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Abstract

Full Text

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Preparation of Diferrocenyl by the Ullmann Reaction

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In a previous paper (1) we described the synthesis of diferrocenyl from diferrocenylmercury by heating it with palladium black. In this case the main reaction product is ferrocene, while diferrocenyl is formed in a yield of only 6% of theory. At the same time as we did, Goldberg and Mayo (2) obtained diferrocenyl by the reaction of a mixture of lithium- and dilithiodiferrocene with tri-*n*-hexylbromosilane. The yield of diferrocenyl is not stated, but apparently it is also low.

In the present work we have shown that diferrocenyl is obtained in 75–80% of the theoretical yield by heating iodoferrocene with Gattermann copper; in this process only small amounts of ferrocene are formed as a by-product.

$$2C_5H_5FeC_5H_4J \xrightarrow{\text{Cu}} C_5H_5FeC_5H_4{-}C_5H_4FeC_5H_5.$$

Earlier (3) we established that the iodine of iodoferrocene is inert in nucleophilic substitution reactions with such reagents as sodium methylate and potassium acetate in an alcoholic medium*. When copper is added as a catalyst, the main reaction product is ferrocene. Copper probably catalyzes the homolytic cleavage of iodoferrocene, and the ferrocenyl radical thereby formed abstracts hydrogen from the solvent; in its absence it dimerizes and only to an insignificant extent abstracts hydrogen from the ferrocenyl nucleus, being converted into ferrocene.

Experimental Part

Preparation of iodoferrocene (3). To a suspension of 10 g (0.023 mole) of thoroughly ground chloromercuriferrocene in 100 ml of xylene, heated with stirring almost to boiling, there was added, with vigorous stirring, a hot solution of 30 g (0.12 mole) of iodine in 100 ml of xylene. Stirring was continued until the mixture had cooled to room temperature. The precipitate was filtered off, washed with xylene and hot alcohol, ground in a mortar, and vigorously stirred for 1.5 hours with a saturated solution of 20–25 ml of sodium thiosulfate. The precipitate was then filtered off, extracted several times with ether, and again stirred with sodium thiosulfate solution for 45 min, after which it was again filtered off and extracted several times with ether. The ether extracts containing iodoferrocene were combined and dried over magnesium sulfate. The ether was distilled off. Iodoferrocene was recrystallized from methyl alcohol (it precipitates on cooling to −10°). M.p. 44–45°. Yield 4.7 g (64% of theory).

Preparation of diferrocenyl. 0.58 g of iodoferrocene in an open test tube was placed in a glycerol bath heated to 100°. When the iodoferrocene had melted, 0.4 g of freshly prepared—

* Under the action of copper salts, as shown by A. N. Nesmeyanov, V. A. Sazonova, and V. N. Drozd ([4]), the halogen in haloferrocenes is exchanged under rather mild conditions.

Gattermann copper; at the same time the temperature in the test tube rose to 120°, and the reaction mixture solidified. The temperature of the bath was then brought to 150° over 15 min, after which the reaction mixture was cooled in air, ground in a mortar, and extracted with petroleum ether. The solution was chromatographed on an alumina column. With petroleum ether, 0.01 g of ferrocene was eluted (yield 3%). M.p. and mixed m.p. 172–173°. With a mixture of benzene and petroleum ether (in a ratio of 2:1), diferrocenyl was eluted, identical with that obtained by us previously ([1]) in m.p. and in the IR spectrum. Yield 0.26 g (79% of theoretical). The m.p. of diferrocenyl and the m.p. of its mixed sample with an authentic specimen were 228–230° (with decomposition).

Heating iodoferrocene in methanol in the presence of copper. 0.2 g of iodoferrocene, 0.1 g of freshly prepared Gattermann copper, and 4 ml of methyl alcohol were heated in a sealed tube for 12 h at 120°. The reaction mixture was then poured into water. The precipitated ferrocene was filtered off and recrystallized from ethyl alcohol. M.p. and mixed m.p. with an authentic specimen of ferrocene 172–173°.

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CITED LITERATURE

[1] O. A. Nesmeyanova, E. G. Perevalova, DAN, **126**, 1007 (1959).
[2] Goldberg, D. W. Mayo, Chem. and Ind., **1959**, 671.
[3] A. N. Nesmeyanov, E. G. Perevalova, O. A. Nesmeyanova, DAN, **100**, 1100 (1955).
[4] A. N. Nesmeyanov, V. A. Sazonova, V. N. Drozd, DAN, **130**, 1030 (1960).

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