

A HIGH YIELD SYNTHESIS OF BIFERROCENYL

ALI R. KORAY, MÜMTAZ ERTAS

Department of Chemistry, Research Institute for Basic Sciences, P.O. Box 74, Gebze-Kocaeli (Turkey)

and ÖZER BEKAROĞLU*

Department of Chemistry, Technical University of Istanbul, Maslak-Istanbul and Research Institute for Basic Sciences, P.O. Box 74, Gebze-Kocaeli (Turkey)

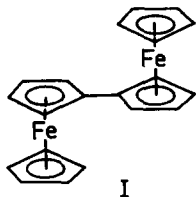
(Received July 21st, 1986)

Summary

Biferrocenyl has been obtained in 78% yield by reaction of monolithioferrocene with *p*-xylene dibromide.

Introduction

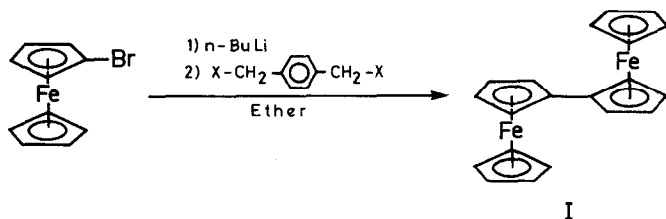
Biferrocenyl (I) first was obtained in small yield from the reaction of lithioferrocenes with trialkylhalosilanes [1,2].



Nesmeyanov et al. prepared biferrocenyl in 52% yield by reaction of ammoniacal silver oxide with ferroceneboronic acid [3]. Other syntheses of this compound, e.g. from ferrocenyl Grignard reagents [4], by Ullmann coupling reactions of haloferrocenes [5], and by thermal decomposition of diferrocenylmercury in the presence of silver or palladium black [6], have also been described. All these routes are, however, somehow circuitous and troublesome, and an easy high yield preparation of biferrocenyl under mild conditions is desirable. We have unexpectedly found a convenient new route to biferrocenyl in high yield, while studying the reactions of lithioferrocenes with *p*-xylene dihalogenids, and we describe this below.

Results and discussion

Our initial study involved the treatment of 1,1'-dilithioferrocene with α,α' -dichloro-*p*-xylene at -12°C ; this gave two products, which were separated by



SCHEME 1

chromatography on silica gel. The first band gave ferrocene and the second band a red-orange compound identified unequivocally as biferrocenyl (in 28% yield) from its melting point, elemental analysis, and ^1H NMR and mass spectra.

This result prompted us to study the reaction of monolithioferrocene (FcLi) with *p*-xylene dichloride. FcLi was prepared by reaction of bromoferrocene with *n*-butyllithium in diethyl ether and was treated in situ with the dichloride, to give biferrocenyl in 39% yield.

Since cleavage of benzyl–bromine bonds occurs more readily than that of benzyl–chlorine bonds, we tried the reaction of FcLi with *p*-xylene dibromide at room temperature, and this gave I in 78% yield.

The isolation of ferrocene and biferrocenyl from the described reactions indicates that ferrocenyl radicals are generated readily in the presence of *p*-xylene dibromide. The results support the suggestion of a Wurtz-type radical mechanism for the formation of biferrocenyl suggested by other research groups [7].

Experimental

All reactions were carried out under prepurified argon. Solvents were purified by distillation from LiAlH_4 and purged with argon before use. Bromoferrocene was prepared by a standard procedure [8].

Preparation of I

n-Butyllithium (3.4 ml, 5.5 mmol) was added slowly from a syringe to a solution of bromoferrocene (1.3 g, 5 mmol) in 40 ml of diethyl ether at -12°C . The mixture was stirred at room temperature for 5 h, during which an orange precipitate of FcLi was formed. This was dissolved in 40 ml of 1,2-dimethoxyethane (DME), and a solution of α, α' -dibromo-*p*-xylene (1.6 g, 6 mmol) in a mixture of 20 ml DME and 20 ml of diethyl ether was added dropwise from a syringe. The colour changed from orange to brown.

After 15 min the mixture was treated with 50 ml of water, and the organic layer was separated and washed with water (2×50 ml). The solvent was removed under reduced pressure and the residue was subjected to flash chromatography on silica. Elution with light petroleum (b.p. $40\text{--}60^\circ\text{C}$) gave some ferrocene followed by 0.7 g (78%) of I. M.p. $237\text{--}238^\circ\text{C}$ (lit. m.p. $238\text{--}239^\circ\text{C}$); MS: m/z , M^+ 370; ^1H NMR (CDCl_3): δ 3.97 (s, 10H), 4.18 (t, 4H), 4.32 (t, 4H) ppm. Analysis. Found: C, 64.89; H, 4.88; Fe, 30.09. $\text{C}_{20}\text{H}_{18}\text{Fe}_2$ calcd.: C, 64.91; H, 4.90; Fe, 30.19%.

Acknowledgement

We are grateful to Prof. Dr. J. Dabrowski and Dr. M. Rentea of the Department of Organic Chemistry, Max-Planck-Institut für medizinische Forschung, Heidelberg (B.R.D.) for the NMR and mass spectra. One of us (Ö.B.) thanks the Deutscher Akademischer Austauschdienst and the Deutsche Gesellschaft für Technische Zusammenarbeit for a valuable gift of an IR spectrophotometer.

References

- 1 M.D. Rausch, M. Vogel, H. Rosenberg, D. Mayo, and P. Shaw, Wright Air Development Center Technical Report 57-62, Part II, February, 1958; ASTIA Document No. 150979.
- 2 S.I. Goldberg, D.W. Mayo, M. Vogel, H. Rosenberg, and M. Rausch, *J. Org. Chem.*, 24 (1959) 824.
- 3 A.N. Nesmeyanov, V.A. Sazonova, and V.N. Drozd, *Chem. Ber.*, 93 (1960) 2717.
- 4 H. Schechter and J.F. Helling, *J. Org. Chem.*, 26 (1961) 1034.
- 5 M.D. Rausch, *J. Am. Chem. Soc.*, 82 (1960) 2080.
- 6 M.D. Rausch, *Inorg. Chem.*, 1 (1962) 414; O.A. Nesmeyanova and E.G. Perevalova, *Dokl. Akad. Nauk SSSR*, 126 (1959) 1007 [*C.A.*, 54, 1478 (1960)].
- 7 K. Hata, I. Motoyama, and H. Watanabe, *Bull. Chem. Soc. Japan*, 37 (1964) 1719.
- 8 R.W. Fish and M. Rosenblum, *J. Org. Chem.*, 30 (1965) 1253.