Studies in Azide Chemistry. Part VI.[1] Some Reactions of Perfluoroazidobenzene and Perfluoro-4-azidotoluene [2]

By **Ronald E. Banks** * and **Ajai Prakash,** Chemistry Department, The University of Manchester Institute of Science and Technology, Manchester M60 1QD

Perfluoroazidobenzene readily undergoes the Staudinger reaction with triphenylphosphine, reacts with dimethyl sulphoxide at elevated temperatures to yield a sulphoximide, partakes in 1,3-dipolar cycloaddition reactions with diphenylacetylene, phenylacetylene, cyclopentadiene dimer, norbornene, and acrylonitrile, and, at 130 °C or above, gives the C–H ' nitrene insertion ' product $C_6F_5 \cdot NHPh$ with benzene, and, *inter alia,* the N–H ' nitrene insertion ' products $C_6F_5 \cdot N \colon NPh$, $C_6F_5 \cdot N \colon N \cdot C_6H_4F \text{-} p$, and $C_6F_5 \cdot N \colon N \cdot C_6F_5$ with aniline, p-fluoroaniline, and pentafluoroaniline, respectively.

Perfluoro-4-azidotoluene reacts with dimethyl sulphoxide, cyclohexane, aniline, and pentafluoroaniline at 160 °C to yield $Ar_F N \colon S(\colon O) Me_2$, $Ar_F NH \cdot C_6 H_{11}$, $Ar_F N \colon NPh$ + anilino-substituted derivatives, and $Ar_F N \colon N \cdot C_6 F_5$, respectively ($Ar_F = p\text{-}F_3C \cdot C_6 F_4$).

The nitrenoid N–H ' insertion ' reactions provide a new method for the synthesis of unsymmetrical polyfluorinated aromatic azo-compounds.

PERFLUOROAZIDOBENZENE was first isolated nearly fifteen years ago by Parkinson,[3,4] who showed only that this azide decomposes smoothly within the temperature range 80—120 °C into nitrogen and a dark brown solid. Very recently, accounts have been published of reactions between perfluoroazidobenzene and benzene,[5] cyclohexene,[6] transition metal complexes,[7] and tri-

phenylarsine;[8] the work now reported in detail,[2,9] is summarised in Scheme 1. The azide, a colourless liquid, b.p. 42—43 °C at 4 mmHg, was prepared by nitrosation of perfluorophenylhydrazine;[3] no reaction appeared to occur when perfluorobenzene was heated

[1] Part V, R. E. Banks and G. R. Sparkes, *J.C.S. Perkin I,* 1972, 2964.

[2] Preliminary communication, R. E. Banks and A. Prakash, *Tetrahedron Letters,* 1973, 99.

[3] J. M. Birchall, R. N. Haszeldine, and A. R. Parkinson, *J. Chem. Soc.,* 1962, 4966.

[4] R. N. Haszeldine, A. R. Parkinson, and J. M. Birchall, U.S.P. 3,238,230/1966.

[5] R. A. Abramovitch, S. R. Challand, and E. F. V. Scriven, *J. Amer. Chem. Soc.,* 1972, **94**, 1374.

[6] R. A. Abramovitch and S. R. Challand, *J.C.S. Chem. Comm.,* 1972, 1160.

[7] J. Ashley-Smith, M. Green, and F. G. A. Stone, *J.C.S. Dalton,* 1972, 1805.

[8] J. I. G. Cadogan and I. Gosney, *J.C.S. Chem. Comm.,* 1973, 586.

[9] A. Prakash, Ph.D. Thesis, University of Manchester, 1972.

with sodium azide in acetonitrile, and use of dimethyl-formamide as solvent [10] gave a product that exploded violently during distillation, presumably owing to the presence of polyazido-compounds.[11]

Like 4-azidotetrafluoropyridine,[1] perfluoroazidoben-zene readily partakes in a Staudinger reaction with

elevated temperatures to give the corresponding sulph-oximide. It does not appear to attack dimethyl sulphoxide at 70—90 °C, but at 120 °C nitrogen is liberated with concomitant formation of the sulphoximide; this suggests [1,12] that thermolysis of perfluoroazido-benzene is a source of singlet perfluorophenylnitrene, a

