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Grignard Reactions of ipso-Methoxynitro-adducts of p-Xylene

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Summary Grignard reactions of the *ipso*-methoxynitroadducts (1a) and (1b) yielded the hydroxylamines (2) and (3) whose configurations were determined by i.r. spectroscopy.

ELECTROPHILIC attack at a substituted (ipso) position of aromatic hydrocarbons is now well established,¹ with *ipso*-nitrations being the most extensively studied. However, difficulties have been encountered in assigning the stereochemistry of *ipso*-nitro adducts and assignments obtained using n.m.r. shift reagents were unreliable.^{2,3} The Grignard reactions investigated here provided key compounds which were used to determine configuration.

Diastereoisomers of methyl 1,4-dimethyl-4-nitro-1,4-dihydrophenyl ether (1a) and (1b)²† were treated with methylmagnesium iodide (10 mol. equiv.) in ether at -40 °C to give the methyl 1,4-dimethyl-4-(*N*-methylhydroxylamino)-1,4-dihydrophenyl ethers (2a) [m.p. 88·0-88·9 °C] and (2b) [m.p. 61·0-62·0 °C], respectively, in 90-95% yields.⁴ I.r. spectra of (2a) and (2b) (0·005 mol 1⁻¹ in CCl₄) exhibited OH bands at 3620 and 3220 cm⁻¹, respectively, indicating strong hydrogen bonding of the OH proton with the methoxy oxygen in (2b) as shown in (4). Hence a *cis*-configuration, with the 4-methyl group *cis* to the 1-methyl group, is assigned to (2b) and hence to (1b) and the *trans* configuration is assigned to (2a) and (1a). These assignments conflict with those proposed for (1a) and (1b) by Fischer and Ramsay using an n.m.r. shift reagent.²



When the concentrations of (2a) and (2b) were increased to $0 \cdot 1 \mod l^{-1}$ the free OH band of (2a) diminished and a broad band appeared at 3320 cm^{-1} , which can be ascribed to intermolecular hydrogen bonding. Increase in the concentration of (2b) caused only a minor change in the i.r. spectrum. These observations are consistent with (2a)having a higher melting point than (2b)

† (1a) and (1b) correspond to the compounds '3a' and '3b' in ref. 2, respectively.

The reactions of (1a) and (1b) with methylmagnesium iodide in tetrahydrofuran in the presence of CuCl (0.2 mol equiv.) afforded the methyl 1,4-dimethyl-4-(hydroxylamino)-1,4-dihydrophenyl ethers (3a) [m.p. $90{\cdot}5{--}91{\cdot}0~{}^\circ\text{C}]$ and (3b)[m.p. 49·1-50·0 °C], respectively, in 80% yields together with 10% of (2a) and (2b). (3b) also has a *cis*-configuration with intramolecular hydrogen bonding as shown by the OH band at 3190 cm^{-1} , which contrasts with the free OH band at 3620 cm^{-1} of the *trans*-isomer (3a). This confirms the configurational assignments of (1a) and (1b).

When heated above 60 °C in hexane for 2 h, (2) and (3) decomposed to *p*-xylene quantitatively.

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¹ R. B. Moodie and K. Schofield, Accounts Chem. Res., 1976, 9, 287.
² A. Fischer and J. N. Ramsay, Canad. J. Chem., 1974, 52, 3960.
³ R. C. Hahn and D. L. Strack, J. Amer. Chem. Soc., 1974, 96, 4335; A. Fischer and R. Röderer, Canad. J. Chem., 1976, 54, 423; A. Fischer and D. R. A. Leonard, *ibid.*, p. 1795.
⁴ Gutman and Muscoplat have obtained hydroxylamine compounds by the Grignard reactions of 2-nitrofluorene and 4-nitrobiphenyls [H. R. Gutman and C. C. Muscoplat, J. Chem. Soc. (C), 1971, 2119].