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.

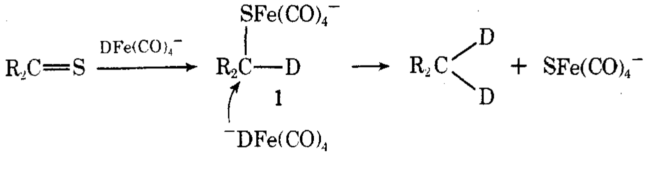
Table I

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



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

(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.

Acknowledgments. The author is grateful to Imperial Oil Limited and to the National Research Council of Canada for support of this research.

References and Notes

(1) H. Alper, *Tetrahedron Lett.*, 2257 (1975).
(2) T. Mitsudo, Y. Watanabe, M. Yamashita, and Y. Takegami, *Chem. Lett.*, 1385 (1974).
(3) G. Cainelli, M. Panunzio, and A. Umani-Ronchi, *Tetrahedron Lett.*, 2491 (1973).
(4) G. P. Boldrini, M. Panunzio, and A. Umani-Ronchi, *J. Chem. Soc., Chem. Commun.*, 359 (1974).
(5) G. P. Boldrini, M. Panunzio, and A. Umani-Ronchi, *Synthesis*, 733 (1974).
(6) Y. Watanabe, M. Yamashita, T. Mitsudo, M. Tanaka, and Y. Takegami, *Tetrahedron Lett.*, 1879 (1974).
(7) Y. Watanabe, T. Mitsudo, M. Yamashita, S. C. Shim, and Y. Takegami, *Chem. Lett.*, 1265 (1974).
(8) R. Noyori, I. Umeda, and T. Ishigami, *J. Org. Chem.*, **37**, 1542 (1972).
(9) H. Alper, *J. Org. Chem.*, **37**, 3972 (1972).

Department of Chemistry
University of Ottawa
Ottawa, Ontario, Canada K1N 6N5

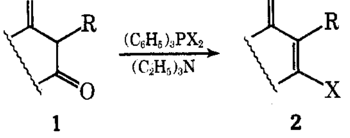
Howard Alper

Received May 27, 1975

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



1 2

Table I
Conversion of β-Bromo α,β-Unsaturated Ketones into β-Alkyl α,β-Unsaturated Ketones

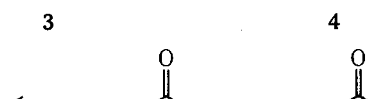
β-Bromo enone	Cuprate reagent[a]	Reaction temp, °C[b]	Yield of β-alkyl enone, %[c]
3	A	0	82
3	B	−20	84
3	C	−78	91
3	D	0	87
5	A	0	70
5	B	−20	87
5	C	−20	82
5	D	0	84
6	A	0	94
6	B	−20	93
6	D	0	89
7	D	22	95
8	A	0	83
9	D	0	89

[a] Reagent A, $C_6H_5S(CH_3)CuLi$; B, $C_6H_5S(n\text{-}C_4H_9)CuLi$; C, $C_6H_5S(sec\text{-}C_4H_9)CuLi$; D, $C_6H_5S(t\text{-}C_4H_9)CuLi$. In all of the experiments with reagent A, 2.0 equiv of cuprate was used; in the other cases, 1.5 equiv was employed. [b] The reaction time was 2.5 hr in each case. [c] Yield of distilled product. In some of the experiments, a small amount (generally <5%) of starting material (β-bromo enone) was recovered.

