO} \arrow[r, "\mathrm{Ar'H}"] & \mathrm{ArAr'CHOH} \arrow[r, "\mathrm{Ar'H}"] \arrow[d, "\mathrm{Fe(CO)_5}"] & \mathrm{ArAr'_2CH} \\
 & & & \mathrm{ArAr'CH^{\bullet}} \arrow[r] & \mathrm{ArAr'CHCHArAr'}
\end{tikzcd}$$

Experimental

Materials

Pentacarbonyliron (E. Merck) was used without further purification. Acid chlorides were prepared by standard procedures. Mircoanalyses were performed by the Australian Microanalytical Services, Melbourne University, Victoria, Australia. Infrared spectra were recorded on a Beckmann IR-10 spectrophotometer. The ^{1}H NMR spectra were recorded on a JEOL 60-HL spectrometer (60 MHz) with tetramethylsilane as the internal standard. Mass spectra were recorded on a Hitachi RMS-4 spectrometer. Melting points are uncorrected.

Reaction of benzoyl chloride with m-xylene in the presence of pentacarbonyliron

A mixture of benzoyl chloride (5 g, 0.036 mol), pentacarbonyliron (9.1 g, 0.046 mol) and *m*-xylene (60 ml) was heated under nitrogen in an oil bath at 140°C for two days. The mixture was cooled and filtered, and evaporation of the filtrate in vacuo gave an oil. This was dissolved in carbon tetrachloride (100 ml), and the solution was washed with water (2 × 100 ml), sodium hydroxide (10%, 2 × 100 ml), and water again (2 × 100 ml), and dried over magnesium sulphate. After removal of the solvent, the residue was chromatographed on silica gel, using hexane/benzene (4/1) as eluent, to give 2,2',4,4'-tetramethyltriphenylmethane (IIa) (1.7 g, 16%); m.p. 123—124°C (Found: C, 92.09; H, 8.12. $C_{23}H_{24}$ calcd.: C, 91.95; H, 8.05%); ν_{max}(KBr) 3060, 2960, 1490, 1450 cm^{-1}; δ(CCl_4) 6.30—7.16 (11 H, m), 5.40 (1 H, s), 2.06 (6 H, s), 2.24 (6 H, s); *m/e* 300. Further elution gave a diastereoisomeric mixture, which was separated by high pressure liquid chromatography into two pure stereoisomers of 1,2-diphenyl-1,2-di(2,4-xylyl)ethanes. One isomer (0.6 g, 9%) melted at 181—182°C (Found: C, 92.34; H, 7.70. $C_{30}H_{30}$ calcd.: C, 92.26; H, 7.74%); ν_{max}(KBr) 3050, 3000, 2930, 1495, 1450 cm^{-1}; δ (CCl_4) 6.60—7.10 (16 H, m), 4.58 (2 H, s), 2.15 (12 H, s); *m/e* 390. The other isomer (0.56 g, 8%), melted at 188—189°C (Found: C, 92.14; H, 7.81. $C_{30}H_{30}$ calcd.: C, 92.26; H, 7.74%); ν_{max}(KBr) 3020, 2930, 1495, 1450 cm^{-1}; δ(CCl_4) 6.68—7.16 (16 H, m), 4.82 (2 H, s), 2.00 (6 H, s); *m/e* 390.

Reaction of benzoyl chloride with o-xylene in the presence of pentacarbonyliron

A similar reaction of benzoyl chloride (5 g, 0.036 mol) and pentacarbonyliron (9.1 g, 0.046 mol) in *o*-xylene (60 ml) gave 3,3'-4,4'-tetramethyltriphenylmethane (IV) (1.5 g, 14.1%); m.p. 70—72°C; ν_{max}(KBr) 3050, 3030, 3000, 2950, 1490, 1450 cm^{-1}; δ($CDCl_3$) 6.62—7.25 (11 H, m), 5.30 (1 H, s), 2.15 (12 H, s); *m/e* 300; and a mixture of stereoisomers, 1,2-diphenyl-1,2-di-(3,4-xylyl)ethanes (V) (0.85 g, 12%), m.p. 204—229°C; ν_{max}(KBr) 3020, 3000, 2950, 1495, 1450 cm^{-1}; δ($CDCl_3$) 6.70—7.25 (16 H, m), 4.55 (2 H, s), 2.05 (12 H, s); *m/e* 390.

