

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

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).

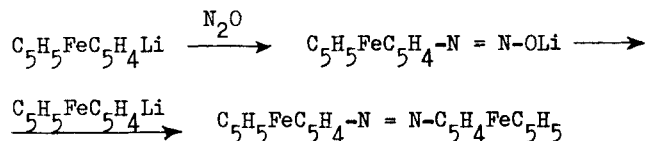
³ G.D. Broadhead and P.L. Pauson, J. Chem. Soc. 367 (1955).

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 C. R. Knox, Proc. Chem. Soc. 56 (1959).

The authors succeeded in preparing azoferrocene by treating lithioferrocene⁷ with N₂O under the conditions reported for phenyllithium and N₂O by Beringer et al.⁸ and Meier.^{9,10}



Azoferrocene was isolated from other reaction products chromatographically (on Al₂O₃). 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. C₂₀H₁₈Fe₂N₂ requires C 60.34; H 4.55; Fe 28.06; N 7.03%). Ultra-violet spectrum of the compound, determined in iso-octane, 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.

⁷ D.W. Mayo, P.D. Shaw and M. Rausch, Chem. & Ind. 1388 (1957).

⁸ F.M. Beringer, J.A. Farr and A. Sauds, J. Amer. Chem. Soc. **75**, 3984 (1953).

⁹ R. Meier, Chem. Ber. **86**, 1483 (1953).

¹⁰ R. Meier and W. Frank, Chem. Ber. **89**, 2747 (1956).