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

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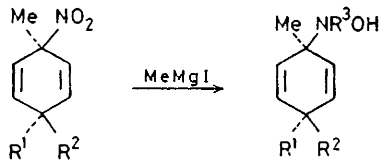
Summary Grignard reactions of the *ipso*-methoxynitro-adducts (**1a**) and (**1b**) yielded the hydroxylamines (**2**) and (**3**) whose configurations were determined by i.r. spectroscopy.

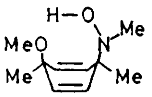
ELECTROPHILIC attack at a substituted (*ipso*) position of aromatic hydrocarbons is now well established,[1] with *ipso*-nitrations being the most extensively studied. However, difficulties have been encountered in assigning the stereochemistry of *ipso*-nitro adducts and assignments obtained using n.m.r. 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 l^{-1} in CCl_4) 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]



(1)a ; R^1 = OMe, R^2 = Me
b ; R^1 = Me, R^2 = OMe

(2)a; R^1 = OMe, R^2 = R^3 = Me
b; R^1 = Me, R^2 = OMe, R^3 = Me
(3)a; R^1 = OMe, R^2 = Me, R^3 = H
b; R^1 = Me, R^2 = OMe, R^3 = H



(4)

When the concentrations of (**2a**) and (**2b**) were increased to 0·1 mol 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**)

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† (**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. 90·5—91·0 °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].