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TRANSITION METAL-PROMOTED REACTIONS

X *. PENTACARBONYLIRON-PROMOTED REDUCTIVE COUPLING OF BENZOYL CHLORIDE IN HALOBENZENES

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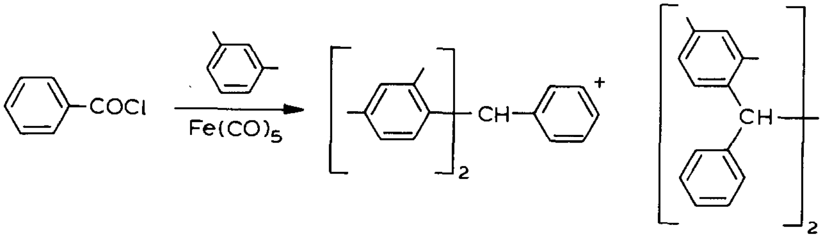
Summary

Reductive coupling of benzoyl chloride to give *trans*- and *cis*-α,α'-stilbenediol dibenzoates is found to be promoted by pentacarbonyliron. The mechanism is briefly discussed.

Introduction

We recently reported that aromatic acid halides react with pentacarbonyliron in aromatic hydrocarbon solvents with benzylic hydrogens (such as xylenes) to give a mixture of the corresponding triarylmethane and tetraarylethanes [2] (eq. 1). The reaction may proceed via an acyl radical intermediate. A similar intermediate may also exist in related reactions. Thus, neat acetyl chloride was reported to be converted into biacetyl on treatment with pentacarbonyliron in a sealed tube [3]. Octanal was recently isolated from a reaction of octanoyl chloride and enneacarbonyl-diiron in diethylether [4]. An ionic reaction mechanism has also been proposed when the corresponding esters were obtained from the reaction of acid chloride and pentacarbonyliron in ether solvents [5]. We now wish to describe our



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* For part IX see ref. 1.

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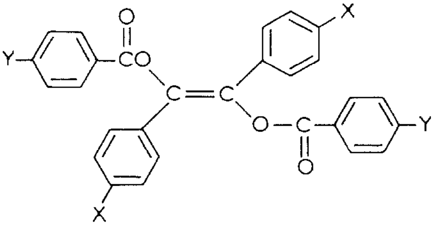
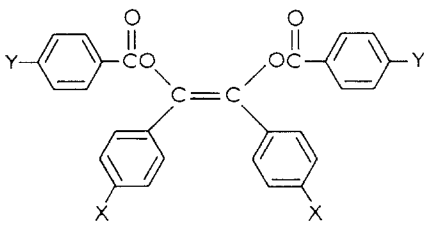
investigation of the reactions of pentacarbonyliron with benzoyl chlorides in halobenzene solvents. Halobenzenes were chosen because they have no active hydrogen(s) and because the aromatic ring is deactivated so that no side reactions such as aromatic substitution would occur.

Results and discussion

On treatment with pentacarbonyliron in bromobenzene at refluxing temperature, benzoyl chloride was smoothly transformed to a mixture of *trans*- and *cis*-α,α'-stilbenediol dibenzoates, **1a** and **2a**, and in 51 and 5% yield, respectively. Comparable results were also obtained when iodobenzene was employed as solvent. The yield was much poorer (ca 13%) when the reaction was carried out in chlorobenzene.

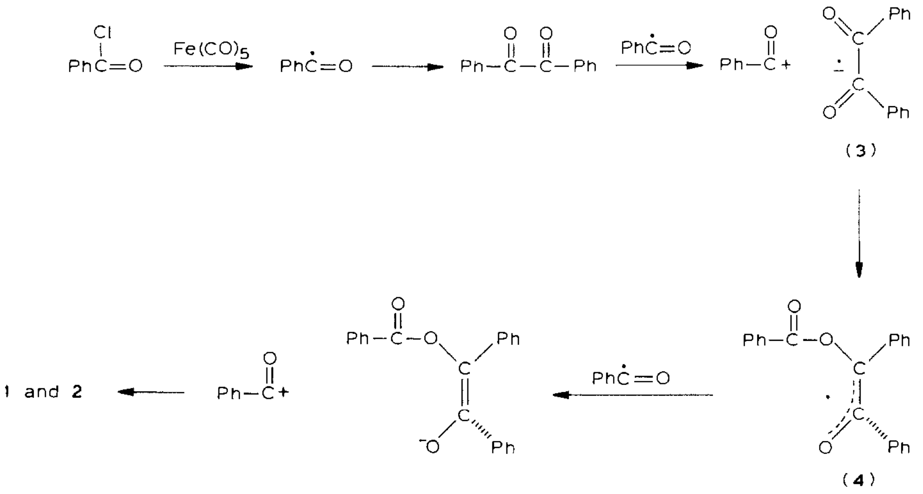


(**1a** , X = Y = H; **1b**, X = Y = D; **1c** , X = H, Y = D)