$Ph_F = 2,3,4,5,6 -$ pentafluorophenyl
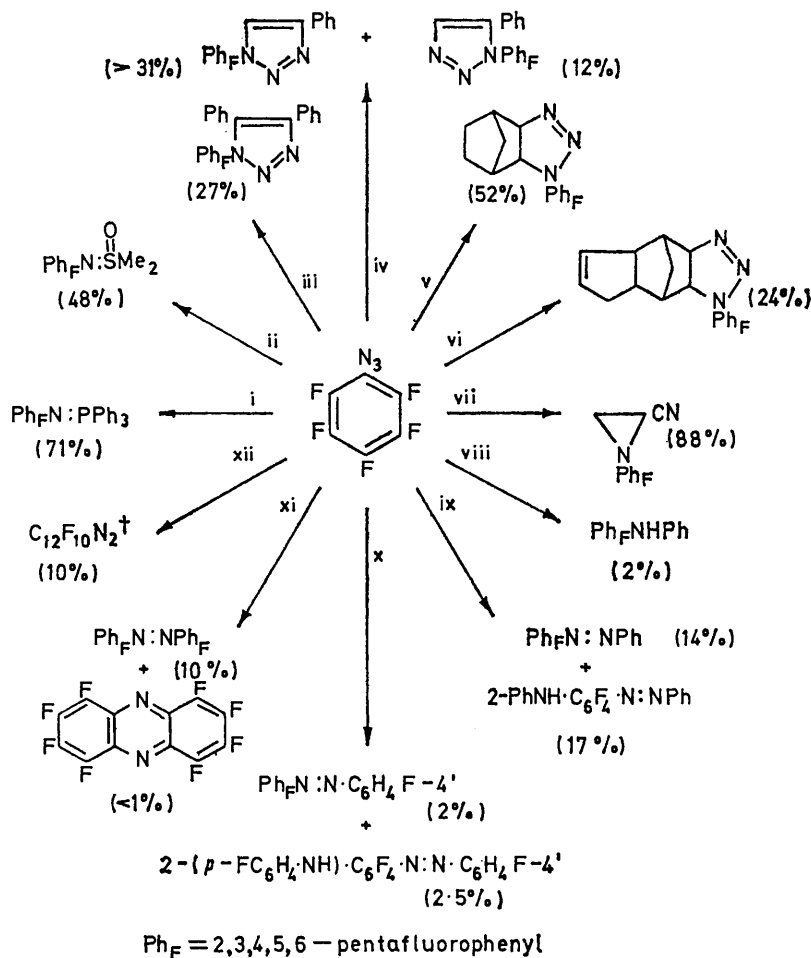
SCHEME 1 Some thermal reactions of perfluoroazidobenzene

Reagents: i, Ph_3P, Et_2O, reflux; ii, Me_2SO, 120 °C; iii, $PhC\vdots CPh$, CCl_4, 77 °C; iv, $PhC\vdots CH$, CCl_4, 77 °C; v, norbornene, ligh petroleum, 21 °C; vi, endo-cyclopentadiene dimer, light petroleum, 21 °C; vii, $CH_2\vdots CH\cdot CN$, 60—65 °C; viii, C_6H_6, 130 °C; ix, $PhNH_2$, 130 °C under N_2; * x, p-$FC_6H_4\cdot NH_2$, 130 °C under N_2; xi, $C_6F_5\cdot NH_2$, 130 °C under N_2; xii, flow pyrolysis at 280—300 °C, N_2, Pt tube.

* With a greater excess of aniline at 150 °C, the only products isolated were 2-$PhNH\cdot C_6F_4\cdot N\vdots NPh$ ($<1\%$) and 2,6-$(PhNH)_2C_6F_3\cdot N\vdots NPh$ (2%). † The structure of this pentafluorophenylnitrene 'dimer' has not been established yet; however, its [19]F n.mr. spectrum seems not inconsistent with perfluoro-2,2'-diazaheptafulvalene.[2]

triphenylphosphine [$Ph_3P\vdots NPh_F$ has also been obtained via attack of Ph_FN_3 on ethylenebis(triphenylphosphine)-nickel [7]], undergoes 1,3-cycloaddition with phenyl- and diphenyl-acetylene, norbornene, and endo-cyclopenta-diene dimer, and reacts with dimethyl sulphoxide at

notion supported [5,13] by the production of the aniline derivative $PhNHPh_F$ and much black tar when the azide is heated with an excess of benzene at 130 °C in the absence of air. The abysmal yield (2%; others [5] quote a similar value) of C–H 'insertion' product in the latter trapping experiment compared with 13% production of $PhNHpy_F$ ($py_F = 2,3,5,6$-tetrafluoropyridyl) in the cor-responding thermolysis of 4-azidotetrafluoropyridine in

[10] A. V. Kashkin, Y. L. Bakhmutov, and N. N. Marchenko, Zhur. Vsesoyuz. Khim. obshch. im. D. I. Mendeleeva, 1970, 15, 591.

[11] Treatment of perfluorobenzene with an excess of sodium azide in Me_2SO at 40 °C yields $C_6F_4(N_3)_2$ (m.p. 78, decomp. 98 °C), $C_6F_2(N_3)_4$ (m.p. 82, decomp. 84 °C; shock sensitive), and, possibly, $C_6(N_3)_6$ (highly shock sensitive) [J. G. Morse and L. P. Kuhn, U.S. Clearinghouse Fed. Sci. Tech. Inform., AD Reports, 1970, No. 713,665 (U.S. Govt. Res. and Development Report, 1970, 70, 60)].

