New Synthesis of α-Diketones from Aldehydes and Alkyl Iodides Using Pentacarbonyliron

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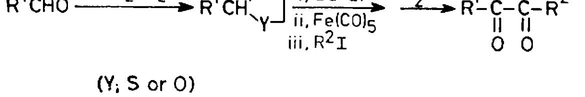
Summary α-Diketones were prepared under mild conditions in high yields from aldehydes and alkyl iodides using pentacarbonyliron.

Known methods[1] for the synthesis of α-diketones, which are useful starting materials in organic syntheses, are restricted to the oxidation of acyloins, ketones, acetylenic compounds, or diols. We now report a novel synthesis of α-diketones from aldehydes and alkyl iodides using pentacarbonyliron as carbonylating agent.



$$R^1CHO \xrightarrow{HYCH_2CH_2YH} R^1CH\langle Y_2C_2H_4\rangle \xrightarrow[\text{ii, Fe(CO)}_5;\ \text{iii, }R^2I]{\text{i, Bu}^n\text{Li}} \xrightarrow{H_2O} R^1\text{–}\overset{O}{\overset{\|}{C}}\text{–}\overset{O}{\overset{\|}{C}}\text{–}R^2 \quad (1)$$

(Y; S or O)

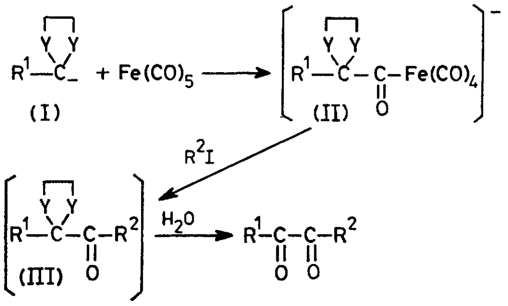
The following procedure is typical [equation (1)]. To a tetrahydrofuran solution (40 ml) of benzaldehyde ethylene dithioacetal (22 mmol), derived from benzaldehyde and ethane-1,2-dithiol, n-butyl-lithium (22 mmol) in hexane was added and the mixture was stirred for 30 min at 0 °C under argon. Pentacarbonyliron (22 mmol) was added, the mixture was stirred for 30 min at room temperature and then methyl iodide (30 mmol) in 1-methylpyrrolidin-2-one (30 ml) was added. After 8 h, solvent was removed under reduced pressure and the residue was hydrolysed. The product was extracted with diethyl ether, the extract was dried (Na_2SO_4) overnight, solvent was removed, and distillation gave pure 1-phenylpropane-1,2-dione (2·21 g, 68% yield based on the acetal), identified by its i.r. and n.m.r. spectra, elemental analysis, and g.l.c. using an authentic sample. Further results are shown in the Table. Ethylene acetals were also employed instead of ethylene dithioacetals, but the yields were rather low.

TABLE. Synthesis of α-diketones

Aldehyde R^1CHO R^1	Alkyl iodide R^2I R^2	% Yield of α-diketone[a] R^1-CO-CO-R^2
Ph	Me	68
Ph[b]	Me	51
Ph	Et	65
Ph[b]	Et	48
Et	Et	70
Pr^n	Me	(80)
Et	Me	(82)
Me	Me	(75)

[a] Isolated yields based on the amount of starting acetal. Yields in parentheses were determined by g.l.c. using internal standards. [b] Ethylene acetals were employed instead of ethylene dithioacetals.

In these reactions, we assume that acyltetracarbonylferrates[2] (II) are formed as intermediates by the reaction of the anion (I)[3] and pentacarbonyliron [equation (2)], which react with alkyl iodides to give (III),[4] hydrolysis of which gives the α-diketones.



(2)

(Y; S or O)

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[2] Treatment of carbanions with pentacarbonyliron gives the corresponding acyltetracarbonylferrates, see M. Ryang, *Organometallic Chem. Rev. A*, 1970, **5**, 67; M. Yamashita, Y. Watanabe, T. Mitsudo, and Y. Takegami, *Tetrahedron Letters*, 1976, 1585.

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