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REACTIONS OF SULFINES WITH IRON AND MANGANESE CARBONYLS; DEXOYGENATION VS. *ortho*-METALATION

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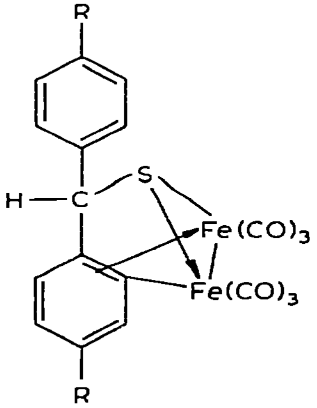
Summary

Diaryl sulfines react with diiron enneacarbonyl in benzene at room temperature to give thiobenzophenones and/or *ortho*-metalated complexes derived from the thioketones, rather than *ortho*-metalated complexes of sulfines. Deoxygenation of sulfines also occurred when dimanganese decacarbonyl was used as the metal carbonyl. These reactions may proceed via initial nucleophilic attack of the sulfine at a terminal metal carbonyl carbon.

Results and discussion

Thiobenzophenones react with iron [1], ruthenium [2], and manganese [3] carbonyls to form sulfur-donor ligand *ortho*-metalated complexes [e.g., I], the latter being useful as intermediates in organic synthesis [1,4].



(I)

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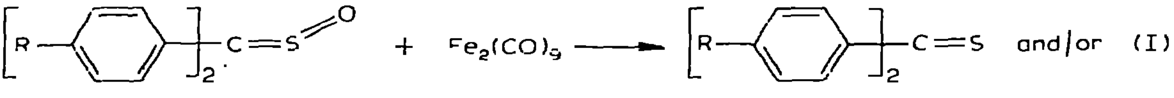
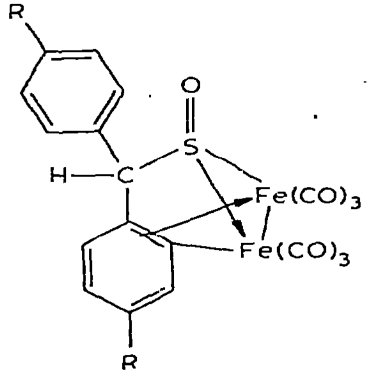
It is also known that iron pentacarbonyl is a convenient reagent for deoxygenating a variety of sulfoxides to sulfides [5]. The *ortho*-metalation and deoxygenation results led to a study of the reactions of sulfines (II) with several metal carbonyls. It was of considerable interest to learn whether preferential deoxygenation or *ortho*-metalation would occur using a sulfine as the organic reactant.

$$R_2S{\to}O + Fe(CO)_5 \xrightarrow{\text{Diglyme or } (n\text{-}C_4H_9)_2O} R_2S$$

Treatment of di(*p*-methoxyphenyl) sulfine [II, R = OCH_3] with diiron enneacarbonyl [$Fe_2(CO)_9$] in benzene at room temperature gave the *ortho*-metalated complex I, R = OCH_3, and/or 4,4'-dimethylthiobenzophenone [III, R = OCH_3], the product distribution subject to the proportion of reactants used. Employing a 2/1 ratio of II/$Fe_2(CO)_9$ gave III, R = OCH_3, in 42% yield and I, R = OCH_3, in 7% yield. The thioketone was obtained in 25% yield and the *ortho*-metalated complex was isolated in 20% yield when equimolar amounts of reactants were used. Use of a 2.5/1.0 mole ratio of $Fe_2(CO)_9$/II gave the *ortho*-metalated complex in 74% yield. Similarly, the following yields of III and/or I [R = CH_3] were realized from reaction of di(*p*-tolyl) sulfine with $Fe_2(CO)_9$:54% III, 10% II [2/1 ratio of II/$Fe_2(CO)_9$]; and 24% III, 32% I [1/1 ratio fo II/$Fe_2(CO)_9$]. Small amounts (4-10%) of benzophenones were obtained in these reactions, presumably due to oxidation of III on work-up. No *ortho*-metalated complex of structural type IV was detected in any of these reactions.



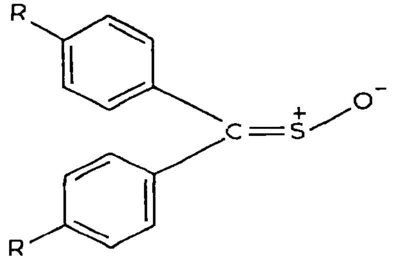
(II) (III)