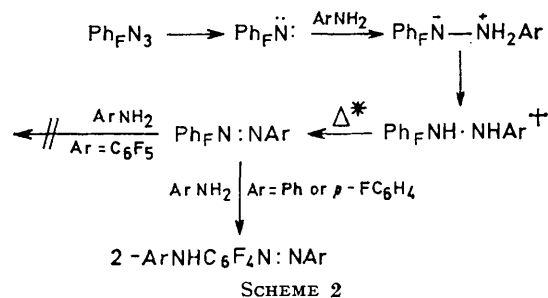[12] D. J. Anderson, D. C. Horwell, E. Stanton, T. L. Gilchrist, and C. W. Rees, J.C.S. Perkin I, 1972, 1317.

[13] R. A. Abramovitch, S. R. Challand, and E. F. V. Scriven, J. Org. Chem., 1972, 37, 2705.

the presence of benzene [1] seems ascribable to the predicted electrophilicity order $py_F\ddot{N}: > Ph_F\ddot{N}:$. Perfluorophenylnitrene is not thought to be involved in the formation of 2-cyano-1-(pentafluorophenyl)aziridine from perfluoroazidobenzene and acrylonitrile at 60—65 °C: not unexpectedly, no reaction seems to occur between this 'unstrained' electron-poor dipolarophile and the azide at 20 °C, and at the higher temperature triazoline production presumably occurs followed by ring contraction via loss of nitrogen.[14,15]

Thermolysis of perfluoroazidobenzene in aniline or p-fluoroaniline did not yield polyfluorinated azepines (azidobenzene decomposes in hot aniline to give 2-anilino-3H-azepine [16]), a rare class of compound.[17] Only unsymmetrical azo-compounds were isolated from the black tars produced, and the difference between perfluoroazidobenzene and azidobenzene in this respect seems best attributed to the much greater electrophilicity of singlet perfluorophenylnitrene, which enables it to be trapped more efficiently than its hydrocarbon analogue by an aromatic amine (see Scheme 2). The proposal that the substituted azo-compounds 2-PhNH·C$_6$F$_4$·N:NPh, 2,6-(PhNH)$_2$C$_6$F$_3$·N:NPh, and 2-(p-FC$_6$H$_4$)·C$_6$F$_4$·N:NPh originated from a simple unsymmetrical azobenzene formed initially, rather than a

$$Ph_FN_3 \longrightarrow Ph_F\ddot{N}: \xrightarrow{ArNH_2} Ph_F\bar{N}-\overset{+}{N}H_2Ar$$

$$\xleftarrow[Ar=C_6F_5]{ArNH_2} \quad Ph_FN:NAr \xleftarrow{\Delta^*} Ph_FNH·NHAr^+$$

$$ArNH_2 \downarrow Ar=Ph \text{ or } p-FC_6H_4$$

$$2\text{-}ArNHC_6F_4N:NAr$$

SCHEME 2

* This change can occur during either the thermolysis experiment or the subsequent work-up procedure. Thermal disproportionation of aromatic hydrazo-compounds [including Ph$_F$NH·NHPh$_F$ (J. Burdon, C. J. Morton, and D. F. Thomas, J. Chem. Soc., 1965, 2621) and C$_6$Cl$_5$·NH·NH·C$_6$Cl$_5$ (E. T. McBee, G. W. Calundann, C. J. Morton, T. Hodgins, and E. P. Wesseler, J. Org. Chem., 1972, 37, 3140)] to the corresponding azo-compounds and anilines is well known. † The hydrazo-compound py$_F$NH·NHPh$_F$ has been successfully isolated from the product obtained by heating 4-azidotetrafluoropyridine with pentafluoroaniline.[19]

step such as $Ph_FN_3 + PhNH_2 \longrightarrow$ 2-PhNH·C$_6$F$_4$·N$_3$, must remain tentative until nucleophilic displacement of fluorine from perfluoroazidobenzene and 2,3,4,5,6-pentafluoroazobenzene by amines has been investigated. Re-
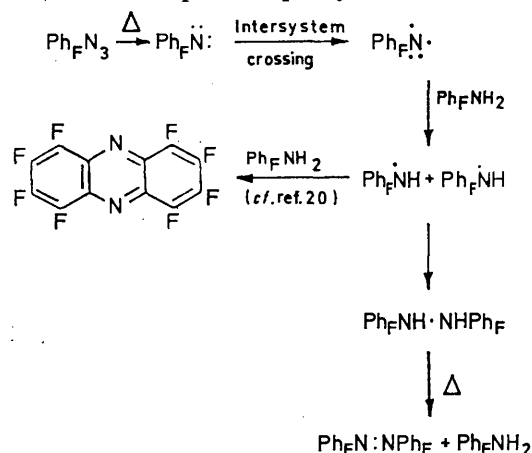
placement of aniline and p-fluoroaniline by the much weaker nucleophile pentafluoroaniline [18] avoided this problem, and only perfluoroazobenzene and traces of perfluorophenazine were isolated; the former product is not thought to have arisen to any extent, or even at all, via dimerisation of perfluorophenylnitrene or its attack

