Communications

The Hydridotetracarbonylferrate Anion, a Convenient Desulfurization Reagent

Summary: Thioketones and thioamides react with $HFe(CO)_4^-$ in 1,2-dimethoxyethane to give hydrocarbons and amines, respectively, in good yield; use of $DFe(CO)_4^-$ as the reagent resulted in incorporation of two deuterium atoms in the product.

Sir: The hydridotetracarbonylferrate anion $[HFe(CO)_4^-]$ is a useful reagent for effecting stereospecific dehalogenation of organic halides,[1] hydroacylation,[2] reductive alkylation,[3,4] amination,[5-7] and hydrogenation of an α,β-unsaturated carbonyl.[8] This communication reports a new, and important, use of the iron hydride as a desulfurization reagent.

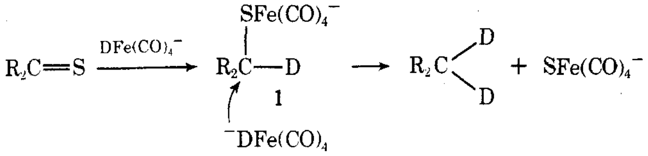
Treatment of an aliphatic or aromatic thioketone with 4 equiv of $HFe(CO)_4^-$ (generated in situ from a 3:1 mixture of KOH and iron pentacarbonyl) in refluxing 1,2-dimethoxyethane (8–12 hr) afforded the desulfurized hydrocarbon in 60–81% yield (Table I). Amines were obtained by use of thioamides as reactant thiones.

Table I
Products Obtained from Reactions of Organosulfur Compounds with $HFe(CO)_4^-$ (A) or $DFe(CO)_4^-$ (B)

Reactant	Iron hydride	Product[a]	Yield, %
$(C_6H_5)_2CS$	A	$(C_6H_5)_2CH_2$	60
$(4\text{-}CH_3C_6H_4)_2CS$	A	$(4\text{-}CH_3C_6H_4)_2CH_2$	61
$(4\text{-}CH_3OC_6H_4)_2CS$	A	$(4\text{-}CH_3OC_6H_4)CH_2$	77
$(4\text{-}CH_3OC_6H_4)_2CS$	B	$(4\text{-}CH_3OC_6H_4)_2CD_2$	74
$(4\text{-}(CH_3)_2NC_6H_4)_2CS$	A	$(4\text{-}(CH_3)_2NC_6H_4)_2CH_2$	81
Adamantanethione	A	Adamantane	74
Adamantanethione	B	2,2-Dideuterioadamantane	78
$C_6H_5CSNHC_6H_5$	A	$C_6H_5CH_2NHC_6H_5$	38
$CH_3CSNHC_6H_5$	A	$C_2H_5NHC_6H_5$	51

[a] Products were characterized by comparison of spectral data with that for authentic samples, as well as by mixture melting points (except for deuterium containing products where mass, NMR, and ir spectroscopy was used for structure elucidation).

Incorporation of two deuterium atoms readily occurred by reaction of 4,4′-dimethoxythiobenzophenone or adamantanethione with $DFe(CO)_4^-$ [from KOD and $Fe(CO)_5$]. Attack of $HFe(CO)_4^-$ [or $DFe(CO)_4^-$] at the thione group of a thioketone to give **1** is probably the first step in the reaction. Addition of a second molecule of iron hydride



$$R_2C{=}S \xrightarrow{DFe(CO)_4^-} R_2\overset{\displaystyle SFe(CO)_4^-}{\underset{\displaystyle \overset{\uparrow}{^-DFe(CO)_4}}{C}}{-}D \;\; \mathbf{1} \longrightarrow R_2C\begin{smallmatrix}D\\D\end{smallmatrix} + SFe(CO)_4^-$$

(or deuteride) would give the product and a sulfur iron carbonyl anion.

A Schiff base is a likely intermediate in the thioamide–$HFe(CO)_4^-$ reaction. The reduction of Schiff bases to amines by the related trinuclear hydride, $HFe_3(CO)_{11}^-$, has been described.[9]

The following procedure is typical. A mixture of $Fe(CO)_5$ (3.0 ml, 22.1 mmol), KOH (3.69 g, 66 mmol), and water (6.0 ml) was refluxed in 1,2-dimethoxyethane (90 ml) for 1.5 hr to generate $HFe(CO)_4^-$. To this solution was added 4,4′-dimethylthiobenzophenone (1.21 g, 5.35 mmol) in 1,2-dimethoxyethane (20 ml), and the resulting mixture was refluxed for 10 hr. The solution was cooled and filtered, and the filtrate was flash evaporated to a brown solid. The latter was treated with ether (200 ml) and filtered; the filtrate was washed three times with water (i.e., until the aqueous layer was colorless). The ether extract was dried ($MgSO_4$), filtered through a short column of Florisil, and concentrated to give 0.69 g (61%) of pure bis(p-tolyl)methane.

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References and Notes

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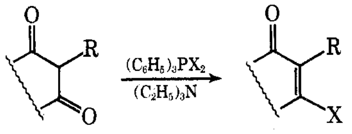
Reaction of Cyclic β-Halo α,β-Unsaturated Ketones with Cuprate Reagents. A New, Efficient Synthesis of β-Alkyl α,β-Unsaturated Ketones

Summary: Reaction of cyclic β-halo α,β-unsaturated ketones with various alkyl cuprate reagents produced the corresponding β-alkyl α,β-unsaturated ketones in high yield.

Sir: Recently, we reported[1] that the reaction of cyclic β diketones **1** with triphenylphosphine dihalides under appropriate conditions produced, in excellent yields, the corresponding β-halo α,β-unsaturated ketones **2**. We report



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