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The synthesis of some ferrocenyl tin hydrides

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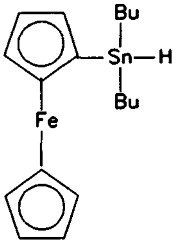
Tin hydrides containing a ferrocenyl (Fc) group have been synthesized. They reduce haloalkanes in good yields and their decomposition products are easily separated from the products by oxidizing the ferrocene compounds to ferrocenium ions.

Keywords: Organometallic free radicals, ferrocene, tin hydrides, ferrocenium

INTRODUCTION

Since the discovery of ferrocene in 1951 by Kealy and Pauson,[1] many aspects of its chemistry have been investigated and reviewed. However, there are few reports in the literature on the involvement of ferrocene or ferrocene derivatives in free-radical reactions. Free radicals can be or have been implicated in the mechanisms of reactions of some ferrocene derivatives[2-16] and we have reported on the reactions of ferrocenyl radicals.[17] Tributyltin hydride has been widely used in organic synthesis from the early 1970s, and is particularly useful for intermolecular and intramolecular free-radical reactions.[18, 19] Separation of the desired products from by-products of the decomposition of tributyltin hydride can be difficult. To overcome such difficulty, it was decided to attempt to synthesize a tin hydride which would give easily removable by-products. Incorporation of a ferrocenyl group ($C_{10}H_9Fe$, Fc) into a hydride would give by-products which would be oxidized readily to ferrocenium species and thus render them water-soluble.

The first hydride synthesized was dibutylferrocenyltin hydride (**1**).



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The synthetic method used for the synthesis of **1** is outlined in the route shown in Scheme 1 and was achieved in an overall yield of 70 % starting from the readiy available compound chloromercuriferrocene, **2**.

$$\mathrm{FcH} \rightarrow \underset{\mathbf{2}}{\mathrm{FcHgCl}} \rightarrow \underset{\mathbf{3}}{\mathrm{FcSnBu_2Cl}} \rightarrow \mathbf{1}$$

Scheme. 1 Route to dibutylferrocenyltin hydride.

Chloromercuriferrocene **2** was synthesized according to the method of Fish and Rosenblum[20] and subsequent reaction of **2** with dibutyltin sulphide gave dibutylferrocenyltin chloride **3**.[21] Reduction of **3** using lithium aluminium hydride gave **1** as a yellow-orange oil. The product was characterized by IR, ^1H, ^{13}C and ^{119}Sn NMR, and mass spectroscopy.

EXPERIMENTAL

Equipment

All reactions were carried out under nitrogen. Infrared spectra were recorded using a Philips Scientific PU 9800 FTIR spectrometer. Mass spectra were determined using an AE1 MS30 instrument at an ionization potential of 70 eV. ^1H and ^{13}C NMR were recorded on a Bruker ACF 250 MHz machine.

Synthesis

Dibutylferrocenyltin hydride (1)
To anhydrous diethyl ether (20 cm^3) in a round-bottomed flask were added lithium aluminium hydride (60 mg, 1.6 mmol) and dibutylferrocenyltin chloride (0.7 g, 1.5 mmol). The mixture was stirred at room temperature for 4 h and then hydrolysed slowly with cold water/ethyl acetate (9:1). After separating the ethereal layer, the aqueous solution was extracted with ether and the combined ether fractions were washed with cold water and then dried over magnesium sulphate. The ether was removed *in vacuo* to leave an

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Table 1 Reduction of alkyl bromides using dibutylferrocenyltin hydride[a]

Alkyl halide	Alkane product	Yield (%)
1-Bromodecane	Decane	90
1-Bromododecane	Dodecane	73
1-Bromoheptane	Heptane	95
1-Bromohexadecane	Hexadecane	96

[a] Reactions were carried out for 4 h at 80 °C by refluxing equimolar amounts of bromoalkane and dibutylferrocenyltin hydride in benzene in the presence of the initiator AIBN. Yields were calculated by GC using the internal standard method.

orange oil, dibutylferrocenyltin hydride (0.5 g, 80%). IR (NaCl), cm^{-1} 2957, 2925, 1833 (Sn–H), 1464, 1260, 1107. ^1H NMR ($CDCl_3$), ppm: 4.42 (t, 2H, C_5H_4), 4.15 (s, 5H, C_5H_5), 4.10 (t, 2H, C_5H_4) 1.40–1.90 (m, 12H, $[CH_2]_3 \times 2$), 1.02 (t, 6H, $CH_3 \times 2$). ^{13}C NMR ($CDCl_3$), ppm: 73.84 (Fc), 71.29 (Fc), 68.42 (Fc), 27.84 (Bu), 27.14 (Bu), 18.31 (Bu), 13.60 (Bu). MS m/z: 420 ($M+1$), 418 ($M-1$), 361 ($M-58$), 305 ($M-114$), 303 ($M-116$), 186 ($M-233$).