(**2a** , X = Y = H; **2b** , X = Y = D; **2c** , X = Y = D)

Presumably, the reaction is temperature dependent. Alternatively, the possibility of carbonyl insertion into the carbon–halogen bond of halobenzene is of concern. It is known that iodobenzene reacts with $Fe_3(CO)_{12}$ to give benzophenone [6]. A σ-acyliron complex was proposed to be the intermediate. This insertion process was ruled out by employing labelled reactants. Thus, 4-deuteriobenzoyl chloride was treated with pentacarbonyliron in bromobenzene or iodobenzene to give exclusively a mixture of **1b** and **2b** with four deuterium atoms on each molecule, which afforded two moles of



SCHEME 1

4-deuteriobenzoic acid and one mole of 4,4′-dideuteriobenzoin upon base hydrolysis.

The mechanism of the reaction is of interest. On treatment with benzoyl chloride and pentacarbonyliron in bromobenzene, benzil was completely transformed to **1a** and **2a**. When 4-deuteriobenzoyl chloride was employed, a mixture of dideuterated **1c** and **2c** and tetradeuterated **1b** and **2b** was obtained. It is interesting to note that no reaction was found from the mixture of benzil and pentacarbonyliron in the absence of acid chloride. Therefore, the possible entity from which benzil might accept electrons would be benzoyl radical which could be formed from the homolytic cleavage of the carbon–chlorine bond of the acid chloride [2,7]. An electron transfer process from benzoyl radical to benzil might be facile, leading to the formation of benzoyl cation and a semidione radical anion **3** which collapses to afford **4**. A similar process might occur again to give **1** and **2**. The overall plausible mechanism is outlined in Scheme 1. This mechanism is compatible with the recent report on the cathodic reductions of aroyl chloride [8].

Experimental

All melting points are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 283 spectrophotometer. NMR spectra were taken on JEOL C-60 HL and FX 90Q spectrometers. Mass spectra were measured on a VG 7070F mass spectrometer.

Reaction of benzoyl chloride with pentacarbonyliron in bromobenzene

Benzoyl chloride (5 g, 0.036 mol) and pentacarbonyliron (9.1 g, 0.046 mol) in bromobenzene (50 ml) were heated under a nitrogen atmosphere in an oil bath at 140°C for two days. The mixture was cooled to room temperature and filtered; removal of solvent in vacuo yielded a brown solid which was chromatographed on silica gel using hexane/benzene (1/1) as eluent. The first band gave *trans*-α,α'-stilbenediol dibenzoate, **1a** (1.9 g, 51%), m.p. 190–191°C (lit. [9] 189°C); ν (KBr) 1740 cm^{-1}; δ ($CDCl_3$) 7.25–8.25 ppm; *m/e* 420, and the second band gave *cis*-α,α'-stilbenediol dibenzoate **2a** (0.17 g, 5%), m.p. 160–161°C (lit. [9] 159°C); ν (KBr) 1730 cm^{-1}; δ ($CDCl_3$) 7.15–8.14 ppm; *m/e* 420.

When iodobenzene was employed as solvent, **1a** and **2a** were obtained in 53% and 5% yields. On the other hand, **1a** was isolated in 13% yield when the reaction was carried out in chlorobenzene.

Reaction of 4-benzoyl chloride-d_1 with pentacarbonyliron in bromobenzene

4-Benzoyl chloride-d_1 (2 g, 0.014 mol) and pentacarbonyliron (3.6 g, 0.018 mol) in bromobenzene (30 ml) were heated under a nitrogen atmosphere in an oil bath at 140°C for two days. The mixture was cooled to room temperature and filtered. Removal of solvent in vacuo yielded a brown solid which upon recrystallization from benzene gave *p*-*trans*-α,α'-stilbenediol dibenzoate-d_4, **1b**, (0.7 g, 47%), *m/e* 424. Removal of the benzene from the mother liquor gave a residue which was recrystallized from ethanol to yield *p*-*cis*-α,α'-stilbenediol dibenzoate-d_4, **2b**, (0.07 g, 5%); *m/e* 424.

Reaction of benzil with benzoyl chloride and pentacarbonyliron in bromobenzene

Benzoyl chloride (5 g, 0.036 mol), benzil (3.7 g, 0.018 mol) and pentacarbonyliron

(9.1 g, 0.046 mol) in bromobenzene (65 ml) were allowed to react and then worked up in the same manner as that described above. *trans*-α,α'-Stilbenediol dibenzoate, **1a**, (3.0 g, 40%) and *cis*-α,α'-stilbenediol, **2a**, (0.65 g, 8%) were obtained.

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