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]

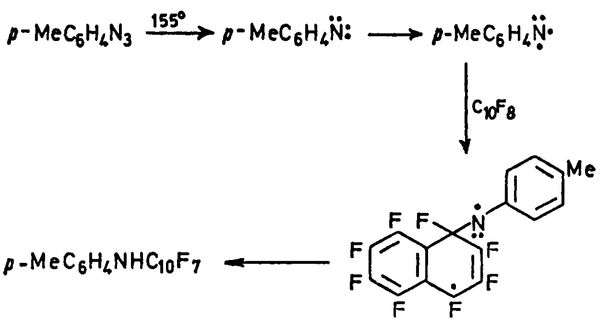
Table

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

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† 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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[1] P. A. S. Smith, in 'Nitrenes', ed. W. Lwowski, Interscience, New York, 1970, p. 47.
[2] P. Walker and W. A. Waters, *J. Chem. Soc.*, 1962, 1632.
[3] R. A. Abramovitch and E. F. V. Scriven, *Chem. Comm.*, 1970, 787.
[4] P. A. Claret, G. H. Williams, and J. Coulson, *J. Chem. Soc.* (*C*), 1968, 341.
[5] L. V. Vlasova, L. S. Kabrina, and G. G. Yakobson, *Zhur. org. Khim.*, 1971, **7**, 1224.
[6] D. Price, H. Suschitzky, and J. I. Hollies, *J. Chem. Soc.* (*C*), 1969, 1967.
[7] J. I. G. Cadogan and S. Kulik, *J. Chem. Soc.* (*C*), 1971, 2621.