RESULTS AND DISCUSSION

The tin hydride **1** reduced various bromoalkanes to their corresponding alkanes in high yields. The results are shown in Table 1.

Reaction of **1** with 4-nitro-2,2,4-trimethylpentane gave a 40 % yield of iso-octane, which is a lower yield than that achieved using tributyltin hydride.[22] The reaction of **1** with 6-bromohex-1-ene gave methylcyclopentane and hex-1-ene.

Removal of the tin by-products from reaction mixtures was readily achieved by washing mixtures with dilute nitric acid. This produced dark blue solutions containing the organic products plus ferrocenium ions. Extraction of the aqueous solutions with diethyl ether provided separation of the organic products from the metal-containing products.

Diphenylferrocenyltin hydride was also synthesized, by first reacting **2** with diphenyltin sulphide to give diphenylferrocenyltin chloride followed by reduction of the chloride using lithium aluminium hydride.

The scope and potential of these new tin hydrides requires further investigation. It may be possible to alter the metal complex in such a way as to allow these types of hydrides to act as radical sources in aqueous reactions.[23]

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REFERENCES

1. Kealy, T J and Pauson, P L *Nature (London)*, 1951, 168: 1039
2. Schechter, H and Helling, J F *J. Org. Chem.*, 1961, 26: 1034
3. Nesmeyanov, A N, Perevalova, E G and Nesmeyanova, O A *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1962, 47
4. Finnegan, R A and Hagen, A W *Tetrahedron Lett.*, 1963, 365
5. Cais, M and Eisenstadt, A *J. Org. Chem.*, 1965, 30: 1148
6. Sato, T, Shimada, S and Hata, K *Bull. Chem. Soc. Jpn.*, 1969, 42: 2731
7. Forrester, A R, Hepburn, S P, Dunlop, R S and Mills, H H *J. Chem. Soc., Chem. Commun.*, 1969, 698
8. Abramovitch, R A, Azogu, C I and Sutherland, R G *J. Chem. Soc., Chem. Commun.*, 1971, 134
9. Neuse, E W *J. Organomet. Chem.*, 1972, 40: 387
10. Kumada, M, Kondo, T, Mimura, K, Yamamoto, K and Ishikowa, M *J. Organomet. Chem.*, 1972, 43: 307
11. Kondo, T, Yamamoto, K and Kumada, M *J. Organomet. Chem.*, 1972, 43: 315
12. Kondo, T, Yamamoto, K, Omura, T and Kumada, M *J. Organomet. Chem.*, 1973, 60: 287
13. Baker, C and Horspool, W M *J. Chem. Soc., Perkin Trans. 1*, 1979, 2294
14. Shibata, K, Saito, Y, Matsui, M and Takase, Y *Bull. Chem. Soc. Jpn.*, 1984, 57: 3349
15. Herberhold, M, Nuyken, O and Pohlmann, T *J. Organomet. Chem.*, 1991, 405: 217
16. Jackson, R A, Scarmoutsos, M and Zarkadis, A K *J. Chem. Soc., Perkin Trans. 2*, 1991, 809
17. Imrie, C, Nonhebel, D C and Pauson, P L *J. Chem. Soc., Perkin Trans. 1*, 1991, 2555
18. Neumann, W P *Synthesis*, 1987, 665
19. Curran, D P *Synthesis*, 1988, 417
20. Fish, R W and Rosenblum, M *J. Org. Chem.*, 1965, 30: 1253
21. Kabouche, Z and Dinh, N H *J. Organomet. Chem.*, 1989, 375: 191
22. Ono, N, Miyake, H, Kamimura, A, Hamamoto, I, Tamura, R and Kaji, A *Tetrahedron*, 1985, 41: 4013
23. Light, J and Breslow, R *Tetrahedron Lett.*, 1990, 31: 2957