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Abstract

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REPLACEMENT OF HALOGEN IN BROMOFERROCENE BY AROMATIC AND HETEROCYCLIC RADICALS

As was shown in our laboratory, tetraphenylborocuprate pyridinate can be used for the phenylation of α, β-unsaturated carbonyl compounds (^{1}). Studying halogen exchange in haloferrocenes in the presence of copper ions, we found that tetraphenylborocuprate pyridinate arylates bromoferrocene, with replacement of bromine by phenyl, at 130°, forming phenylferrocene.

$$C_5H_5FeC_5H_4Br \xrightarrow{CuB(C_6H_5)_4} C_5H_5FeC_5H_4{-}C_6H_5.$$

The reaction is accompanied by reduction of bromoferrocene to ferrocene and by the formation of a number of by-products—diferrocenyl and, probably, polyarylated ferrocenes, which were not studied in detail. It is more convenient to carry out the reaction using not pyridinate $CuB(C_6H_5)_4$, but a mixture of $(C_6H_5)_4BK$ (^{2}) and Cu_2Br_2, which has almost no effect on the yield of phenylferrocene.

We applied this method to the preparation of n-tolylferrocene, as well as heterocyclylferrocenes, which cannot be obtained by the most commonly used method for the synthesis of arylferrocenes—arylation of ferrocene with aryldiazonium salts (^{3,4}). We succeeded in obtaining α-thienylferrocene and N-indolylferrocene in yields of 81% and 35%, respectively, by heating bromoferrocene with a mixture of tetra-(α-thienyl)boropotassium (^{5}) and Cu_2Br_2 and tetra-(indolyl-1)-boropotassium (^{6}) with Cu_2Br_2 at 130°.

$$C_5H_5FeC_5H_4Br + KB\,(\alpha\text{-thienyl})_4 \xrightarrow{Cu_2Br_2} \alpha\text{-thienylferrocene}$$

$$C_5H_5FeC_5H_4Br + KB\,(\text{indolyl-1})_4 \xrightarrow{Cu_2Br_2} \text{N-indolylferrocene}$$

N-Pyrrylferrocene is formed in 17% yield upon heating bromoferrocene with a mixture of sodium pyrrole and Cu_2Br_2.

$$C_5H_5FeC_5H_4Br + \text{sodium pyrrole} \xrightarrow{Cu_2Br_2} \text{N-pyrrylferrocene}$$

The absence in the IR spectra of N-indolylferrocene and N-pyrrylferrocene of an absorption band at 3400-3440 cm^{-1}, characteristic of the NH bond of the pyrrole ring, confirms their structure as N-substituted compounds.

Copper phenylacetylide reacts with bromoferrocene in boiling dimethylformamide, forming ferrocenylphenylacetylene.

Experimental Section

Phenylferrocene. a) A mixture of 0.3 g of bromoferrocene and 1.8 g of tetraphenylborocuprate pyridinate is heated under nitrogen at 125–130° for 30 min; the reaction mixture is cooled and washed with ether. The ethereal sol-

The solution is washed with water, 10% H_2SO_4, again with water, dried over $MgSO_4$, the ether is distilled off, and the residue is chromatographed on Al_2O_3 in heptane: first a mixture of ferrocene and bromoferrocene is eluted, and then 0.17 g (57% of theory) of phenylferrocene, m.p. 110-111° (from alcohol), is obtained. Literature data: m.p. 110-111° (^{4}). Other reaction products were not investigated.

b) A mixture of 0.2 g of bromoferrocene, 0.54 g of potassium tetraphenylborate, and 0.22 g of Cu_2Br_2, moistened with 0.8 ml of pyridine, is heated under nitrogen at 125-130° for 30 min. After analogous work-up, 0.11 g (56% of theory) of phenylferrocene, m.p. 110-111° (from alcohol), is obtained.

***p*-Tolylferrocene.** In an analogous manner, from 0.2 g of bromoferrocene, 0.45 g of tetra-*p*-tolylsodium borate (^{7}), and 0.17 g of Cu_2Br_2, 0.11 g (53% of theory) of *p*-tolylferrocene is obtained, m.p. 138-139° (from alcohol). Literature data: m.p. 139-140° (^{3}).

α-Thienylferrocene. In an analogous manner, from a mixture of 0.4 g of bromoferrocene, 0.65 g of tetra-(α-thienyl)potassium borate, and 0.25 g of Cu_2Br_2, moistened with 0.6 ml of pyridine, 0.32 g (81% of theory) of α-thienylferrocene is obtained, m.p. 116.5-117.5° (from alcohol).

Found, %: C 62.85, 62.64; H 4.74, 4.56; Fe 20.80, 20.71; S 11.89, 11.94
$C_{14}H_{12}FeS$. Calculated, %: C 62.70; H 4.51; Fe 20.83; S 11.96

N-Pyrrylferrocene. A mixture of 0.5 g of bromoferrocene, 0.78 g of sodium pyrrolide, and 1.10 g of Cu_2Br_2 is heated under nitrogen at 120° for 30 min. The reaction mixture is cooled and washed with hot benzene. After distilling off the benzene, the residue is chromatographed on Al_2O_3; heptane first elutes 0.10 g of ferrocene, then a mixture of N-pyrrylferrocene and diferrocenyl, and then 0.15 g of diferrocenyl, which is better eluted with benzene. N-Pyrrylferrocene cannot be separated from diferrocenyl by chromatography on Al_2O_3 because of their close R_f values; but after sublimation at 90°/13 mm, 0.08 g (17% of theory) of N-pyrrylferrocene is obtained, m.p. 83-83.5° (from alcohol).

Found, %: C 67.15, 67.28; H 5.39, 5.42; Fe 22.48, 22.50; N 5.50, 5.65
$C_{14}H_{13}FeN$. Calculated, %: C 66.96; H 5.22; Fe 22.24; N 5.58

N-Indolylferrocene. In an analogous manner to the first three experiments, from a mixture of 0.80 g of bromoferrocene, 1.60 g of tetra-(indolyl-1)potassium borate, and 0.56 g of Cu_2Br_2, moistened with 1.4 ml of pyridine, 0.32 g (35% of theory) of N-indolylferrocene is obtained, m.p. 89–90° (from alcohol).

Found, %: C 72.16, 71.93; H 5.08, 5.15; Fe 18.48, 18.31; N 4.79, 4.71
$C_{18}H_{15}FeN$. Calculated, %: C 71.78; H 5.02; Fe 18.55; N 4.65

Ferrocenylphenylacetylene. To a solution of 0.5 g of bromoferrocene in 10 ml of dimethylformamide, 1 g of copper phenylacetylide is added, and the mixture is boiled under nitrogen on an oil bath for 3 h. After cooling, the reaction mixture is diluted with water and filtered; the precipitate on the filter is washed with ether. The ether extracts are washed with 10% H_2SO_4, water, 10% KOH, water, and dried over $MgSO_4$. After removal of the ether, the residue is chromatographed on Al_2O_3 in heptane; first a mixture of bromoferrocene and ferrocene is eluted, and then ferrocenylphenylacetylene. Yield 0.26 g (48% of theory), m.p. 126–127° (from alcohol).

Found, %: C 75.34, 75.67; H 4.96, 5.08; Fe 19.47, 19.24
$C_{18}H_{14}Fe$. Calculated, %: C 75.55; H 4.93; Fe 19.52

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