

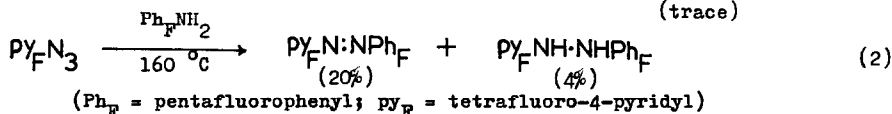
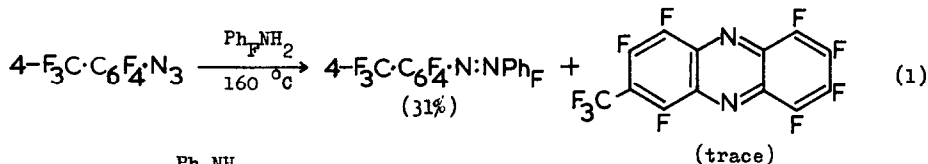
NEW REACTIONS OF AZIDOPENTAFLUOROBENZENE; INTERMOLECULAR 'INSERTIONS' INTO N-H BONDS

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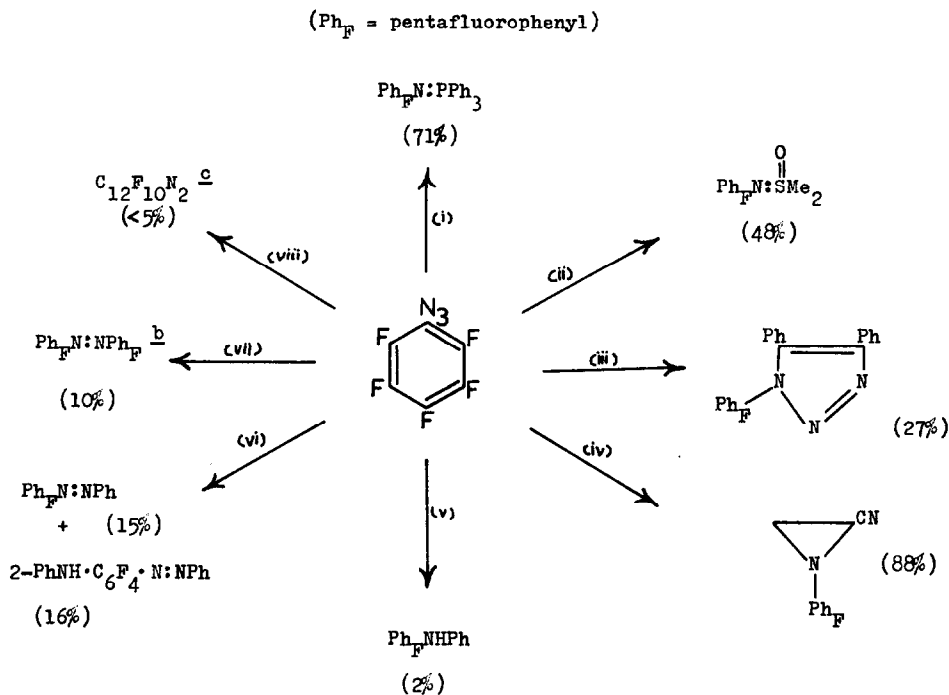
Azidopentafluorobenzene was first isolated more than a decade ago and shown to decompose smoothly within the temperature range 80-120 °C into nitrogen and an unidentified brown solid;^{1*} during the interim, but only recently, accounts have appeared of reactions between this azide and benzene,³ cyclohexene,⁴ and transition metal complexes.⁵ The current scope of our studies on thermal conversions of azidopentafluorobenzene is indicated by Scheme 1; the novel reaction involving pentafluoroaniline is of interest from a synthetic as well as a mechanistic viewpoint, since its extension to other aromatic azides of the fluorocarbon class provides unsymmetrical azo-compounds, ** e.g.,⁶



Azidopentafluorobenzene undergoes a Staudinger reaction with triphenylphosphine, and readily partakes in 1,3-dipolar cycloadditions with common dipolarophiles such as norbornene, *endo*-dicyclopentadiene, acrylonitrile, styrene, tolan, and phenylacetylene. It does not appear to attack dimethyl sulphoxide at 70 °C, but reaction occurs at 120 °C with the formation of SS-dimethyl-N-(pentafluorophenyl)sulphoximide; this suggests⁷ that

*No details of experimental work associated with the claims² regarding formation of a triazole or an aziridine from azidopentafluorobenzene and acetylene (thermally) or *p*-benzoquinone (photochemically), respectively, seem to exist.

**The formation of azo-compounds of the type ArN:N·C₆F₅ via thermal reactions between non-fluorinated azidoarenes and pentafluoroaniline has been studied independently by V. Garner, E.F.V. Scriven, and H. Suschitzky (see the adjacent letter).



