The Oxidative Coupling of Butyrophenone by Ferric Chloride

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(Received September 4, 1971)

We wish to report a novel oxidative coupling of enolizable ketone, butyrophenone (I), which takes place thermochemically and photochemically in the presence of ferric chloride, leading to the formation of the γ-diketone, 3,4-benzoylhexane (II), accompanied by chlorination in the α-position of the carbonyl group to give α-chlorobutyrophenone (III).

A solution of 0.22 g (1.34 mmol) of anhydrous ferric chloride in 5 m*l* of I was heated at 70—80°C for 48 hr. During the course of the reaction, ferric chloride was reduced to ferrous chloride in a 67% yield. The two products of II and III were isolated by gas chromatography after work-up; II (yield, 49%) exhibited NMR (CCl_4) signals at 0.7—1.3 (*m*, 6H, CH_3), 1.6—2.1 (*m*, 4H, CH_2), 4.05 and 5.55 (*q* and *t*, 2H, CH), and 6.9—8.0 (*m*, 10H, aromatic protons), and an IR (liquid film) peak at 1680 cm^{-1} (CO). Mass *m/e*; 294 (parent peak).

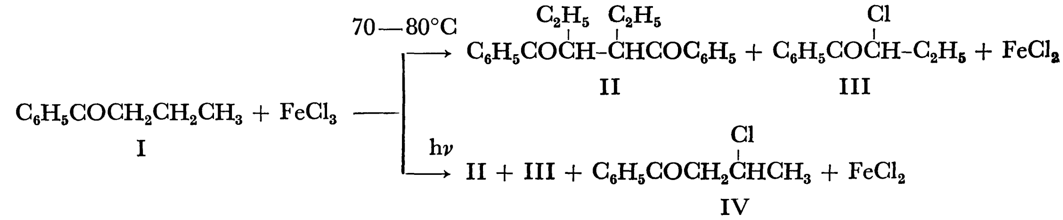
Found: C, 81.56; H, 7.55%. Calcd for $C_{20}H_{22}O_2$: C, 81.60; H, 7.53%.

III[1] (yield, 31%) exhibited NMR (CCl_4) signals at 1.05 (*t*, 3H, CH_3), 1.7—2.3 (*m*, 2H, CH_2), 4.75 (*t*, 1H, CH), and 7.2—7.9 (*m*, 5H, aromatic protons), and an IR (liquid film) peak at 1693 cm^{-1} (CO).

The yields of II and III, which were calculated by 200×(the number of moles of the product / that of ferric chloride), increased as the reaction time proceeded and then became constant after 3 hr. Over 3 hr, III was not converted to II. When a mixture of 0.11 g (0.58 mmol) of III and 0.063 g (0.48 mmol) of ferrous chloride in 5 m*l* of I was heated at 70°C, II was not obtained, but III was recovered unchanged. These facts indicate that the coupling reaction does not proceed *via* the process involving the reduction of III by ferrous chloride. The yield of II increased with an increase in the concentration of ferric chloride up to the saturation of ferric chloride. Furthermore, the addition of pyridine to the ferric chloride - I system resulted in a decrease in the yield of II. With the molar ratio of pyridine to ferric chloride of 1: 1, III was obtained selectively in a 64% yield.

On the other hand, a solution of 0.21 g (1.27 mmol) of ferric chloride in 5 m*l* of I, which had been placed in a quartz tube, was irradiated with a 100-W high-pressure mercury lamp at a distance of 4 cm under an atmosphere of air at room temperature for 24 hr. During the course of this reaction, white crystals of ferrous chloride precipitated (yield, 83%). The reaction products were II, III, β-chlorobutyrophenone (IV), and acetophenone, which were obtained in 26, 26, 14, and 31% yields respectively. The formation of ethylene was also confirmed by converting the ethylene to 1,2-dibromoethane. Acetophenone and ethylene were produced after the complete conversion of ferric chloride to ferrous chloride. When pyridine was added to the reaction system, with the molar ratio of pyridine to ferric chloride of 1: 1, III, IV, and crotophenone were obtained in 48, 14, and 6% yields respectively after irradiation for 24 hr.

The formation of II and III indicates that the initial step involves the oxidation of the ketone by ferric chloride, thus leading to the α-keto radical. Such a process has been found in the oxidation of ketones by either manganic or ceric ions.[2-4] The α-keto radicals couple with each other to form II or are oxidized by the ferric chloride to give α-chloroketone (III).[5] Further work is in progress and will be reported in the future.



$$\underset{\text{I}}{C_6H_5COCH_2CH_2CH_3} + FeCl_3 \xrightarrow{70\text{—}80^\circ C} \underset{\text{II}}{C_6H_5CO\overset{C_2H_5}{C}H\text{-}\overset{C_2H_5}{C}HCOC_6H_5} + \underset{\text{III}}{C_6H_5CO\overset{Cl}{C}H\text{-}C_2H_5} + FeCl_2$$

$$\xrightarrow{h\nu} \text{II} + \text{III} + \underset{\text{IV}}{C_6H_5COCH_2\overset{Cl}{C}HCH_3} + FeCl_2$$

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