

DEHALOGENATION OF ORGANIC HALIDES  
BY THE HYDRIDOTETRACARBONYLFERRATE ANION

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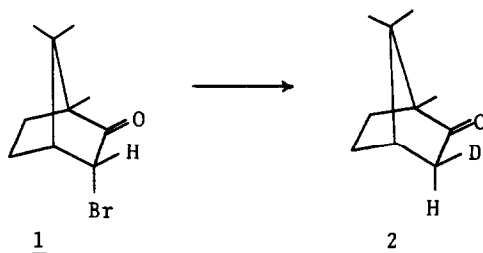
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There has been considerable recent interest in the use of the *in situ* generated hydridotetracarbonylferrate anion  $[\text{HFe}(\text{CO})_4^-]$  for effecting reductive alkylation,<sup>1,2</sup> amination,<sup>3-5</sup> hydroacylation,<sup>6</sup> and for hydrogenation of the carbon-carbon double bond of an  $\alpha, \beta$ -unsaturated carbonyl.<sup>7</sup> The related  $\text{HFe}_3(\text{CO})_{11}^-$  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  $\text{HFe}(\text{CO})_4^-$ ) 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>  $\text{HFe}(\text{CO})_4^-$  effects debromination rather than hydrogenation of bromomaleic anhydride.

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



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

The halide- $\text{HFe}(\text{CO})_4^-$  reaction may occur via initial  $\text{S}_\text{N}2$  displacement of the halide to give 3 which can then collapse to product, the latter step occurring with retention of configuration.

TABLE I  
Products Obtained from Reaction of Halides with  $\text{HFe}(\text{CO})_4^-$

| 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        | 85                     |
| 1-Adamantyl bromomethyl ketone | 1-Adamantyl methyl ketone    | 64                     |
| 9-Bromofluorene                | Fluorene                     | 84                     |
| Dichlorodiphenylmethane        | Diphenylmethane <sup>b</sup> | 83                     |
| Bromomaleic anhydride          | Maleic Anhydride             | 81                     |
| $\alpha$ -Bromocamphor         | Camphor                      | 59                     |
| 1-Bromoadamantane              | Adamantane                   | 0                      |

<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.



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