Intramolecular Cyclisation of Phenolic Oximes with Manganese(III) Tris(acetylacetonate)

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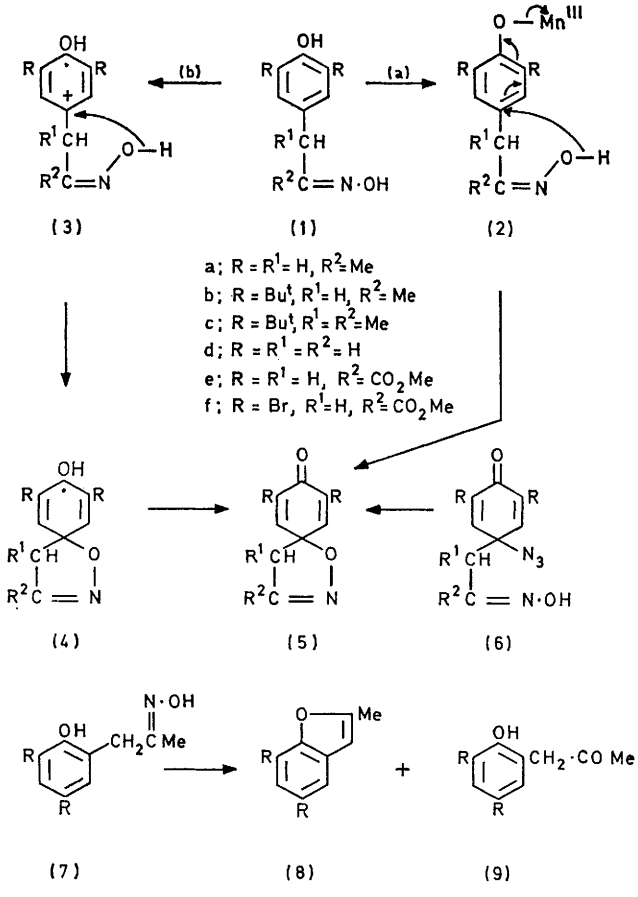
Summary Oxidative intramolecular cyclisation of a series of *p*-hydroxybenzyl ketoximes to spiro-isoxazolines has been effected with manganese(III) tris(acetylacetonate).

Manganese(III) tris(acetylacetonate) (MTA) is a useful oxidative coupling reagent for phenols;[1] dimeric phenols are formed in high yield by coupling of intermediate aroxyls. We now report that MTA can effect intramolecular cyclisation of phenolic oximes, not by coupling of aroxyl and iminoxyl radicals (*cf.* ref. 2), but by intramolecular capture of either an incipient phenoxonium ion or a phenol radical-cation.

Spiro-isoxazolines† (**5**) were obtained in 20—50% yield by treatment of the phenolic oximes (**1**) (1 mol) with MTA (2·2 mol) in acetonitrile under reflux during 5 h. The structures of the products followed from their i.r. (*ca.* 1670 and 1640 cm^{-1}; no OH absorption), u.v. ($\lambda_{max.}$ *ca.* 240 nm), n.m.r., and mass spectra. With typical one-electron oxidants, such as alkaline ferricyanide and silver oxide, either intractable products or benzoquinones were formed. Formation of the spiro-dienones (**5**) can be accounted for in two ways. Either the manganese–phenol complex (**2**) undergoes heterolysis, as indicated, with simultaneous nucleophilic attack by the oxime hydroxy-group at the *para*-carbon and disproportionation of Mn^{I} [$Mn^{I} + Mn^{III} \rightarrow 2Mn^{II}$] (path a), or the radical cation (**3**), formed by electron transfer, cyclises to give the radical (**4**) which is then further oxidised to (**5**) (path b). Both routes involve nucleophilic attack at the position *para* to the hydroxy and this step is supported by the observation that when the phenol (**1**; R = Bu^t, R^1 = H, R^2 = Me) was oxidised with MTA in a solution of sodium azide in dimethyl sulphoxide–acetonitrile the yield of spiro-isoxazoline was depressed to 10% and an organic azide was also formed. This showed (i.r.) hydroxy, dienone, and azide absorption but could not be satisfactorily



† Satisfactory elemental analyses and spectroscopic data were obtained for all new compounds.

purified because it was transformed during isolation into (**5**; R = Bu^t, R^1 = H, R^2 = Me). We consider that this intermediate is the azido-dienone (**6**) formed by the azide anion competing with the oxime hydroxy-group at the cyclisation step of paths a or b.

Treatment of the *ortho*-analogues (**7**; R = Bu^t and H) with MTA under a variety of conditions gave none of the spiro-isoxazolines. Instead the benzofurans (**8**; R = Bu^t and H) (35 and 25%, respectively) were the main products accompanied in one case by the parent ketone (**9**; R = Bu^t) (11%).

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