α-Pyridylferrocene and 1,1$'$-di-(α-pyridyl)-ferrocene

Academician A. N. Nesmeyanov, V. A. Sazonova, A. V. Gerasimenko

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Abstract

Full Text

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The formation of diferrocenyl upon interaction of ferrocenylboronic acid with certain copper salts indicates the intermediate appearance of the ferrocenyl radical ([1]). The ability of the latter to abstract a hydrogen atom particularly readily from the solvent, and in the absence of the latter—from the ferrocene derivatives themselves, has been studied in detail by one of us, E. G. Perevalova, and O. A. Nesmeyanova ([2]), in studying reactions of organomercury compounds of ferrocene and iodoferrocene.

In the present work it is shown that the ferrocenyl radical can be "introduced" into pyridine. Thus, on heating 1,1′-ferrocenylenediboronic acid with cupric carbonate in pyridine, together with ferrocene a small amount of α-pyridylferrocene is formed. Traces of the latter can also be detected on heating ferrocenylboronic acid under the same conditions. The yield of α-pyridylferrocene is very small, since the reaction is directed mainly toward the formation of ferrocene. α-Pyridylferrocene is obtained rather readily, together with 1,1′-di-(α-pyridyl)-ferrocene, by the action of a mixture of lithium- and 1,1′-dilithioferrocenes on pyridine. The reaction proceeds in ethereal solution

$$C_5H_5FeC_5H_4Li \xrightarrow{C_5H_5N} (\alpha\text{-pyridyl})-C_5H_4FeC_5H_5$$

$$LiC_5H_4FeC_5H_4Li \xrightarrow{C_5H_5N} (\alpha\text{-pyridyl})-C_5H_4FeC_5H_4-(\alpha\text{-pyridyl})$$

After oxidation of the pyridylferrocene obtained with potassium permanganate in an acidic medium, picolinic acid was detected, which indicates the α-position of the ferrocenyl radical in pyridylferrocene.

When dry hydrogen chloride is passed into an ethereal solution of α-pyridylferrocene, a red precipitate of α-pyridylferrocene hydrochloride separates. The latter is readily soluble in water; upon addition of a solution of sodium tetraphenylborate it immediately gives the tetraphenylborate. Aqueous solutions of α-pyridylferrocene hydrochloride are unstable and gradually decompose.

Experimental Part

1. α-Pyridylferrocene (interaction of 1,1′-ferrocenylenediboronic acid with pyridine in the presence of cupric carbonate). A mixture of 3 g of 1,1′-ferrocenylenediboronic acid and 6 g of cupric carbonate was heated (to boiling) in 20 ml of pyridine in a stream of nitrogen for 30 min. The color changed from blue to dark brown. After cooling, ether was added to the mixture, and the precipitate was filtered off and washed several times with ether. The combined ethereal extracts were washed with water; ether and pyridine were removed in vacuo. The solid residue was dissolved in heptane and chromatographed on alumina. With heptane

ferrocene was eluted; then, with ether—α-pyridylferrocene. It was obtained in an amount of 0.03 g, m.p. 87–89° (from aqueous alcohol).

Found, %: C 68.21; 68.37; H 5.07; 5.14; Fe 20.65; 20.94; N 5.28; 5.29
$C_{15}H_{13}FeN$. Calculated, %: C 68.45; H 4.98; Fe 21.23; N 5.32

2. α-Pyridylferrocene and 1,1′-di-(α-pyridyl)ferrocene (from a mixture of lithium and 1,1′-dilithioferrocene and pyridine). The reaction is carried out in a stream of pure dry nitrogen. To a flask containing an ethereal solution of ferrocenyllithium, obtained by 5-hour heating of 8.8 g of ferrocene with butyllithium (3.8 g of lithium, 21 ml of butyl chloride in 100 ml of abs. ether), 20 ml of pyridine was added dropwise with cooling. The reaction mixture was heated for 3 hours, during which the color changed from yellow to dark red. Then water was added with cooling. The ether layer was separated and washed several times with water. The ether and pyridine were removed in vacuo. The residue was chromatographed on alumina. First ferrocene was eluted with heptane, then α-pyridylferrocene with a mixture of heptane and an equal volume of diethyl ether, and 1,1′-di-(α-pyridyl)ferrocene with pure diethyl ether. After removal of the corresponding solvent, there were obtained: 1) 2.95 g of α-pyridylferrocene (24% of theory), m.p. 87–89° (from aqueous alcohol); a mixed sample with the α-pyridylferrocene obtained in the preceding experiment melts at the same temperature; 2) 0.47 g of 1,1′-di-(α-pyridyl)ferrocene (3% of theory, calculated on the ferrocene taken), m.p. 179–180° (in a sealed capillary, under nitrogen), crystallizes from a mixture of benzene and heptane.

Found, %: C 70.28; 70.28; H 4.88; 4.91; Fe 16.35; 16.43; N 8.08; 8.18
$C_{20}H_{16}FeN_2$. Calculated, %: C 70.61; H 4.74; Fe 16.42; N 8.23

After oxidation of α-pyridylferrocene with potassium permanganate in an acidic medium, picolinic acid ([3]) was detected by paper chromatography ([4]) and by a qualitative reaction with ferrous sulfate (yellow coloration).

3. Salts of α-pyridylferrocene. a) Hydrochloride. Dry hydrogen chloride is passed through an ethereal solution of α-pyridylferrocene; a red precipitate of α-pyridylferrocene hydrochloride is precipitated quantitatively.

Found, %: C 59.63; 59.76; H 5.00; 5.09; N 4.65; 4.75; Cl 11.97; 12.33; Fe 18.37;

18.13
$C_{15}H_{14}FeNCl$. Calculated, %: C 60.15; H 4.71; N 4.68; Cl 11.84; Fe 18.64

b) Tetraphenylborate. A red solution of α-pyridylferrocene hydrochloride was poured into a solution of sodium tetraphenylborate. A tetraphenylborate precipitate formed immediately. After repeated washing with water and drying in a vacuum desiccator over P_2O_5, the salt was analyzed.

Found, %: C 80.25; 80.20; H 5.89; 6.12; Fe 9.71; B 1.84; N 2.59; 2.51
$C_{39}H_{34}FeBN$. Calculated, %: C 80.30; H 5.87; Fe 9.57; B 1.84; N 2.40

The study of the properties of pyridylferrocenes is continuing.

Moscow State University
named after M. V. Lomonosov

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Note: Figure translations are in progress. See original paper for figures.