Reaction of benzoyl chloride with mesitylene in the presence of pentacarbonyliron

A similar reaction between benzoyl chloride (5 g, 0.036 mol) and pentacarbonyliron (9.1 g, 0.046 mol) in mesitylene (60 ml) gave a stereoisomeric mixture of 1,2-diphenyl-1,2-di-(2,4,6-mesityl)ethane (VI) (0.5 g, 6.7%); m.p. 170—197°C (Found: C, 91.78; H, 8.13. $C_{32}H_{34}$ calcd.: C, 91.81; H, 8.19%); ν_{max}(KBr) 3040, 2980, 2940, 1600, 1450 cm^{-1}; δ($CDCl_3$) 6.5—6.98 (14 H, m), 5.42 (2 H, s), 2.05, 2.16 and 2.25 (18 H, s); *m/e* 2.10 ($M - C_{16}H_{16}$).

Reaction of p-bromobenzoyl chloride with m-xylene in the presence of pentacarbonyliron

Reaction of *p*-bromobenzoyl chloride (5 g, 0.023 mol) and pentacarbonyliron (5.8 g, 0.030 mol) in *m*-xylene (60 ml) as described above gave 4-bromophenyl-di-(2,4-xylyl)methane (IIb) (1.58 g, 18%); m.p. 155—157°C (Found: C, 72.93; H, 6.12. $C_{23}H_{23}Br$ calcd.: C, 72.82; H, 6.11%); ν_{max}(KBr) 3065, 3010, 2990, 2950, 2900, 1485, 1450 cm^{-1}; δ(CCl_4) 6.40—7.42 (10 H, m), 5.8 (1 H, s), 2.05 (6 H, s), 2.24 (6 H, s); *m/e* 380, 378; and a stereoisomeric mixture of 1,2-di-(4-bromophenyl)-1,2-di-(2,4-xylyl)ethanes (IIIb) (1.14 g, 18%); m.p. 198—220°C (Found: C, 65.65; H, 5.20. $C_{30}H_{28}Br_2$ calcd.: C, 65.71; H, 5.15%); ν_{max}(KBr 3020, 2940, 1480, 1410 cm^{-1}; δ(CCl_4) 6.56—7.22 (14 H, m), 4.55 and 4.76 (2 H, 2s), 2.00, 2.10 and 2.18 (12 H, 3s).

Reaction of p-methylbenzoyl chloride with m-xylene in the presence of pentacarbonyliron

The reaction between *p*-methylbenzoyl chloride (5 g, 0.032 mol) and pentacarbonyliron (8.2 g, 0.042 mol) in *m*-xylene (60 ml) as described above gave 4-methylphenyl-di(2,4-xylyl)methane (IIc) (1.35 g, 13%); m.p. 153—154°C (Found: C, 91.56; H, 8.40. $C_{24}H_{26}$ calcd.: C, 91.67; H, 8.33%); ν_{max}(KBr) 3040, 3000, 2940, 2900, 1500, 1450 cm^{-1}; δ(CCl_4) 6.40—6.80 (10 H, m), 5.35 (1 H, s), 2.00 (6 H, s), 2.20 (6 H, s), 2.25 (3 H, s); *m/e* 314; and two stereoisomers of 1,2-di-(4-methylphenyl)-1,2-di-(2,4-xylyl)ethane (IIIc) (0.95 g, 14%), m.p. 150—183°C (Found: C, 91.84; H, 8.15. $C_{32}H_{34}$ calcd.: C, 91.81; H, 8.19%); ν_{max}(KBr) 3020, 2950, 1500, 1450 cm^{-1}; δ($CDCl_3$) 6.65—7.30 (14 H, m), 4.68 and 4.85 (2 H, 2s), 2.05, 2.15 and 2.20 (18 H, 3s); *m/e* 418.

Reaction of p-methoxybenzoyl chloride with m-xylene in the presence of pentacarbonyliron

p-Methoxybenzoyl chloride (5 g, 0.029 mol) and pentacarbonyliron (7.5 g, 0.038 mol) in *m*-xylene (60 ml) were treated as described above to give two stereoisomers of 1,2-di(4-methoxyphenyl)-1,2-di-(2,4-xylyl)ethane (IIId). One isomer (0.77 g, 6%), melts at 210—212°C (Found: C, 85.59; H, 7.80. $C_{32}H_{34}O_2$ calcd.: C, 85.29; H, 7.61; O, 7.10%); ν_{max}(KBr) 3000, 1600, 1590, 1500, 1450 cm^{-1}; δ($CDCl_3$) 6.32—7.20 (14 H, m), 4.72 (2 H, s), 3.54 (6 H, s), 2.12 (6 H, s), 2.00 (6 H, s); *m/e* 450. The other isomer (0.67 g, 5%), melts at 201—204°C (Found: C, 85.23; H, 7.56. $C_{32}H_{34}O_2$ calcd.: C, 85.29; H, 7.61%); ν_{max}(KBr) 3010, 2930, 2860, 1585, 1490, 1450 cm^{-1}; δ(CCl_4) 6.25—6.90 (14 H, m), 4.42 (2 H, s), 2.10 (12 H, s), 3.55 (6 H, s); *m/e* 450.