SCHEME 3

on undissociated azide, since thermolysis of perfluoro-p-azidotoluene or 4-azidotetrafluoropyridine [19] in the presence of an excess of pentafluoroaniline yielded only unsymmetrical azo-compounds (4-F$_3$C·C$_6$F$_4$·N:NPh$_F$ and py$_F$N:NPh$_F$, respectively).

Although involvement of only singlet perfluorophenylnitrene is depicted in Scheme 2, neither an 'assisted' nitrenoid mechanism nor a contribution from a triplet process (e.g. see Scheme 3) can be discounted on the present evidence. The trapping stage involving pentafluoroaniline can be expected to lie further along the mechanistic continuum of Scheme 4 than that involving aniline, and the formation of perfluorophenazine, which suggests [20,21] the generation of pentafluorophenylaminyl radical, lends supports to the formation of solvated singlet perfluorophenylnitrene which has the opportunity to cross to the triplet state. Formerly, thermally-initiated intermolecular N–H 'insertion' reactions between organic azides and amines were somewhat rare,[22-24] but recently studies on the thermolysis of azidoarenes [p-XC$_6$H$_4$·N$_3$ (X = H, Me, OMe, Cl, or NO$_2$), m-XC$_6$H$_4$·N$_3$ (X = Me or NO$_2$), or o-MeC$_6$H$_4$·N$_3$], in anilines [ArNH$_2$ (Ar = Ph, p-MeC$_6$H$_4$, p-MeO·C$_6$H$_4$, p-ClC$_6$H$_4$, or C$_6$F$_5$)] have been described.[25] The formation of unsymmetrical azo-compounds was observed

[14] W. Broeckx, N. Overbergh, C. Samyn, G. Smets, and G. L'abbé, Tetrahedron, 1971, 27, 3527.

[15] For a detailed review of Δ^2-1,2,3-triazoline decomposition see P. Scheiner in 'Selective Organic Transformations,' ed. B. S. Thyagarajan, Wiley-Interscience, New York, 1970, vol. 1, p. 327.

[16] R. A. Abramovitch and E. P. Kyba, in 'The Chemistry of the Azido Group,' ed. S. Patai, Wiley-Interscience, London, 1971, p. 257.

[17] Perfluoro-N-cyanoazepine has been synthesised via reaction of perfluorobenzene with cyanonitrene (F. D. Marsh and H. E. Simmons, J. Amer. Chem. Soc., 1965, 87, 3529; F. D. Marsh, U.S.P. 3,268,512/1966). Other routes to polyfluoroazepines are being sought (R. E. Banks and T. J. Noakes, work in progress).

[18] R. E. Banks, 'Fluorocarbons and their Derivatives,' Macdonald Technical & Scientific Press, London, 1970, p. 217.

[19] R. E. Banks and T. J. Noakes, unpublished work.

[20] A. G. Hudson, A. E. Pedler, and J. C. Tatlow, Tetrahedron Letters, 1968, 2143; M. Wilkinson, Ph.D. Thesis, University of Manchester, 1966.

[21] J. M. Birchall, R. N. Haszeldine, and J. E. G. Kemp, J. Chem. Soc. (C), 1970, 449.

[22] P. A. Smith and H. Dounchis, J. Org. Chem., 1973, 38, 2958.

[23] K. Hafner, D. Zinser, and K. L. Moritz, Tetrahedron Letters, 1964, 1733.

[24] R. Huisgen and K. v. Fraunberg, Tetrahedron Letters, 1969, 2595.

[25] E. F. V. Scriven, H. Suschitzky, and G. V. Garner, Tetrahedron Letters, 1973, 103.

only when a p-substituted azide was employed, and with an ease dependent on the electronic characteristics of the $para$-substituents in the reactants; *i.e.*, for an azide p-XC$_6$H$_4$·N$_3$, where X is strongly electron-withdrawing, reaction proceeds successfully only with p-YC$_6$H$_4$·NH$_2$, where Y is electron-donating (or H), and *vice versa*. Clearly the systems C$_6$F$_5$·N$_3$/C$_6$F$_5$·NH$_2$ and p-F$_3$C·C$_6$F$_4$·N$_3$/C$_6$F$_5$·NH$_2$ (see below) do not comply with this 'rule.' Thermolysis of the azide p-MeO·C$_6$H$_4$·N$_3$ in pentafluoroaniline was found to yield the corresponding unsymmetrical azo-compound and phenazine plus the

high field designated positive). The usual precautions [1] were taken to minimise possible explosion damage.

