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Abstract

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SOME REACTIONS OF HALOGEN DERIVATIVES OF FERROCENE

FERROCENYLAMINE. FERROCENYL ACETATE

The haloferrocenes obtained by one of us together with Perevalova and Nesmeyanova [1] proved incapable of exchanging the halogen for hydroxyl, acyloxy, and similar groups in reactions with NaOH, CH_3COONa, and analogous salts of alkali metals. In reactions under Ullmann conditions, replacement of the halogen by a residue bonded to sodium likewise does not occur; instead, elimination of the halogen takes place, with formation of diferrocenyl and ferrocene (Z. G. Perevalova, O. A. Nesmeyanova—private communication).

In our preceding papers we described the preparation of chloro- and bromo derivatives of ferrocene from ferroceneboronic acid [2] and the replacement of bromine in bromoferrocene by an acetoxy group in the reaction with copper acetate (135-140°, yield of ferrocenyl acetate 55%) [3]. As our further work has shown, the method of exchanging halogen in haloferrocenes by reaction with a salt of divalent (and monovalent $Cu_2(CN)_2$) copper is a general method for replacing a halogen atom in the ferrocene nucleus by residues bonded to copper.

Replacement of the halogen in haloferrocenes by an acetoxy group proceeds even more smoothly than we previously described, in aqueous-alcoholic solution on boiling with copper acetate for 15 min. (yield of ferrocenyl acetate 90%)

$$\Phi X \xrightarrow{\text{Cu(OCOCH}_3)_2} \Phi OCOCH_3,$$

where X is halogen; Φ is ferrocenyl, $C_5H_5FeC_5H_4$.

On heating (135-140°) a mixture of haloferrocene with copper phthalimide, N-ferrocenylphthalimide is obtained

$$\Phi X + \text{Cu}\left(-\text{N}\begin{matrix}\text{CO}\\ \\ \text{CO}\end{matrix}\right)_2 \longrightarrow \left(\begin{matrix}\text{CO}\\ \\ \text{CO}\end{matrix}\quad \text{N}-\Phi\right) \longrightarrow \Phi\text{NH}_2.$$

N-Ferrocenylphthalimide is readily converted by the action of hydrazine hydrate into ferrocenylamine, with an overall yield, already in the first experiments, of 50%, calculated on bromoferrocene. Ferrocenylamine was identified in the form of N-acetylferrocenylamine. Replacement of the halogen by a phthalimide residue can also be carried out in aqueous-alcoholic solution on boiling for two hours.

Ferrocenylamine had previously been obtained by the interaction of ferrocenyl lithium with benzyl ether of hydroxylamine [4] and from the azide of ferrocenecarboxylic acid [5]. The route described here is undoubtedly more accessible than the others.

Bromoferrocene reacts with cuprous cyanide, giving the nitrile of ferrocenecarboxylic acid in good yield. This reaction is somewhat more difficult ···

proceeds with chloroferrocene. The nitrile of ferrocenecarboxylic acid had previously been obtained from the acid amide (6) and from formylferrocene oxime (7).

Experimental Part

Ferrocenyl acetate. Bromoferrocene (0.30 g) and 1 g of copper acetate were boiled in 30 ml of 50% alcohol for 15 min. The mixture was then diluted with water and extracted with ether. The ether was washed with water, 5% alkali solution, water, and evaporated. This gave 0.25 g of ferrocenyl acetate (90% of theory), m.p. 60-62°; the halogen test was negative. After recrystallization from alcohol, m.p. 64.5-66.5°; a mixed sample with authentic ferrocenyl acetate melted at the same temperature. After hydrolysis of ferrocenyl acetate to oxyferrocene and subsequent benzoylation by the Schotten-Baumann method, ferrocenyl benzoate was obtained, m.p. 108.5-109.5° (3). Similarly, from 0.30 g of chloroferrocene and 1 g of copper acetate in 30 ml of 50% alcohol, 0.28 g of ferrocenyl acetate was obtained (84% of theory).

N-Ferrocenylphthalimide. A mixture of 0.60 g of bromoferrocene and 1.5 g of copper phthalimide was heated in an oil bath at 135-140° for 2 h. The mixture was then repeatedly washed with ether. The red ethereal solution was washed with water, 10% KOH solution, again with water, and evaporated. This gave 0.48 g of N-ferrocenylphthalimide (64% of theory), m.p. 150-153°. After recrystallization from alcohol, m.p. 156-157°.

$C_{18}H_{13}O_2NFe$. Found, %: C 65.25; 65.51; H 3.95; 3.89; Fe 16.93; 16.98; N 4.23; 4.29;
Calculated, %: C 65.30; H 3.96; Fe 16.87; N 4.23.

N-Ferrocenylphthalimide is a red crystalline substance, soluble in ether, acetone, chloroform, and benzene; less readily soluble in alcohol. Similarly, from 0.30 g of chloroferrocene and 1.5 g of copper phthalimide, 0.24 g of N-ferrocenylphthalimide was obtained (53% of theory).

Ferrocenylamine. N-Ferrocenylphthalimide (0.30 g) was boiled (under nitrogen) with 0.5 ml of hydrazine hydrate in 5 ml of alcohol for 40 min. The mixture was then diluted with water and extracted with ether; the ether was washed with water, 10% KOH, and water, and ferrocenylamine was extracted with 10% HCl, precipitated with 10% alkali solution, filtered off, washed with water, and dried in a vacuum desiccator over P_2O_5. This gave 0.15 g (82% of theory) of ferrocenylamine, m.p. 153-155°. Literature data: m.p. 153-155° (4), 155° (5).

N-Acetylferrocenylamine. Ferrocenylamine (0.08 g) was dissolved in 0.5 ml of acetic anhydride and 1 ml of pyridine. The solution was left at room temperature for several hours. The mixture was diluted with water and extracted with ether. The ether was washed with water, 10% H_2SO_4, and water, and evaporated. This gave 0.08 g of N-acetylferrocenylamine (82% of theory), m.p. 166-168°; after recrystallization from benzene, m.p. 169-171°. Literature data: m.p. 167-168° (4); 170.5-172° (5).

Nitrile of ferrocenecarboxylic acid. 1) A mixture of 0.30 g of bromoferrocene with 2 g of cuprous cyanide was heated for 2 h in an oil bath at 135-140°. The mixture was then repeatedly washed with ether, and the ether was evaporated. This gave 0.20 g of the nitrile of ferrocenecarboxylic acid (84% of theory), m.p. 101-103°; the halogen test was negative. After recrystallization from heptane, m.p. 105.5-106.5°; a mixed sample with authentic nitrile melted without depression. Literature data: m.p. 107-108° (6); 103-104° (7).

2) A mixture of 0.30 g of chloroferrocene with 1.5 g of cuprous cyanide in 2 ml of dry pyridine was heated for 3 h in an oil bath at 140-145° with addition of 3-4 mg of nitrile (8) of ferrocenecarboxylic acid. The mixture was washed with ether, and the ether was evaporated. The remaining crystals were washed with cold hep-

with methane. 0.12 g of ferrocenecarboxylic acid nitrile was obtained, m.p. 100-102° (42% of theory); test for halogen negative; after recrystallization from heptane, m.p. 105.5-106.5°.

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