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**Abstract**

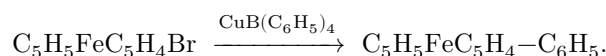
**Full Text**

**CHEMISTRY**

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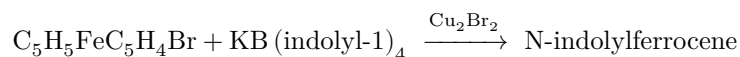
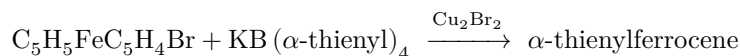
## REPLACEMENT OF HALOGEN IN BROMO-FERROCENE BY AROMATIC AND HETERO-CYCLIC RADICALS

As was shown in our laboratory, tetraphenylborocuprate pyridinate can be used for the phenylation of  $\alpha, \beta$ -unsaturated carbonyl compounds (<sup>1</sup>). 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.



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  $\text{CuB}(\text{C}_6\text{H}_5)_4$ , but a mixture of  $(\text{C}_6\text{H}_5)_4\text{BK}$  (<sup>2</sup>) and  $\text{Cu}_2\text{Br}_2$ , 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 (<sup>3,4</sup>). We succeeded in obtaining  $\alpha$ -thienylferrocene and N-indolylferrocene in yields of 81% and 35%, respectively, by heating bromoferrocene with a mixture of tetra-( $\alpha$ -thienyl)boropotassium (<sup>5</sup>) and  $\text{Cu}_2\text{Br}_2$  and tetra-(indolyl-1)-boropotassium (<sup>6</sup>) with  $\text{Cu}_2\text{Br}_2$  at 130°.



N-Pyrrylferrocene is formed in 17% yield upon heating bromoferrocene with a mixture of sodium pyrrole and  $\text{Cu}_2\text{Br}_2$ .



The absence in the IR spectra of N-indolyferrocene and N-pyrrolyferrocene of an absorption band at 3400–3440  $\text{cm}^{-1}$ , 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 ferrocenyphenylacetylene.

## 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° (<sup>4</sup>). 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 (<sup>7</sup>), 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° (<sup>3</sup>).

**$\alpha$ -Thienylferrocene.** In an analogous manner, from a mixture of 0.4 g of bromoferrocene, 0.65 g of tetra-( $\alpha$ -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  $\alpha$ -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-Pyrrolyferrocene.** 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-pyrrolyferrocene and diferrocenyl, and then 0.15 g of diferrocenyl, which is better eluted with benzene. N-Pyrrolyferrocene 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-pyrrolyferrocene 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-Indolyferrocene.** 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-indolyferrocene 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 phenylacetylde 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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 named after M. V. Lomonosov

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

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