Perfluoroazidobenzene was prepared by nitrosation of pentafluorophenylhydrazine.[3]

Perfluoro-4-azidotoluene.—A mixture of perfluorotoluene (10·0 g, 42·5 mmol), sodium azide (3·2 g, 49 mmol), and acetonitrile (150 cm³) was stirred at 20 °C for 15 h then at 70 °C for 8 h. The product was filtered and the filtrate evaporated at reduced pressure; vacuum distillation of the oily residue gave perfluoro-4-azidotoluene (8·3 g, 29 mmol, 67%) (Found: C, 32·6; F, 51·3; N, 16·3. Calc. for C$_7$F$_7$N$_3$: C, 32·4; F, 51·4; N, 16·2%), b.p. 60 °C at 6 mmHg

Scheme 4

Scheme 5
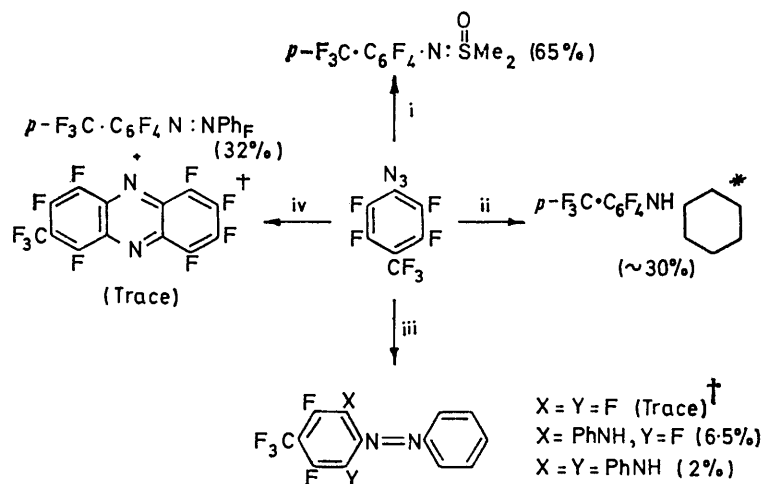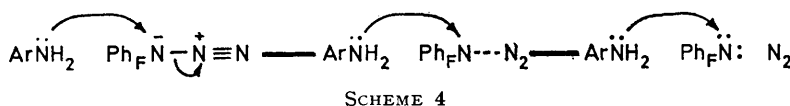
Reagents: i, Me$_2$SO, 160 °C; ii, cyclo-C$_6$H$_{12}$, 160 °C; iii, PhNH$_2$, 160 °C, under N$_2$; iv, C$_6$F$_5$·NH$_2$, 160 °C, under N$_2$.

* An authentic sample of this compound was prepared from perfluorotoluene and cyclohexylamine. Only an intractable tar formed when the azide was decomposed in the presence of undecafluorocyclohexane. † Identified only tentatively.

aniline p-MeO·C$_6$H$_4$·NH$_2$ and the substituted azo-compound 2-(p-YC$_6$H$_4$·NH)·C$_6$F$_4$·N:N·C$_6$H$_4$Y-p (Y = OMe); that the last product could have arisen *via* nucleophilic displacement of fluorine from the azo-compound C$_6$F$_5$·N:N·C$_6$H$_4$Y-p by the aniline formed was demonstrated by heating C$_6$F$_5$·N:N·C$_6$H$_4$·OMe-p with p-MeO·C$_6$H$_4$·NH$_2$ in a separate experiment.[25]

Perfluoro-4-azidotoluene.—This azide, obtained in 67% yield by treating perfluorotoluene with sodium azide in acetonitrile at 20—70 °C (*cf.* ref. 10), is a colourless liquid (b.p. 60 °C at 6 mmHg) that darkens when heated to 140 °C and visibly releases nitrogen at 160 °C with concomitant formation of a dark brown solid. The thermal transformations shown in Scheme 5 are consistent with the intermediacy of perfluoro-p-tolylnitrene.

EXPERIMENTAL

Spectroscopic analyses were performed with the instruments described in Part V;[1] [19]F and [1]H n.m.r. chemical shifts were determined with respect to external trifluoroacetic acid and benzene references, respectively (shifts to

(lit.,[10] 54—55 °C at 5 mmHg), $\lambda_{max.}$ (film) 4·65 μm (N$_3$ asym. str.) (lit.,[10] 4·68 μm), δ_F −20·5 (t, CF$_3$), +67·0 (m, 2- and 6-F), and +77·5 (m, 3- and 5-F) p.p.m. (rel. int. 3 : 2 : 2).