Reaction of benzaldehyde with m-xylene in the presence of pentacarbonyliron

Benzoyl chloride (5 g, 0.036 mol), benzaldehyde (3.8 h, 0.036 mol) and pentacarbonyliron (9.1 g, 0.046 mol) in *m*-xylene (65 ml) were heated together under nitrogen in an oil bath at 140°C for two days. The mixture was cooled, filtered, and evaporated in vacuo to give an oil. This was dissolved in carbon tetrachloride (100 ml), and the solution was washed with water (2 × 100 ml), sodium hydroxide (10%, 2 × 100 ml) and water again (2 × 100 ml), and dried over magnesium sulphate. After removal of the solvent, the residue was chromatographed on silica gel with hexane/benzene (4/1) as eluent to give compound IIa (3.2 g, 30%) and a diastereoisomeric mixture of IIIa (2.8 g, 40%).

Reaction of benzaldehyde with p-bromobenzoyl chloride and m-xylene in the presence of pentacarbonyliron

p-Bromobenzoyl chloride (5 g, 0.023 mol), benzaldehyde (2.4 g, 0.023 mol) and pentacarbonyliron (5.8 g, 0.030 mol) in *m*-xylene (65 ml) were heated under nitrogen on an oil bath at 140°C for two days. The products were separated and purified as described above to give compound IIa (1.9 g, 28%) and a diastereomeric mixture of IIIa (1.9 g, 42%).

Reaction of p-chlorobenzaldehyde with benzoyl chloride and m-xylene in the presence of pentacarbonyliron

Benzoyl chloride (5 g, 0.036 mol) and *p*-chlorobenzaldehyde (5 g, 0.036 mol) and pentacarbonyliron (9.1 g, 0.046 mol) in *m*-xylene (70 ml) were treated as described above to afford 4-chloro-2′,2″,4′,4″-tetramethyltriphenylmethane (5.4 g, 45%), m.p. 150—151° C (Found: C, 82.47; H, 6.94. $C_{23}H_{23}Cl$ calcd.: C, 82.49; H, 6.92%); ν_{max}(KBr) 3020, 3000, 2940, 2880, 1485, 1450 cm^{-1}; δ($CDCl_3$) 6.45—7.25 (10 H, m), 5.52 (1 H, s), 2.15 (6 H, s), 2.08 (6 H, s); *m/e* 336; and a stereoisomeric mixture of 1,2-di-(4-chlorophenyl)-1,2-di(2,4-xylyl)ethanes (2.6 g, 23%) m.p. 186—213°C (Found: C, 78.30; H, 6.33. $C_{30}H_{28}Cl_2$ calcd.: C, 78.42; H, 6.14%); ν_{max}(KBr) 3020, 2880, 1490 cm^{-1}; δ($CDCl_3$) 6.62—7.18 (14 H, m), 4.60 and 4.82 (2 H, 2s), 2.02 and 2.15 (12 H, 2s).

Reaction of diphenylmethanol with m-xylene and benzoyl chloride in the presence of pentacarbonyliron

Diphenylmethanol (6.5 g, 0.035 mol), benzoyl chloride (5 g, 0.036 mol) and pentacarbonyliron (9.1 g, 0.046 mol) were heated together under nitrogen atmosphere in an oil bath at 140°C for two days. The mixture was cooled and filtered. After evaporation of the solvent in vacuo, the residue was dissolved in carbon tetrachloride (100 ml) and the solution was washed with water (2 × 100 ml), sodium hydroxide (10%, 2 × 100 ml) and water again (2 × 100 ml), and dried over magnesium sulphate. After removal of the solvent, the residue was chromatographed on a silica gel column using hexane/benzene (4/1) as eluent to give 2,4-dimethyltriphenylmethane (3.1 g, 32%) and tetraphenylethane (2.1 g, 45%), m.p. 213—215°C, (lit. [9] 214—215°C).

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