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Oxidation by Iron(III) Complexes. IX.[1] The Preparation of α-Diketones by the Oxidation of Enolizable Ketones with the Iron(III) Chloride-Pyridine Complex under Oxygen

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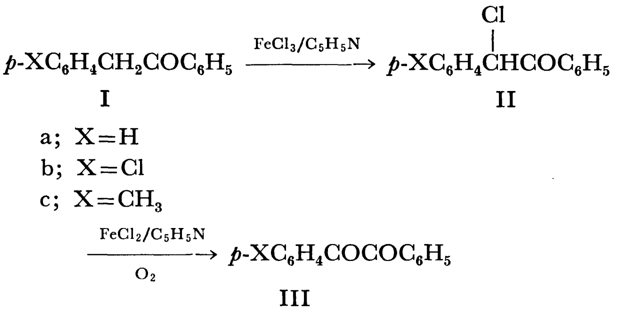
Synopsis. The oxidation of deoxybenzoin and *p*-substituted deoxybenzoins with an iron(III) chloride-pyridine complex under air or oxygen was investigated. The reaction afforded the corresponding α-diketones in a satisfactory yield.

We have recently reported that enolizable deoxybenzoin (Ia) is oxidized with iron(III) chloride dispersed in benzene to undergo direct arylation with benzene at the α-position of the carbonyl group.[2] In the course of our studies, we found that the reaction pathway alters in the direction of the formation of an α-diketone, benzil(IIIa), upon the addition of pyridine to the reaction system, and that the reaction proceeds *via* the formation of an intermediate, α-chlorodeoxybenzoin(IIa), followed by the oxidation of IIa with oxygen in the presence of iron(II) chloride and pyridine. We wish to report here a novel method for the preparation of α-diketones from I.



$$p\text{-}XC_6H_4CH_2COC_6H_5 \xrightarrow{FeCl_3/C_5H_5N} p\text{-}XC_6H_4\overset{\overset{Cl}{|}}{C}HCOC_6H_5$$

I II

a; X=H

b; X=Cl

c; $X=CH_3$

$$\xrightarrow[O_2]{FeCl_2/C_5H_5N} p\text{-}XC_6H_4COCOC_6H_5$$

III

Results and Discussion

The Formation of α-Diketone. When pyridine was added to dry benzene containing the dispersed anhydrous iron(III) chloride (in the pyridine/iron(III) chloride molar ratio of 1: 1), the iron(III) chloride solid changed to a black-brown paste which adhered to the wall of the reaction vessel. Ia was then added to the reaction system, and the solution was heated at 80 °C under an atmosphere of air. As the reaction time proceeded, the paste changed to a black-brown solid containing an iron(III) ion and pyridine as the major components. Ia was converted to IIIa, along with the by-products of benzaldehyde, benzoic acid, and 2,2-diphenylacetophenone(IV), as is shown in Table 1. The other products were a high-melting material and a tarry matter, although the structures of the products are still uncertain. In the absence of the iron(III) chloride and/or pyridine, IIIa was not obtained at all. When the reaction was carried out under oxygen, the yield of IIIa became higher than that in the case of air (Table 1). The substituted deoxybenzoins (Ib and Ic) were also converted to the corresponding α-diketones (IIIb and IIIc). In the case of propiophenone, however, the α-diketone was not obtained under similar conditions, although α-chloropropiophenone was produced in a good yield.[2] Thus, the existence of the phenyl group at the α-position of the carbonyl group is required for the formation of the α-diketone.

TABLE 1. THE REACTION OF I WITH AN IRON(III) CHLORIDE-PYRIDINE (1 : 1) COMPLEX UNDER AIR OR OXYGEN[a)]

Ketone	Atmosphere	Yield, %	
		III	*p*-XPhCHO
Ia[b)]	Air	56	11
Ia	O_2	73	2
Ib	O_2	78	7
Ic	O_2	67	8

a) The reaction time: 24 hr. The remaining I was not detected after 24 hr. b) IV was obtained in 8% yield. In a large scale reaction benzoic acid was isolated in 4% yield.

Catalytic Behavior. The oxidation of Ia with the iron(III) chloride–pyridine complex under air was carried out in the molar ratio of Ia, iron(III) chloride, and pyridine of 10 : 1 : 1. After a reaction of 118 hr, IIIa was produced in a 56% yield (based on Ia). This means that the iron(III) complex acts as a catalyst for the formation of IIIa.

Reaction Pathway. In the initial period of the reaction, IIa was detected by means of glc, although the amount produced was very small. After a long reaction, however, IIa could not be detected at all. This fact suggests that IIa is produced as an intermediate in the formation of IIIa. The reaction of Ia with the iron(III) chloride–pyridine (1: 1) complex under nitrogen at 80 °C for 24 hr afforded only IIa in a 56% yield, with a 35% recovery of Ia. In this reaction, the iron(III) ion was reduced to the iron(II) ion in a 55% yield. In addition, IIa was oxidized with oxygen in the presence of the hydrated iron(II) chloride and pyridine to afford IIIa in a good yield (Table 2), along with an iron(III) complex. In the absence of iron(II) chloride and pyridine, IIIa was not obtained at all. These facts led to the conclusion that IIIa is produced *via* the formation of IIa, followed by the oxidation of IIa with oxygen in the presence of the iron(II) complex produced.