Reactions of Perfluoroazidobenzene.—(a) *With triphenylphosphine.* A yellow colour appeared immediately when a solution of triphenylphosphine (0·78 g, 2·96 mmol) in ether (20 cm³) was added dropwise to a solution of the azide (0·6 g, 2·87 mmol) in ether (25 cm³). The yellow mixture was heated under reflux (3 h) then evaporated by distillation; the residue was recrystallised from ether to give (2,3,4,5,6-pentafluorophenylimino)triphenylphosphorane (0·95 g, 2·14 mmol, 71%) (Found: C, 64·8; H, 3·6; F, 21·7; N, 3·3. Calc. for C$_{24}$H$_{15}$F$_5$NP: C, 65·0; H, 3·4; F, 21·4; N, 3·2%), white needles, m.p. 134—136 °C, δ_H (*ca.* 10% soln. in CDCl$_3$) −0·9, δ_F (same soln.) +76·0 (m, 2- and 6-F), +90·6 (m, 3- and 5-F), and +98·0 (t of t, 4-F) p.p.m. (rel. int. 2 : 2 : 1). The [19]F n.m.r. data agree with those reported previously.[7]

(b) *With dimethyl sulphoxide.* The azide (1·0 g, 4·8 mmol) was heated with dimethyl sulphoxide (5 cm³) in a flask connected to a nitrometer. No nitrogen collected and no change in the reactants (as indicated by i.r. analysis) occurred during 15 days at 70 °C or a further 10 days at 90 °C. At 120 °C, however, 4·8 mmol of nitrogen collected

during 15 h; the organic product was worked up as described [1] for the reaction between 4-azidotetrafluoropyridine and dimethyl sulphoxide, to give SS-*dimethyl*-N-(*pentafluorophenyl*)*sulphoximide* (0·6 g, 2·3 mmol, 48%) (Found: C, 37·3; H, 2·4; F, 36·2; N, 5·4. $C_8H_6F_5NOS$ requires C, 37·0; H, 2·3; F, 36·7; N, 5·4%), white crystals, m.p. 120—121 °C (from ether), $\lambda_{max.}$ (mull) 8·12, 8·18 (d, S=O str.), and 8·52 (S=N str.) μm, δ_H (*ca.* 10% soln. in $CDCl_3$) +3·24 (s), δ_F (same soln.) +71·9 (m, 2- and 6-F) and +86·5 (m, 3-, 4-, and 5-F) p.p.m. (rel int. 2 : 3).

(c) *With diphenylacetylene.* The azide (1·0 g, 4·8 mmol), diphenylacetylene (0·9 g, 5·05 mmol), and carbon tetrachloride (30 cm³) were heated under reflux for 10 days. Solvent was distilled from the product, and the brown oily residue was triturated with light petroleum (b.p. 60—80 °C). A solid which separated was sublimed to give (at 170—180 °C and <1 mmHg) 1-*pentafluorophenyl*-4,5-*diphenyl*-1,2,3-*triazole* (0·5 g, 1·3 mmol, 27%) (Found: C, 62·1; H, 2·8; F, 25·0; N, 10·9. $C_{20}H_{10}F_5N_3$ requires C, 62·0; H, 2·6; F, 24·5; N, 10·8%), white crystals, m.p. 220—221 °C.

(d) *With phenylacetylene.* No reaction occurred during 70 h at 20 °C between the azide (1·7 g, 8·1 mmol) and phenylacetylene (0·82 g, 8·0 mmol) in carbon tetrachloride (30 cm³), as revealed by i.r. and t.l.c. analysis. The mixture was heated under reflux for 50 h then distilled. The oily distillation residue partly solidified when cooled to 20 °C; recrystallisation of the solid material from light petroleum (b.p. 60—80 °C) gave 1-*pentafluorophenyl*-4-*phenyl*-1,2,3-*triazole* (0·8 g, 2·5 mmol, 31%) (Found: C, 54·2; H, 2·2; F, 30·2; N, 13·6. $C_{14}H_6F_5N_3$ requires C, 54·1; H, 1·9; F, 30·5; N, 13·5%), white plates, m.p. 130—131 °C, δ_H (*ca.* 30% soln. in Me_2CO) −1·75 (m, =CH·N=), −0·97 (m, *o*-H), and −0·50 (m, *m*- and *p*-H) p.p.m. (rel. int. 1 : 2 : 3), δ_F (same soln.) +70·5 (m, 2- and 6-F), +76·0 (m, 4-F), and +85·5 (m, 3- and 5-F) p.p.m. (rel. int. 2 : 1 : 2). The remainder of the distillation residue was cooled to 0 °C; the brown solid that precipitated was sublimed to provide (at 100—110 °C and <1 mmHg) pale yellow material, which was separated by column chromatography (silica gel, 3 : 1 v/v light petroleum–chloroform) into 1-pentafluorophenyl-4-phenyl-1,2,3-triazole and 1-*pentafluorophenyl*-5-*phenyl*-1,2,3-*triazole* (0·3 g, 1·0 mmol, 12%) (Found: C, 54·1; H, 2·2; F, 30·3; N, 13·6. $C_{14}H_6F_5N_3$ requires C, 54·1; H, 1·9; F, 30·5; N, 13·5%), m.p. 142—143 °C, δ_H (*ca.* 15% soln. in Me_2CO) −1·05 (s, =CH·N=) and −0·35 (s, Ph) (rel. int. 1 : 5), δ_F (same soln.) +69·5 (m, 2- and 6-F), +74·5 (t of t, 4-F), and +84·5 (m, 3- and 5-F) p.p.m. (rel. int. 2 : 1 : 2).