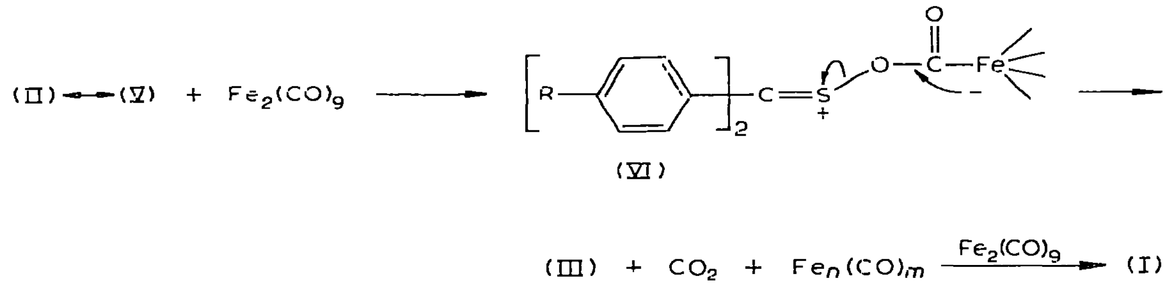
(IV)

Deoxygenation of sulfines was also observed with dimanganese decacarbonyl [$Mn_2(CO)_{10}$]. 4,4'-Dimethoxythiobenzophenone [III, R = OCH_3] was obtained in 51% yield by treatment of II, R = OCH_3, with $Mn_2(CO)_{10}$, and III, R = CH_3, was formed in 48% yield when II, R = CH_3, was used as the reactant sulfine. By-products of both reactions were tetraarylethylenes, which were also isolated from the reaction of III with $Mn_2(CO)_{10}$.

The results described above clearly demonstrate that when both deoxygenation and *ortho*-metalation are possible, deoxygenation is the preferred reaction pathway. An accounting of these results can be made on the basis that V makes an important contribution to the resonance hybrid of II [6]. The initial step in the *ortho*-metalation reaction of thiobenzophenones probably involves attack of a lone pair of sulfur on the metal carbonyl. Such a reaction pathway is less likely for sulfines due to the presence of a positive charge at sulfur in V. Instead, nucleophilic attack by the sulfine, at one of the terminal metal carbonyl carbons. [e.g., of $Fe_2(CO)_9$] to give VI, and subsequent loss of carbon dioxide, would afford the deoxygenated material. The latter can undergo further reaction [e.g., III → I] in the presence of more metal carbonyl. The deoxygenations of sulfoxides and nitrile oxides [7] likely occur by a pathway analogous to that described herein. In addition, this mechanism is similar to that proposed for the deoxygenation of amine oxides, azoxy benzenes and nitrones by iron pentacarbonyl [8].



(V)



Experimental

Melting points were measured using a Fisher—Johns apparatus and are uncorrected. Infrared spectra were obtained on a Perkin—Elmer 457 grating spectrophotometer. Nuclear magnetic resonance spectra were determined on a Varian A-60 spectrometer with tetramethylsilane as the internal standard. All reactions were run under an atmosphere of dry nitrogen.

Diiron enneacarbonyl and dimanganese decacarbonyl were purchased from Pressure Chemical Company and used as received. 4,4'-Dimethylthiobenzophenone was purchased from Aldrich Chemical Company and 4,4'-dimethylthiobenzophenone was synthesized according to the method of Scheeren and co-workers [9].

Sulfines

Sulfines were prepared by oxidation of the corresponding thioketone with *m*-chloroperbenzoic acid. This method is superior to that using mono-perphthalic acid [10], because *m*-chloroperbenzoic acid is commercially available (Aldrich Chemical Co.) and because the reaction is simple to carry out and affords high yields of sulfines. The following general procedure was used: An ether solution [20-35 ml] of *m*-chloroperbenzoic acid [5-15 mmol] was added dropwise to an ice-cold ether solution [50-100 ml] containing an equimolar amount of the thiobenzophenone. After addition was complete, the solution was transferred to a separating funnel and washed successively with aqueous sodium bisulfite, aqueous sodium bicarbonate, and then twice with water. The ether layer was dried over Na_2SO_4, and the sulfine was obtained by flash evaporation of the solvent. In this manner, di(*p*-methoxyphenyl) sulfine [II, R = OCH_3, m.p. 84-86° (lit. [10] m.p. 84-85°)] and di(*p*-tolyl) sulfine [II, R = CH_3, m.p. 93-94° (lit. [11] m.p. 92-93°)] were prepared in 86% and 83% yields, respectively.

General procedures for reactions of sulfines with metal carbonyls

(i). Diiron enneacarbonyl. A mixture of the sulfine and $Fe_2(CO)_9$ in dry benzene was stirred at room temperature for 36 h. The solution was filtered, and the filtrate was evaporated in vacuo. The residue from flash evaporation was dissolved in pentane and chromatographed on Florisil. Elution with pentane gave the *ortho*-metalated complex, followed by thioketone (if present). Elution with benzene afforded, in several instances, minor amounts of ketone.

(ii). Dimanganese decacarbonyl. A mixture of the sulfine and $Mn_2(CO)_{10}$ was refluxed with stirring in isooctane or in n-heptane for 24-26 h. The solution was cooled, filtered from some tetraarylethylene, and the filtrate evaporated in vacuo. The resulting residue was dissolved in benzene and chromatographed on neutral alumina. Elution with benzene first gave the thioketone, followed by tetraarylethylene (if any).

The products obtained from each of the above reactions were identified by mixed melting points with authentic samples, and by their infrared and nuclear magnetic resonance spectral properties.

Acknowledgment

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