Substitution of Perfluoronaphthalenes by Aryl-nitrenes

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Summary Thermolysis of certain aryl azides in perfluoronaphthalenes gives the corresponding *N*-aryl-1-heptafluoronaphthylamines.

Thermal decomposition of the *p*-tolyl and the *p*-anisyl azide in perfluoronaphthalene gave the products as listed in the Table. The azobenzenes and anilines (*cf.* Table) are typical of nitrene reactions[1] and 2,6-dimethoxyphenazine has been observed before under similar conditions.[2] Interest lies, however, in the formation of *N*-*p*-tolyl- (I)† (3·9%) and *N*-*p*-anisyl-heptafluoronaphthylamine (II) (3·2%) during thermolysis under nitrogen. The complete absence of (I) in the thermolysis of *p*-tolyl azide in air suggests intermediacy of a triplet nitrene leading to (I), or (II), respectively, which can be quenched by aerial oxygen. Nitrene participation in this reaction was confirmed by a kinetic study, since the rate of decomposition of *p*-tolyl azide (0·2 mol) was found to be the same ($1 \times 10^{-4}\ s^{-1}$, at 155°) in bromobenzene and in bromobenzene containing perfluoronaphthalene (0·2 mol). The possibility that substitution to give (I) and (II) is by a singlet nitrene, and that oxygen suppresses the formation of (I) by promoting singlet triplet intersystem crossing is unlikely, as has been demonstrated for closely analogous thermolyses.[3]

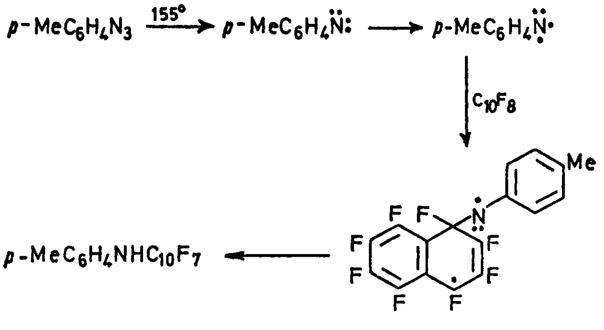
Table

Thermolysis of aryl azides in perfluoronaphthalene at 155° *under nitrogen or in air*

Azide (RN_3)	Products; Yield (%)				
R	1-Naphthylamine $R\text{–}NH\text{–}C_{10}F_7$		RN=NR	RNH_2	Others[c]
p-Tolyl[a]	(I)	3·9	21	18·7	—
p-Tolyl[b]	—		2·9	trace	—
p-Anisyl[a]	(II)	3·2	25·8	trace	2,6-dimethoxyphenazine 1·3

[a] Under nitrogen. [b] In air. [c] All reactions were accompanied by much tarring.

The formation of (I) and (II) can be interpreted as attack by a triplet nitrene on perfluoronaphthalene (Scheme). Indirect support comes from the work of Williams *et al.*,[4] who have shown that phenyl radicals attack hexafluorobenzene, and, more pertinently, from the observation of Yacobsen *et al.*[5] of almost exclusive 1-substitution by phenyl and benzoyloxy-radicals in perfluoronaphthalene. Nucleophilic attack by the aryl-nitrenes, or by arylamines derived from them, can be ruled out since this would occur exclusively at the 2-position.[6]



Scheme

† The ^{19}F n.m.r. spectra of (I) and (II) were in agreement with the suggested structure. Also, authentic samples of the corresponding 2-substituted isomers obtained by nucleophilic substitution were different.

Thermolysis of *p*-tosyl azide and benzyl azide under similar conditions gave only products of hydrogen abstraction and no substitution.

The only reaction between a nitrene and a C–halogen bond (C–Cl) observed so far was recently reported by Cadogan and Kulik.[7]

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