(e) *With norbornene.* A solution of the azide (2·0 g, 9·6 mmol) and norbornene (0·94 g, 10·0 mmol) in light petroleum (b.p. 60—80 °C; 100 cm³) was stored at room temperature until no free azide could be detected by i.r. spectroscopy (70 h). Evaporation of the solvent *in vacuo* at room temperature, followed by recrystallisation of the residue from light petroleum (b.p. 60—80 °C), gave 5-*pentafluorophenyl*-3,4,5-*triazatricyclo*[5.2.1.0²,⁶]*dec*-3-ene (1·5 g, 4·95 mmol, 52%) (Found: C, 51·6; H, 3·4; F, 31·0; N, 14·1. $C_{13}H_{10}F_5N_3$ requires C, 51·5; H, 3·3; F, 31·3; N, 13·9%), white crystals, m.p. 51—52 °C, δ_H (*ca.* 30% soln. in CCl_4) *ca.* +2 to +6 (br, complex), δ_F (same soln.) +68·5 (m, 2- and 6-F), +80·5 (m, 4-F), and +84·0 (m, 3- and 5-F) p.p.m. (rel. int. 2 : 1 : 2).

(f) *With dicyclopentadiene.* A solution of the azide (1·3 g, 6·2 mmol) and *endo*-dicyclopentadiene (0·8 g, 6·2

mmol) in light petroleum (b.p. 60—80 °C; 50 cm³) was stirred at room temperature for 4 days, by which time the reaction mixture showed no i.r. absorption in the azide region. The product was evaporated at 20 °C under reduced pressure, leaving an oily solid that was recrystallized from light petroleum (b.p. 60—80 °C) to give 5-(pentafluorophenyl)-3,4,5-triazatetracyclo[5.5.1.0²,⁶.0⁸,¹²]trideca-3,9(and/or 3,10)-diene (0·9 g, 2·64 mmol, 24%) (Found: C, 56·0; H, 3·7; F, 27·7; N, 12·4. Calc. for $C_{16}H_{12}F_5N_3$: C, 56·2; H, 3·5; F, 27·9; N, 12·3%), as white crystals.

(g) *With acrylonitrile.* No reaction occurred between the azide (0·6 g, 2·9 mmol) and an excess of acrylonitrile (5 cm³) at 20 °C during 70 h, as revealed by i.r. and t.l.c. analysis of the mixture. At 60—65 °C, however, *ca.* 3 mmol of nitrogen was evolved during 50 h. The liquid product was distilled to remove acrylonitrile and the solid residue was recrystallised from light petroleum (b.p. 60—80 °C), to give 2-*cyano*-1-(*pentafluorophenyl*)*aziridine* (0·6 g, 2·5 mmol, 88%) (Found: C, 46·4; H, 1·5; F, 40·2; N, 12·3. $C_9H_3F_5N_2$ requires C, 46·1; H, 1·3; F, 40·5; N, 12·0%), white needles, m.p. 73—74 °C, $\lambda_{max.}$ (mull) 4·42 and 4·45 (d, C≡N str.) μm, δ_H (*ca.* 15% soln. in $CDCl_3$) +3·4 to +3·9 (complex, aziridine ring C–H [26]), δ_F (same soln.) +76·6 (m, 2- and 6-F) and +86·2 (m, 3-, 4-, and 5-F) p.p.m. (rel. int. 2 : 3).

