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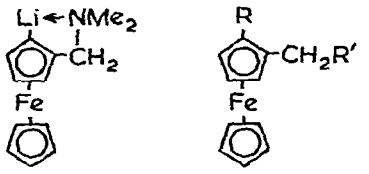
[2-(Dimethylamino)methyl]ferroceneboronic acid as a convenient intermediate in the synthesis of 1,2-disubstituted ferrocenes

Ferroceneboronic acid[1] and [(dimethylamino)methyl]ferrocene[2] have been shown to act as versatile intermediates in the synthesis of mono-substituted ferrocenes. We now describe the preparation of the title compound and its application to the synthesis of 1,2-disubstituted ferrocenes. The amino-acid, [II; $R = B(OH)_2$, $R' = NMe_2$], m.p. 177–178°, was obtained from [(dimethylamino)methyl]ferrocene[3] by condensation of the recently described 2-lithio-amine (I)[4] with tri-n-butyl borate at −78°. The product was isolated in 92% yield* by chromatography on alumina (78% overall yield from ferrocene). As expected it was soluble in aqueous mineral acids and bases and passed through an isoelectric point. The amino-acid gave a methiodide, [II; $R = B(OH)_2$, $R' = NMe_3I$], under mild conditions and this derivative was smoothly degraded to ferrocenemethanol and ferrocenemethylmethyl ether by boiling with aqueous base and aqueous/methanolic base respectively. Stirring the amino-acid, [II; $R = B(OH)_2$, $R' = NMe_2$], with aqueous cupric chloride at 50° gave the chloro-amine (II; $R = Cl$, $R' = NMe_2$), m.p. 42–43°, in 88% yield. We have been informed recently of the independent preparation of this compound by a different route[5]. The same reaction with cupric bromide gave the bromo-amine, (II; $R = Br$, $R' = NMe_2$), m.p. 46–48°, in 95% yield.



(I) (II)

Each of the halo-amines was converted to other 2-halo derivatives through the nucleophilic substitution reactions of the corresponding methiodides, (II; $R = Cl$, Br; $R' = NMe_3I$). Thus the chloro-alcohol, (II; $R = Cl$, $R' = OH$), m.p. 56.5–59°, and the chloro-ether, (II; $R = Cl$, $R' = OPh$), m.p. 78–78.5°, were prepared by heating the methiodide, (II; $R = Cl$, $R' = NMe_3I$), under reflux with aqueous sodium hydroxide and aqueous sodium phenoxide respectively. Similar reactions of the methiodide of the bromo-amine, (II; $R = Br$, $R' = NMe_3I$), gave the bromo-alcohol, (II; $R = Br$, $R' = OH$), m.p. 70–71°, and the bromo-ether, (II; $R = Br$, $R' = OPh$), m.p. 71–72°.

All new compounds gave satisfactory analyses for three or more elements and exhibited the expected infrared absorption spectra.

Further reactions of the amino-acid are under investigation.

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* Yields were based on unrecovered starting material.

1 A. N. NESMEYANOV, V. A. SAZONOVA AND V. N. DROZD, *Dokl. Akad. Nauk SSSR*, 126 (1959) 1004; *Chem. Ber.*, 93 (1960) 2717.
2 M. ROSENBLUM, *Chemistry of the Iron Group Metallocenes*, Part I, Interscience, New York, 1965, pp. 138–140.
3 C. R. HAUSER AND J. K. LINDSAY, *J. Org. Chem.*, 21 (1956) 382.
4 D. W. SLOCUM, B. W. ROCKETT AND C. R. HAUSER, *Chem. Ind. (London)*, (1964) 1831; *J. Am. Chem. Soc.*, 87 (1965) 1241.
5 R. L. GAY, T. F. CRIMMINS AND C. R. HAUSER, *Chem. Ind. (London)*, in press (private communication).

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