# DEHALOGENATION OF ORGANIC HALIDES BY THE HYDRIDOTETRACARBONYLFERRATE ANION

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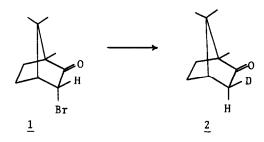
(Received in USA 7 March 1975; received in UK for publication 20 May 1975)

There has been considerable recent interest in the use of the <u>in situ</u> generated hydridotetracarbonylferrate anion  $[HFe(CO)_4]$  for effecting reductive alkylation,<sup>1,2</sup> amination,<sup>3-5</sup> hydroacylation,<sup>6</sup> and for hydrogenation of the carboncarbon double bond of an  $\alpha,\beta$ -unsaturated carbonyl.<sup>7</sup> The related  $HFe_3(CO)_{11}$  anion can reduce the carbon-nitrogen double bond of a diazine or a Schiff base.<sup>8</sup> This communication describes a simple, mild and stereospecific method for dehalogenating organic halides.

Treatment of a halide with a 3:1 mixture of KOH and iron pentacarbonyl (i.e. conditions which generate  $HFe(CO)_4$ ) in 1,2-dimethoxyethane (DME)-ethanol, or in DME containing a small amount of water, at room temperature, gave the dehalogenated product in good - excellent yields (Table I). The reaction occurs in the presence of olefin, ketone, anhydride, methoxy, and aromatic bromide functionalities. The only unreactive non-aromatic halide was 1-bromoadamantane.

The iron hydride has advantages over other dehalogenating reagents. For instance while zinc dust in acetic acid would reduce the double bond of an  $\alpha$ ,  $\beta$ -unsaturated dicarbonyl,<sup>9</sup> HFe(CO)<sub>4</sub> effects debromination rather than hydrogenation of bromomaleic anhydride.

Use of  $DFe(CO)_4$  instead of  $HFe(CO)_4$  resulted in monodeuteration. For example, 9-deuteriofluorene was obtained in 82% yield by reaction of 9-bromo-fluorene with  $DFe(CO)_4$ . This reaction is stereospecific as witnessed by the conversion of  $\alpha$ -bromocamphor (<u>1</u>) to camphor-3-exo-d[<u>2</u>, 60% yield]<sup>10</sup> by  $DFe(CO)_4$ .



Camphor-3-<u>endo</u>-d was not detected, the reaction therefore occurring with complete inversion of configuration.

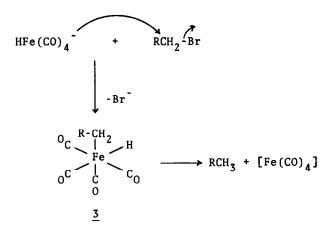
The halide-HFe(CO)<sub>4</sub> reaction may occur <u>via</u> initial Sn2 displacement of the halide to give <u>3</u> which can then collapse to product, the latter step occurring with retention of configuration.

Reactant	Product <sup>a</sup>	Yield (%) <sup>C</sup>
2-Bromo-4'-phenylacetophenone	4-Phenylacetophenone	82
2,4'-Dibromoacetophenone	4-Bromoacetophenone	66
2-Bromo-4'-methoxyacetophenone	4-Methoxyacetophenone	8 5
1-Adamantyl bromomethyl ketone	1-Adamanty1 methy1 ketone	64
9-Bromofluorene	Fluorene	84
Dichlorodiphenylmethane	Dipheny1methane $^{b}$	83
Bromomaleic anhydride	Maleic Anhydride	81
a-Bromocamphor	Camphor	59
l-Bromoadamantane	Adamantane	0

## TABLE I

Products Obtained from Reaction of Halides with HFe(CO)

<sup>a</sup> Products were characterized by comparison of spectral data with that for authentic samples, as well as by mixed melting points.
<sup>b</sup> A 2:1 ratio of iron hydride to halide was used here.
<sup>c</sup> Yields are of pure materials.



The following general procedure was used. The iron hydride was generated by refluxing a mixture of  $Fe(CO)_5$  [1.0 ml., 7.37 mmol], KOH [1.23 g., 22.0 mmol] and ethanol [45 - 70 ml]for 1.5 - 2.0 hr. The solution was cooled to room temperature. The halide [7.37] mmol , dissolved in the minimum amount of DME, was added to the hydride, and the resulting mixture was stirred at room temperature for 1 - 3 days. The solution was filtered and the residue obtained on flash evaporation of the filtrate was treated with benzene (80 - 100 ml.) and filtered. This filtrate was washed 2 - 3 times with equal volumes of water, dried, and concentrated <u>in vacuo</u> to give the product. A 15:1 ratio of DME to water (V/V) was used when aqueous DME was employed as the reaction solvent.

### ACKNOWLEDGEMENTS

Acknowledgement is made to the University of Ottawa (Rector's Fund) for support of this research. I am grateful to Mr. R. Capoor for recording nmr spectra on the HA-100 spectrometer.

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#### REFERENCES

- 1. G. Cainelli, M. Panunzio and A. Umani-Ronchi, Tetrahedron Lett., 2491 (1973).
- 2. G.P. Boldrini, M. Panunzio and A. Umani-Ronchi, J.C.S. Chem. Comm., 359 (1974)
- Y. Watanabe, M. Yamashita, T. Mitsudo, M. Tanaka and Y. Takegami, <u>Tetrahedron</u> Lett., 1879 (1974).
- 4. Y. Watanabe, T. Mitsudo, M. Yamashita, S.C. Shim and Y. Takegami, <u>Chem</u>. <u>Lett</u>. 1265 (1974).
- 5. G.P. Boldrini, M. Panunzio and A. Umani-Ronchi, Synthesis, 733 (1974).
- T. Mitsudo, Y. Watanabe, M. Yamashita and Y. Takegami, <u>Chem. Lett.</u>, 1385 (1974).
- 7. R. Noyori, I. Umeda and T. Ishigami, <u>J. Org. Chem.</u>, <u>37</u>, 1542 (1972).
- 8. H. Alper, J. Org. Chem., 37, 3972 (1972).
- 9. J. Elks, R.M. Evans, A.G. Long, and G.H. Thomas, J. Chem. Soc., 451 (1954).
- Spectral properties and melting point were in full accord with literature data - R.R. Sauers and C.K. Hu, <u>J. Org. Chem.</u>, <u>36</u>, 1153 (1971).