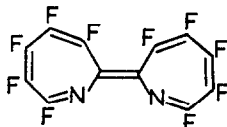
Some thermal reactions of azidopentafluorobenzene ^a

Reagents : (i) Ph₃P, Et₂O, reflux; (ii) Me₂SO, 120 °C; (iii) PhC≡CPh, CCl₄, reflux; (iv) CH₂=CH·CN, 60–65 °C; (v) C₆H₆, 130 °C; (vi) PhNH₂, 130 °C, under N₂; (vii) Ph_FNH₂, 130 °C, under N₂; (viii) flow pyrolysis at 280–300 °C at 1 atm. in Pt tube.

^a Products were identified by elemental analysis and/or spectroscopic methods (i.r., n.m.r., and mass).

^b Perfluorophenazine (<1%) was also isolated.

^c The structure of this pentafluorophenylnitrene 'dimer' [Found: M (mass spec.) 362], an orange solid, m.p. 118–120 °C, has not yet been established; however, its ¹⁹F n.m.r. spectrum seems not inconsistent with the diazaheptafulvalene

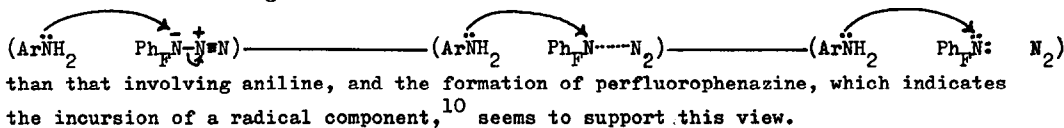


Work on this product is still in progress.

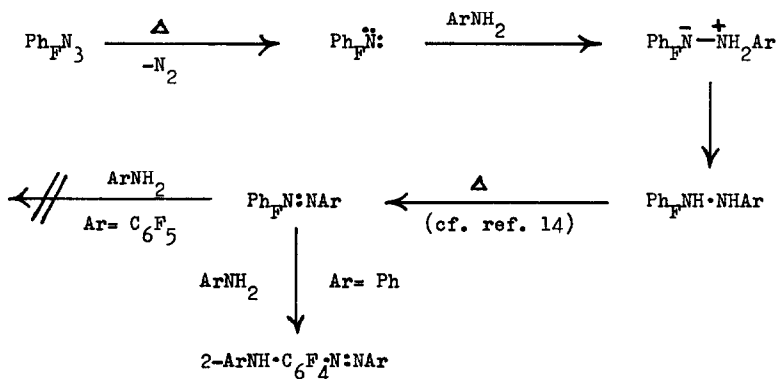
initially thermolysis of azidopentafluorobenzene is a source of singlet pentafluorophenyl-nitrene, a notion supported^{3,8} by the formation of *N*-(pentafluorophenyl)aniline and much black tar when the azide is heated with benzene at 130 °C.

The formation of tar and a mixture of the azo-compounds $C_6F_5 \cdot N:NPh$ and $2-PhNH \cdot C_6F_4 \cdot N:NPh$ when a solution of azidopentafluorobenzene in aniline is heated at 130 °C under nitrogen contrasts markedly with the production of 2-anilino-3H-azepine in the analogous reaction involving azidobenzene;⁹ this difference is tentatively ascribed to the greater electrophilicity of singlet pentafluorophenyl nitrene, which enables it to be trapped more efficiently than its hydrocarbon counterpart by the amine (see Scheme 2). Replacement of aniline by the weaker nucleophile pentafluoroaniline avoids the complication of displacement of nuclear fluorine from the azo-compound formed initially [at 150 °C only a mixture of $2-PhNH \cdot C_6F_4 \cdot N:NPh$ and $2,6-(PhNH)_2 C_6F_3 \cdot N:NPh$ is obtained], so only perfluoroazobenzene and traces of perfluorophenazine are obtained; the isolation of only mixed azo-compounds from products obtained by heating perfluoro-*p*-azidotoluene or perfluoro-4-azidopyridine with pentafluoroaniline (eq. 1,2) indicates that the perfluoro-azobenzene is not formed to any extent, or even at all, via dimerization of pentafluorophenyl nitrene.

Although involvement of only singlet pentafluorophenyl nitrene is depicted in Scheme 2, neither an 'assisted' nitrene mechanism nor a contribution from a triplet process ($Ph_F \ddot{N}: \rightarrow Ph_F \dot{N} \cdot$; $Ph_F \dot{N} \cdot + ArNH_2 \rightarrow Ph_F \dot{N}H + Ar\dot{N}H \rightarrow Ph_F NH \cdot NHAr$) can be discounted on the present evidence. The trapping stage involving pentafluoroaniline should be further along the continuum



Thermally-initiated intermolecular N-H 'insertion' reactions between organo-azides and amines are not well known, having been observed, it seems, for only the systems 3,5-dimethyl-4-azidopyrazole/aniline (\rightarrow azo-compound),¹¹ ethyl azidoformate/aniline or *N*-methylaniline (\rightarrow hydrazo-compounds),¹² and 2-azido-4,6-dimethylpyrimidine/aniline (\rightarrow hydrazo- plus azo-compound),¹³ *i.e.*, cases where a singlet nitrene of greater electrophilicity than $Ph\ddot{N}:$ can be envisaged as an intermediate.



SCHEME 2

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