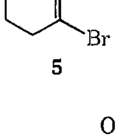
herein that the latter compounds **2** react smoothly with a variety of organocuprate reagents to produce efficiently the corresponding cyclic β-alkyl α,β-unsaturated ketones.[2]

Most of our experiments thus far have employed β-bromo enones as starting materials, although preliminary investigations have indicated that the corresponding chloro or iodo derivatives could also be used. In fact, in some cases, the best results were obtained from the appropriate iodo derivative. However, in general, the β-bromo enones appeared to be superior to the chloro compounds and, compared with the iodo derivatives, were more convenient to prepare[1] and were easier to handle experimentally. Furthermore, we have found that, although lithium dialkylcuprate reagents could be employed to convert the β-bromo enones into the corresponding β-alkyl enones, in most cases a more efficient and less cumbersome transformation could be achieved by use of lithium phenylthio(alkyl)cuprate reagents.[11,12]

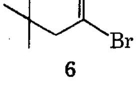
Treatment of 3-bromo-2-cyclohexen-1-one (**3**) with 2.0 equiv of lithium phenylthio(methyl)cuprate in THF at 0° for 2.5 hr afforded, in 82% yield, 3-methyl-2-cyclohexen-1-one (**4**, R = CH_3).[13] In similar fashion, reaction of **3** with the corresponding *n*-butyl-, *sec*-butyl-, and *tert*-butylcuprates gave the enones **4** (R = $n\text{-}C_4H_9$, $sec\text{-}C_4H_9$, and $t\text{-}C_4H_9$, respectively) in high yield. Extension of these studies to the β-bromo enones **5–9**, inclusive, afforded comparable results, some of which are summarized in Table I.[13]



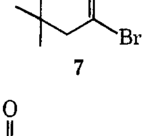
3 **4**



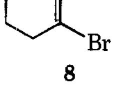
5



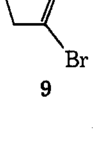
6



7



8

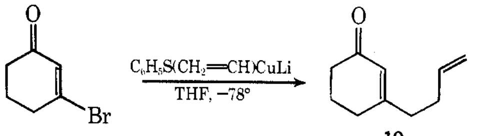


9

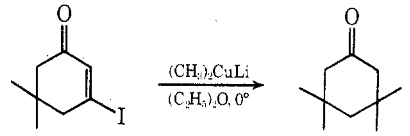
Although, in some of the experiments recorded in Table I, small amounts of starting material (<5%) were recovered along with the product, in no case were we able to detect any product resulting from further addition to the initially formed β-alkyl enone. It is also appropriate to emphasize the rather remarkable efficiency with which the β-*tert*-butyl enones were formed. Although some of the *tert*-butyl products had previously been prepared via entirely different synthetic processes, the yields were generally low.[14] In contrast, the present method not only provided high yields of product in each of these cases, but even the relatively highly hindered β-bromo enones **5** and **7** reacted smoothly with lithium phenylthio(*tert*-butyl)cuprate to provide the corresponding β-*tert*-butyl enones (previously unknown compounds[13]) in yields >80%.

Reaction of the β-bromo enone **3** with 1.3 equiv of lithium phenylthio(vinyl)cuprate in THF at −78° gave, in addition to starting material, the unsaturated ketone **10** (ratio ~7:2, respectively). Obviously, 1,6 addition of the cuprate reagent to the initially formed 3-vinyl-2-cyclohexen-1-one occurred at a rate faster than the original 1,4 addition to **3**. Treatment of **3** with 3.0 equiv of the vinylcuprate reagent afforded **10**[13] in 70% yield.

Finally, it should be mentioned that β,β-dialkylcycloalkanones can be prepared directly from the appropriate β-halo enone by reaction of the latter with an excess of lithium dialkylcuprate. For example, when 3-iodo-5,5-dimethyl-2-cyclohexen-1-one (**11**)[1] was allowed to react with 3.0 equiv of lithium dimethylcuprate in ether at 0°, 3,3,5,5-tetramethylcyclohexanone (**12**)[13] was formed in 84% yield.



