

NITROFERROCENE

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NUMEROUS attempts to prepare nitroferrocene have been reported to be unsuccessful, both by direct nitration of ferrocene,^{1,2,3,4} and from nitrocyclopentadiene.¹ This compound has now been prepared in low yield by treatment of lithioferrocene^{5,6,7} with n-propyl nitrate at -70° . The compound forms deep purple needles; a sample twice-sublimed and recrystallized from cyclohexane had m.p. 130° . (Found: C, 52.06; H, 3.95; N, 5.95; Fe, 24.20. $C_{10}H_9FeNO_2$ requires C, 51.99; H, 3.93; N, 6.06; Fe, 24.18%). Nitroferrocene is stable in air, but decomposes slowly above 190° .

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- ¹ M. Rosenblum, Ph.D. Thesis, Harvard University, August, 1953.
 - ² P. L. Pauson, Quart. Rev. 9, 391 (1955).
 - ³ E. O. Fischer and H. P. Fritz, Advanc. Inorg. Chem. Radiochem. 1, 55 (1959).
 - ⁴ P. W. K. Woo and K. L. Rinehart, Jr., Unpublished results.
 - ⁵ R. A. Benkeser, D. Goggin and G. Schroll, J. Amer. Chem. Soc. 76, 4025 (1954).
 - ⁶ A. N. Nesmeyanov, E. G. Perevalova, R. V. Golovnya and O. A. Nesmeyanova, Dokl. Akad. Nauk SSSR 97, 459 (1954).
 - ⁷ D. W. Mayo, P. D. Shaw and M. Rausch, Chem. & Ind. 1388 (1957).

It is soluble in benzene, cyclohexane, ether and alcohol, but not in water; ethanolic solutions decompose slowly.

The structure of nitroferrocene was demonstrated by its spectral properties and a derivative. An infrared spectrum of the compound (KBr pellet) shows bands at 1507 (nitro),⁸ 1425, 1369, 1348, 1330, 1107 (unsubstituted cyclopentadienyl ring), and 820 cm^{-1} (ferrocene). Its ultraviolet spectrum, determined in ethanol, contains maxima at 242, 270 (Sh), 372 and 495 μ . Reduction of nitroferrocene with iron and hydrochloric acid gives aminoferrocene,⁹ sublimed sample m.p. 154° (lit.¹⁰ m.p. 153-155°).

Studies are in progress concerned with other products from this and related reactions, as well as with additional physical and chemical properties of nitroferrocene.

⁸ L. J. Bellamy, The Infrared Spectra of Complex Molecules (2nd Ed.). John Wiley, New York (1958).

⁹ The method of choice for the preparation of aminoferrocene has been shown recently to be the reaction of lithioferrocene with methoxyamine (L. Westman and K. L. Rinehart, Jr., Unpublished results).

¹⁰ A. N. Nesmeyanov, E. G. Perevalova, R. V. Golovnya and L. S. Shilovtseva, Dokl. Akad. Nauk SSSR 102, 535 (1955).