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, although examples of the addition of ethoxycarbonyl nitrene to olefins are well known. 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.

The electrophilic aryl nitrene obtained by deoxygenation of pentafluoronitrosobenzene, undergoes addition to aromatic bonds. 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%), and the desired aziridine (4) (30.5%) m.p. $71-72^{\circ}$.‡ (3) was

$$C_6F_5-N=N-C_6F_5$$
 C_6F_5-N-1 C_6F_5-N C_6F_5-N

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).

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

[‡] 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

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of (1) in the presence of trans-but-2-ene in CH₂Cl₂ 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.

C₆F₅N 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.

This work was supported by a grant from the National Science Foundation.

(Received, 22nd August 1972; Com. 1475.)

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