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AZOFERROCENE

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IT has been reported that all attempts to prepare azo-derivatives of ferrocene either by direct coupling of diazonium salts with ferrocene, or indirectly from aminoferrocene via ferrocenyldiazonium, were unsuccessful.

As shown by the authors,[1,2] and later by Broadhead and Pauson,[3] and Weinmayr,[4] ferrocene treated with diazonium salts in an acid medium yields nothing but arylated ferrocenes. Diazotization of aminoferrocene destroyed completely the ferrocene nucleus of the molecule.[5]

A direct synthesis of methyl- and phenylazoferrocene from methyl- and phenylazocyclopentadienyllithium has been recently described by Knox.[6]

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[1] A. N. Nesmeyanov, E. G. Perevalova, R. V. Golovnya and O. A. Nesmeyanova, Dokl. Akad. Nauk SSSR 97, 459 (1954).

[2] A. N. Nesmeyanov, E. G. Perevalova and R. V. Golovnya, Dokl. Akad. Nauk SSSR 99, 539 (1954).

[3] G.D. Broadhead and P.L. Pauson, J. Chem. Soc. 367 (1955).

[4] V. Weinmayr, J. Amer. Chem. Soc. 77, 3012 (1955).

[5] A. N. Nesmeyanov, E. G. Perevalova, R. V. Golovnya and L. S. Shilovtseva, Dokl. Akad. Nauk SSSR 102, 535 (1955).

[6] G. R. Knox, Proc. Chem. Soc. 56 (1959).

The authors succeeded in preparing azoferrocene by treating lithioferrocene[7] with N_2O under the conditions reported for phenyllithium and N_2O by Beringer <u>et al.</u>[8] and Meier.[9,10]

$$C_5H_5FeC_5H_4Li \xrightarrow{N_2O} C_5H_5FeC_5H_4\text{-}N = N\text{-}OLi \longrightarrow$$

$$\xrightarrow{C_5H_5FeC_5H_4Li} C_5H_5FeC_5H_4\text{-}N = N\text{-}C_5H_4FeC_5H_5$$

Azoferrocene was isolated from other reaction products chromatographically (on Al_2O_3). The yield was as high as 30% (based on unrecovered ferrocene). The compound is stable in air, soluble in ether, ligroin, benzene, ethanol, when crystallized from benzene it gives deep violet crystals m.p. 256-258° dec. - (in a sealed capillary) (Found: C 60.10; H 4.79; Fe 28.11; N 7.27. $C_{20}H_{18}Fe_2N_2$ requires C 60.34; H 4.55; Fe 28.06; N 7.03%). Ultra-violet spectrum of the compound, determined in isooctane, contains maxima at 315, 375 and 510 m (log. ϵ max. 2.55, 1.88 and 1.91).

The structure of azoferrocene was confirmed by hydrogenation on Pt-catalyst in glacial acetic acid to aminoferrocene identical with the sample previously prepared by the authors.[5]

The other products of the reaction are being studied.

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[7] D.W. Mayo, P.D. Shaw and M. Rausch, <u>Chem. & Ind.</u> 1388 (1957).

[8] F.M. Beringer, J.A. Farr and A. Sauds, <u>J. Amer. Chem. Soc.</u> **75**, 3984 (1953).

[9] R. Meier, <u>Chem. Ber.</u> **86**, 1483 (1953).

[10] R. Meier and W. Frank, <u>Chem. Ber.</u> **89**, 2747 (1956).