Synthesis of Spiroheterocycles by Oxidative Coupling of Phenolic Sulphonamides

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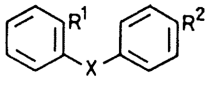
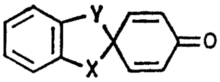
Summary Secondary aromatic sulphonamides have been used as phenol equivalents in intramolecular oxidative coupling reactions leading to the spirobenzoxazole (**2a**) and spiroimidazoles (**2b**) and (**3**).

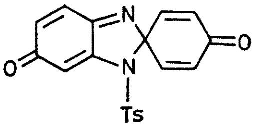
THE spirobenzoxazole (**2a**) has been prepared[1] by oxidation with active manganese dioxide of the dihydroxydiphenylamine (**1a**). The synthesis of the diphenylamine, though efficient, is somewhat laborious, and its conversion into (**2a**) is very dependent on the activity of the manganese dioxide used. In contrast, the 2-sulphonamido-4′-hydroxydiphenyl ether (**1e**)† is readily obtainable *via* compounds (**1b**)—(**1d**), and on treatment with active manganese dioxide reproducibly gives the dienone (**2a**) in reasonable (*ca.* 50%) yield. Although the oxidation of aromatic sulphonamides to quinone imides and di-imides has been extensively studied,[2] the use of a sulphonamide substituent as a 'phenol equivalent' in an oxidative coupling reaction appears to be novel and of some synthetic potential. Thus, oxidation with manganese dioxide of the 2-sulphonamido-4′-hydroxydiphenylamine (**1f**) gave the spirobenzimidazole (**2b**) (58%) [ν_{max} (KBr) 1682, 1643, and 1618 cm^{-1} (cyclohexadienone); τ ($CDCl_3$) 2·21—3·32 (12H, m, ArH), 3·45 and 3·78 (4H, 2×d, *J* 10 Hz, =CH), and 7·62 (6H, s, Ar*Me*)] a novel ring system not readily available by other means. When compounds (**1g**) and (**1h**) are subjected to oxidation with manganese dioxide, the major product isolated is the iminoquinone (**3**), ν_{max} (KBr) 1678, 1630, and 1608 cm^{-1} (cyclohexadienone); τ ($CDCl_3$) 1·96—2·72 (4H, 2 × d, ArH), 3·18—3·8 (7H, m, =CH), and 7·54 (3H, s, Ar*Me*), *m/e* 366.0701; calc. 366.0675, presumably arising by further oxidation of an initial product (**2c**). This is common[3] in the oxidation of amino-functions, but is prevented by the use of secondary sulphonamides; the versatility of these latter compounds in oxidative couplings is under investigation.


(1)

a; $R^1 = R^2 = OH$, $X = NTs$
b; $R^1 = NO_2$, $R^2 = OCH_2Ph$, $X = O$
c; $R^1 = NH_2$, $R^2 = OCH_2Ph$, $X = O$
d; $R^1 = NHTs$, $R^2 = OCH_2Ph$, $X = O$
e; $R^1 = NHTs$, $R^2 = OH$, $X = O$
f; $R^1 = NHTs$, $R^2 = OH$, $X = NTs$
g; $R^1 = NH_2$, $R^2 = OH$, $X = NTs$
h; $R^1 = NHTs$, $R^2 = OH$, $X = NH$


(2)

a; $X = O$, $Y = NTs$
b; $X = Y = NTs$
c; $X = NTs$, $Y = NH$


(3)

$Ts = 4\text{-}MeC_6H_4SO_2$

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† Satisfactory analytical and spectral data were obtained for all new compounds.

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