

Reactions of *o*-Alkenyloxyarenediazonium Fluoroborates and Related Species with Nitroxides

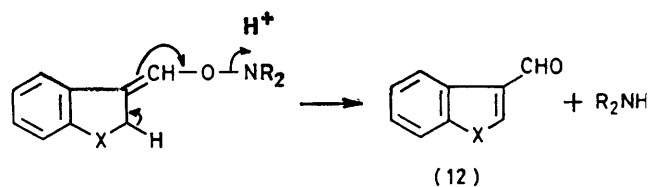
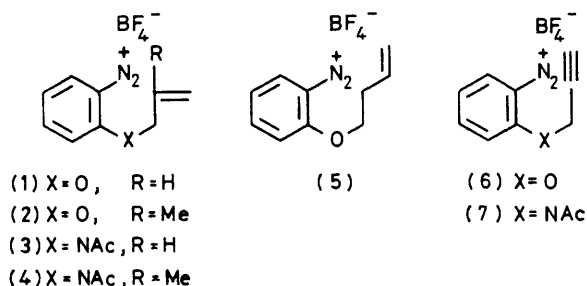
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Summary Treatment of arenediazonium fluoroborates bearing suitable alkenyloxy- or alkenylamino-*ortho*-substituents affords ring-closed hydroxylamine deriva-

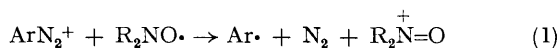
tives *via* a free-radical mechanism: similar treatment of *o*-alkynyloxy- or *o*-alkynylamino-arenediazonium salts gives aldehydes.

ALTHOUGH 'homosolvolysis'¹ of arenediazonium salts is believed to involve the intermediacy of free aryl radicals,^{1,2} an attempt to form fluorenone from diazotised *o*-aminobenzophenone by this method was unsuccessful.¹ However, we have now found that ring-closure of the *o*-allyloxyphenyl radical (**13**) and similar species generated by interaction of suitable diazonium salts with either of the nitroxides (**8**) or (**9**) proceeds efficiently and affords *ONN*-trisubstituted hydroxylamines in fair to good yield (see Table).



SCHEME 1.

The mechanism of the reaction of diazonium salts with nitroxides probably involves an initial electron-transfer to afford aryl radicals [reaction (1)].^{1,2} Ring-closure of the



radicals (*e.g.*, **13**) so formed occurs, as expected,^{4,5} exclusively in the *exo*-mode to afford cyclised species (*e.g.*, **14**) which then couple with nitroxide to give *ONN*-trisubstituted hydroxylamines (Scheme 2). A significant feature of the

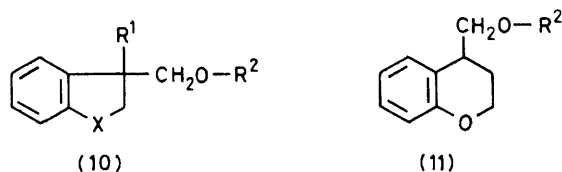


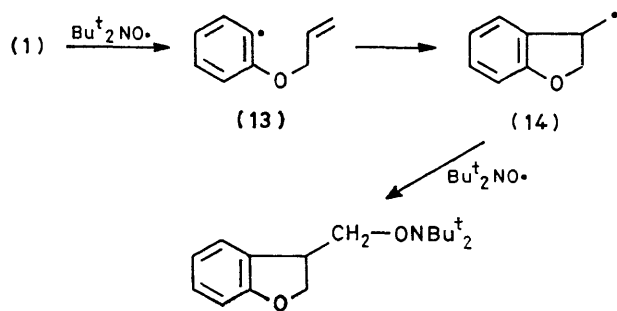
TABLE. Reactions of diazonium fluoroborates with nitroxides.

Salt	Nitroxide	Product ^a				% Yield
		X	R ¹	R ²		
(1)	(8)	(10)	O	H	DBA	76
(1)	(9)	(10)	O	H	TMP	84
(2)	(8)	(10)	O	Me	DBA	68
(2)	(9)	(10)	O	Me	TMP	82
(3)	(8)	(10)	NAc	H	DBA	75
(3)	(9)	(10)	NAc	H	TMP	80
(4)	(8)	(10)	NAc	Me	DBA	35
(4)	(9)	(10)	NAc	Me	TMP	51
(5)	(9)	(11)	—	—	TMP	59
(6)	(8)	(12)	O	—	—	57
(6)	(9)	(12)	O	—	—	62
(7)	(8)	(12)	NAc	—	—	28
(7)	(9)	(12)	NAc	—	—	48

^a DBA \equiv di-*t*-butylamino; TMP \equiv 2,2,6,6-tetramethylpiperidin-1-yl.

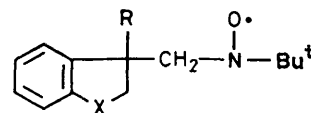
In a typical experiment the diazonium salt (**1**) was added to the nitroxide (**9**; 2.1 mol equiv.) in acetone, the mixture was boiled for 15 min, ascorbic acid was added,^{3†} and the product was then isolated by flash chromatography. Reduction of the product with zinc in acetic acid gave the

† Ascorbic acid does not play a part in the reaction. However, its addition to the mixture facilitates the isolation of products.



SCHEME 2.

reaction is that ring-closure, even of the *o*-butenyloxyphenyl radical derived from (**5**), occurs sufficiently rapidly⁴ to compete effectively with trapping of the uncyclised species by nitroxide.



(15) X = O, R = H: *aH*(1) 11.38, *aH*(1) 13.25, *aN* 15.50 G
 (16) X = O, R = Me: *aH*(1) 5.50, *aH*(1) 15.75, *aN* 15.25 G
 (17) X = NAc, R = H: *aH*(2) 12.30, *aN* 15.45 G

When the reaction of the diazonium salts (1)—(7) with nitroxides is conducted in the presence of a suitable spin trap, *e.g.*, 2-methyl-2-nitrosopropane, the adduct radicals (*e.g.*, 15—17) can be detected by e.s.r. spectroscopy. The same species can be readily generated by reduction of diazonium salts in acetone with potassium xanthate in the presence of 2-methyl-2-nitrosopropane.

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