# Addition of Aryl Nitrenes to Olefins

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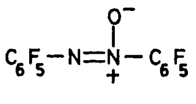
*Summary* Triethyl phosphite deoxygenation of pentafluoronitrosobenzene in the presence of 2,3-dimethylbut-2-ene *cis*- and *trans*-but-2-ene, *trans*-stilbene, and cyclohexene gives the aziridines expected from stereospecific addition of a singlet aryl nitrene to the olefin.

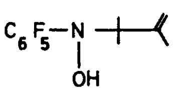
ADDITION of ferrocenyl nitrene to cyclohexene is the only reported example of the addition of a 'free' aryl nitrene to an olefinic bond to yield an aziridine derivative,[1] although examples of the addition of ethoxycarbonyl nitrene to olefins are well known.[2] The difficulty is that azides, the usual aryl nitrene precursors, themselves add to olefins at temperatures lower than those required to generate the corresponding nitrene, to give 1,2,3-triazolines which may subsequently lose nitrogen to give an aziridine.[3]

The electrophilic aryl nitrene obtained by deoxygenation of pentafluoronitrosobenzene, undergoes addition to aromatic bonds.[4] Intermolecular addition of this nitrene to olefins, especially those containing electron-releasing substituents, might be expected: this is indeed found. Addition of pentafluoronitrosobenzene (**1**) to triethyl phosphite in tetramethylethylene† gave decafluoroazoxybenzene (**2**) (14·0%), the hydroxylamine (**3**), (5·5%),[5] and the desired aziridine (**4**) (30·5%) m.p. 71—72°.‡ (**3**) was unaffected by triethyl phosphite under these reaction conditions and is thus ruled out as a precursor of (**4**). A nitrene seems likely as the origin of the aziridine but the possibility of a dipolar addition of the nitrene precursor (**5**), followed by elimination of triethyl phosphate cannot, at present, be excluded (Scheme).

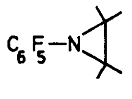


$C_6F_5-N=\overset{O^-}{\underset{+}{N}}-C_6F_5$

(2)



(3)



(4)

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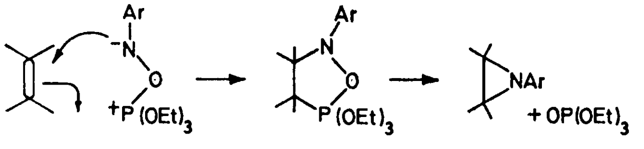
† Inverse addition was necessary in this reaction since (**1**) reacts with 2,3-dimethylbut-2-ene, even at low temperature.[5]

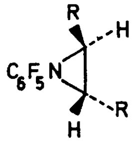
‡ All new compounds have been satisfactorily characterized.

Addition by way of singlet nitrene or of (**5**) should be stereospecific (though some rotation might be expected if loss of phosphate according to the Scheme is a stepwise process); if the triplet nitrene is involved, some stereochemical scrambling should be observed.[6] Deoxygenation of (**1**) in the presence of *trans*-but-2-ene in $CH_2Cl_2$ solution gave only one adduct (**6**) (18·0%) along with (**2**) (35·2%). Similarly, *cis*-but-2-ene gave (**2**) (26·8%) and a single adduct (**7**) (17·3%) having i.r. and n.m.r. spectra and gas chromatographic properties different from those of (**6**). The complete stereospecificity observed and the fact that no aziridine appears to be formed from nitrosobenzene and triethyl phosphite in 2,3-dimethylbut-2-ene speak in favour of the singlet nitrene mechanism.

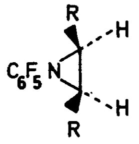


(5)

SCHEME



(**6**; R = Me)
(**8**; R = Ph)



(**7**; R = Me)
(**9**; RR = -[CH$_2$]$_4$-)

$C_6F_5N$ has also been found to add stereospecifically to *trans*-stilbene and to cyclohexene to give (**8**) (26%) and (**9**) (35%), respectively. (**9**) has also been obtained (38·6%) by photolysis of pentafluorophenyl azide in cyclohexene, again arguing for nitrene intermediacy in the deoxygenation reaction.

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