

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

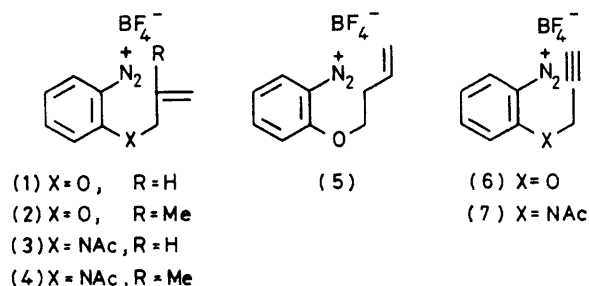
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Summary Treatment of arenediazonium fluoroborates bearing suitable alkenyloxy- or alkenylamino-*ortho*-substituents affords ring-closed hydroxylamine deriva-

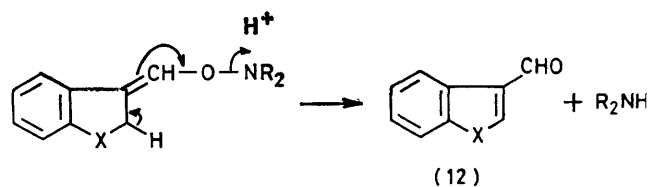
tives *via* a free-radical mechanism: similar treatment of *o*-alkynyloxy- or *o*-alkynylamino-arenediazonium salts gives aldehydes.

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).



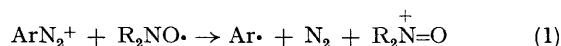
alcohol (**10**; X = O, R¹ = R² = H) in 77% yield. Similar treatment of the hydroxylamine obtained from (**3**) gave the alcohol (**10**; X = NAc, R¹ = R² = H).

Treatment of the diazonium salts (**6**) or (**7**) containing an alkynyl group with either of the nitroxides (**8**) or (**9**) gave the aldehydes (**12**, X = O) or (**12**, X = NAc) respectively, the formation of which is attributed to acid-catalysed elimination of amine from initially formed *O*-vinylhydroxylamines (Scheme 1).



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

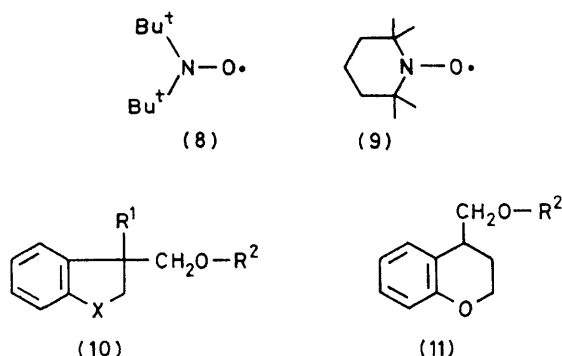
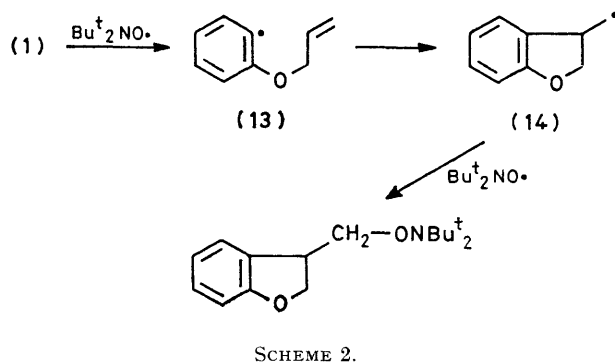


TABLE. Reactions of diazonium fluoroborates with nitroxides.

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

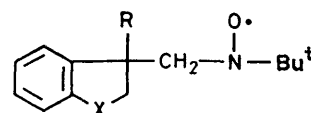
^a DBA ≡ di-*t*-butylamino; TMP ≡ 2,2,6,6-tetramethylpiperidin-1-yl.

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



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

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

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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