3 **10**



11 **12**

A typical experimental procedure, involving conversion of **3** into **4** (R = $t\text{-}C_4H_9$), follows. To a stirred suspension of phenylthiocopper[12] (260 mg, 1.5 mmol) in 10 ml of dry THF at −20° was added dropwise 1.28 ml of 1.17 *M* *tert*-butyllithium in pentane. The resulting clear solution was stirred at −20° for 5 min and then cooled to −78°. After 3-bromo-2-cyclohexen-1-one (**3**, 175 mg, 1.0 mmol) had been added, the solution was allowed to warm to 0° and was kept at this temperature for 2.5 hr. During this time, the solution became dark green. Methanol (1.0 ml) and saturated aqueous ammonium chloride (0.5 ml) were added, followed after ~1 min by magnesium sulfate (4.0 g) and ether (10 ml). The resulting mixture was filtered through a short column of silica gel (10 g) and the column was eluted with an additional 100 ml of ether. The combined eluants were concentrated and the residual oil was distilled (air-bath temperature 75–85°, 9.0 Torr) to give 132 mg (87%) of 3-*tert*-butyl-2-cyclohexen-1-one: ir (film) 1680, 1608 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.13 (s, 9 H), 1.66–2.54 (diffuse, 6 H), 5.97 (s, 1 H).

Acknowledgment. We are grateful to the National Research Council of Canada for financial support.

References and Notes

(1) E. Piers and I. Nagakura, *Synth. Commun.*, **5**, 193 (1975).

(2) Although cyclic β-chloro α,β-unsaturated ketones have recently served as starting materials for the synthesis of a series of structurally diverse and potentially fruitful synthetic intermediates,[3-9] their reaction with cuprate reagents has not been reported.[10] Reports concerning the use of β-bromo or β-iodo α,β-unsaturated ketones as precursors have been rare or nonexistent, respectively.

(3) E. Ee. van Tamelen, M. P. Seiler, and W. Wierenga, *J. Am. Chem. Soc.*, **94**, 8229 (1972).

(4) J. L. Herrmann, J. E. Richman, and R. H. Schlessinger, *Tetrahedron Lett.*, 2599 (1973).

(5) R. D. Clark and C. H. Heathcock, *J. Org. Chem.*, **38**, 3658 (1973).

(6) Y. Tamura, T. Miyamoto, T. Nishimura, J. Eiho, and Y. Kita, *J. Chem. Soc., Perkin Trans. 1*, 102 (1974).

(7) J. P. Marino and T. Kaneko, *J. Org. Chem.*, **39**, 3175 (1974).

(8) R. J. Chorvat and R. Pappo, *Tetrahedron Lett.*, 623 (1975).

(9) E. Vedejs and J. P. Bershas, *Tetrahedron Lett.*, 1359 (1975).

(10) It should be noted that the overall conversion of 5,5-dimethyl-1,3-cyclohexanedione and 2-methyl-1,3-cyclopentanedione into 3,5,5-trimethyl-2-cyclohexen-1-one and 2,3-dimethyl-2-cyclopenten-1-one, respectively, has been accomplished via the reaction of the corresponding enol acetates with lithium dimethylcuprate: C. P. Casey, D. F. Marten, and R. A. Boggs, *Tetrahedron Lett.*, 2071 (1973).

(11) G. H. Posner, C. E. Whitten, and J. J. Sterling, *J. Am. Chem. Soc.*, **95**, 7788 (1973).

(12) G. H. Posner, D. J. Brunelle, and L. Sinoway, *Synthesis*, 662 (1974).

(13) All products exhibited spectral data (uv, ir, ^{1}H NMR) in full accord with the assigned structures. New compounds were fully characterized and gave satisfactory elemental analyses (±0.3%).

(14) For example: 3-*tert*-butyl-2-cyclohexen-1-one, 19%;[15] 3-*tert*-butyl-5,5-dimethyl-2-cyclohexen-1-one, 7%;[16] 3-*tert*-butyl-2-cyclopenten-1-one, 54%.[17]

(15) W. G. Dauben, G. W. Shaffer, and N. D. Vietmeyer, *J. Org. Chem.*, **33**, 4060 (1968).

(16) N. F. Firrell and P. W. Hickmott, *J. Chem. Soc. C*, 716 (1970).

(17) T. S. Sorensen and K. Rajeswari, *J. Am. Chem. Soc.*, **93**, 4222 (1971).

Department of Chemistry
University of British Columbia
Vancouver, Canada V6T 1W5

Edward Piers*
Isao Nagakura

Received April 17, 1975