On the other hand, the yields of benzaldehyde and benzoic acid became higher in a homogeneous reaction

TABLE 2. THE REACTION OF Ia OR IIa WITH THE Fe(II) OR Fe(III) COMPLEX[a)]

Ketone	Fe(II) or Fe(III) complex	Atmosphere	Time hr	Yield, %		Recovery, % Ketone
				IIIa	PhCHO	
Ia[b)]	$FeCl_3/CH_3CN$	Air	24	15	38	10
Ia[c)]	$[Fe(DMF)_3Cl_2][FeCl_4]$	Air	96	26	58	9
IIa[c,d)]	$FeCl_2/C_5H_5N$	O_2	24	83	0	0

a) The molar ratio of Ia or IIa to Fe(II) or Fe(III) ion: 1 : 2. b) IIa and benzoic acid were isolated in 14 and 20% yields, respectively. c) The solvent: benzene. The temperature: 80 °C. d) The Fe(II) ion was oxidized to the Fe(III) ion in 90% yield. The $FeCl_2/C_5H_5N$ molar ratio: 1.

of Ia with iron(III) chloride in acetonitrile under an atmosphere of air. A similar phenomenon was observed in the reaction of Ia with $[Fe(DMF)_3Cl_2][FeCl_4]$[3] dispersed in benzene (Table 2). Thus, the yields of IIIa and benzaldehyde can be altered by changing the structure of the iron(III) complex. Benzaldehyde and benzoic acid are produced by the carbon-carbon cleavage of the $-CH_2-CO-$ bond, although the mechanism is ambiguous.

Experimental

Materials. The anhydrous iron(III) chloride was prepared by the method described in a previous paper.[1] The hydrated iron(II) chloride, $FeCl_2 \cdot 5H_2O$, was prepared by the recrystallization of commercial iron(II) chloride from water. The Ia, Ib, Ic, IIa, IIIb, and IIIc were prepared by the methods described in the literature.[4]

Oxidation. *By Iron(III) Chloride-Pyridine Complex*: Similar procedures were used for all the reactions. Pyridine (1 mmol) was added to dry benzene (5 ml) containing the dispersed iron(III) chloride (1 mmol). Ia (0.5 mmol) was then added to the solution. The resulting solution was heated at 80 °C under an atmosphere of air, oxygen, or nitrogen for the desired time. In the case of a nitrogen atmosphere, the reaction tube was degassed by the freeze-thaw method and then sealed. After the reaction, 2 ml of water was added to the resulting mixture, and then an internal standard, biphenyl, was added. The benzene layer was analyzed by glc. The products were identified by a comparison of their retention times in glc with those of authentic specimens, and their amounts were determined by means of glc. The products were isolated out by the following method. To dry benzene (40 ml) containing the dispersed iron(III) chloride (1.36 g), we added pyridine (0.64 g) and then Ia (0.85 g), after which the solution was heated at 80 °C under air. After a 24-hr reaction, a black-brown solid (2.08 g) was collected from the brown solution by filtration and washed with benzene. Found: C, 28.08; H, 2.58; N, 5.40; Cl, 38,45; Fe(II), 2.4; Fe(III), 15.27%. The combined benzene solution was extracted with a 10% sodium bicarbonate solution and then subjected to chromatography on alumina. Elution with benzene gave 0.025 g (3%) of the unreacted Ia and 0.1 g (8%) of IV. The formation of benzaldehyde was confirmed by means of glc. Elution with methanol gave 0.47 g (52%) of IIIa (mp 94—95 °C). Elution with methanol-water gave 0.26 g of a white, amorphous product (mp>280 °C), which did not become crystalline, along with a tarry matter. The white product exhibited an IR spectrum with broad peaks at 3050, 1660, 1600, 1550, 1410, 1210, 1180, 1070, 880, 840, 800, 703, and 680 cm^{-1}. The sodium bicarbonate solution was acidified with dilute aqueous hydrochloric acid and extracted several times with benzene. The benzene extracts were then combined and the solvent removed to yield 0.021 g (4%) of benzoic acid. IIIb (mp 71—72 °C) and IIIc (mp 30—31 °C) were isolated and identified by a method similar to that used in the case of IIIa.

By $[Fe(DMF)_3Cl_2][FeCl_4]$: A solution of Ia (0.53 mmol) in benzene (5 ml) containing the iron(III) complex (1.1 mmol) was heated at 80 °C for 96 hr. The amounts of IIIa and benzaldehyde were then determined by means of glc.

By Iron(III) Chloride in Acetonitrile: An acetonitrile solution (30 ml) of a mixture of Ia (3.2 mmol) and iron(III) chloride (6.3 mmol) was refluxed under air for 24 hr. After the subsequent removal of the acetonitrile, the residue was added to benzene. The amounts of the products were determined by means of glc.

Analyses. The iron(II) or iron(III) complex isolated was analyzed by the methods described in a previous paper.[5] Analytical determinations of the products were carried out using a Hitachi K-53 gas chromatograph fitted with a 3 mm × 1 m stainless steel column packed with 30% high-vacuum silicon grease on Celite 545.

References

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