(h) *With benzene.* A solution of the azide (1·5 g, 7·2 mmol) in benzene (15 cm³) was heated at 130 °C for 16 h in a Pyrex ampoule (250 cm³) in the absence of air. Benzene was removed from the product by distillation, leaving a dark brown oily residue that solidified when cooled to 0 °C. The solid was triturated with light petroleum (b.p. 60—80 °C) and the insoluble material (*ca.* 1·3 g) was heated in a sublimation apparatus; no sublimate collected on the probe even with a bath temperature of 250 °C and at 0·1 mmHg pressure. Evaporation of the light petroleum extract gave a black slime which was shown by i.r. and n.m.r. spectroscopy to contain much 1-anilino-2,3,4,5,6-pentafluorobenzene (*ca.* 0·04 g, 0·15 mmol, 2%). An authentic sample of this anilino-derivative (Found: C, 55·9; H, 2·6; F, 36·7; N, 5·2. Calc. for $C_{12}H_6F_5N$: C, 55·6; H, 2·3; F, 36·7; N, 5·4%), m.p. 68—70 °C (from ethanol) was prepared by treating hexafluorobenzene with the sodium salt of aniline in tetrahydrofuran at 50 °C.

(i) *With aniline.* The azide (1·5 g, 7·2 mmol) was added slowly (3 h) to hot (130 °C) aniline (10 cm³), stirred magnetically under a nitrogen atmosphere. The mixture was kept at 130 °C for 1 h then poured into water. The aqueous product was extracted with ether (4 × 150 cm³) and the extract, after evaporation to reduce the volume to *ca.* 100 cm³, was shaken with 2M-hydrochloric acid (2 × 50 cm³) then washed with water and dried (MgSO₄). Distillation of ether from the extract left a dark brown solid (0·8 g) which was subjected to vacuum sublimation. Material which sublimed at 120—130 °C and 0·2 mmHg was subjected to column chromatography (silica gel); elution with light petroleum (b.p. 60—80 °C), followed by recrystallisation from aqueous ethanol, provided orange crystals of 2,3,4,5,6-*pentafluoroazobenzene* (0·3 g, 1·1 mmol, 14%) (Found: C, 53·3; H, 2·2; F, 35·0; N, 9·9. $C_{12}H_5F_5N_2$ requires C, 53·0; H, 1·8; F, 35·0; N, 10·3%), m.p. 92—93 °C, δ_H (*ca.* 5% soln. in $CDCl_3$) −1·35 (m, *o*-H) and −0·95 (m, *m*- and *p*-H) (rel. int. 2 : 3), δ_F (same soln.) +74·0 (m, 2- and 6-F), +76·5 (m, 4-F), and +86·0 (m, 3- and 5-F) p.p.m. (rel. int. 2 : 1 : 2); subsequent elution with

[26] G. Szeimies and R. Huisgen, *Chem. Ber.*, 1966, **99**, 491.

light petroleum (b.p. 60—80 °C)–chloroform (9 : 1 v/v), followed by recrystallisation from aqueous ethanol, gave light red needles of 2-anilino-3,4,5,6-tetrafluoroazobenzene (0·4 g, 1·2 mmol, 17%) (Found: C, 61·8; H, 3·3; F, 22·3; N, 12·2. $C_{18}H_{11}F_4N_3$ requires C, 62·5; H, 3·2; F, 22·0; N, 12·2%), m.p. 120—121 °C, δ_F (ca. 3% soln. in $CDCl_3$; 94·10 MHz spectrum, $CF_3 \cdot CO_2H$ lock) +67·6 (m, 3- and 6-F), +72·4 (m, 4-F), and +91·5 (m, 5-F) p.p.m. (rel. int. 2 : 1 : 1).

Similar work-up of the black slimy product obtained by heating perfluoroazidobenzene (1·5 g, 7·2 mmol) in aniline (25 cm³) at 150 °C for 4 h under nitrogen gave 2-anilino-3,4,5,6-tetrafluoroazobenzene (0·01 g) and dark red crystals of 2,6-dianilino-3,4,5-trifluoroazobenzene (0·05 g, 0·12 mmol, 2%), m.p. 160—162 °C, δ_F (5% soln. in Me_2SO; 94·10 MHz spectrum, $CF_3 \cdot CO_2H$ lock) +71·4 (d, $J_{3,4}$ 22 Hz, 3- and 5-F) and +75·3 (t, 4-F) p.p.m. (rel. int. 2 : 1), δ_H (same soln.; 100 Hz spectrum, Me_2SO lock, shifts converted to the ext. benzene scale by subtracting 3·9 p.p.m.) −3·2 (s, NH), and −1·6 to −0·6 (complex, Ph groups) (rel. int. 2 : 15).

(j) With p-fluoroaniline. Perfluoroazidobenzene (1·5 g, 7·2 mmol) was decomposed at 125—130 °C in p-fluoroaniline (5 g) as described in (i). The product was worked up as before; elution of the chromatography column with light petroleum (b.p. 60—80 °C) gave 2,3,4,4′,5,6-hexafluoroazobenzene (0·04 g, 0·14 mmol, 2%), orange crystals, m.p. 100—101 °C, δ_H (ca. 5% soln. in Me_2CO) −0·85 (m) and −0·14 (m) (AA′BB′ portion of an AA′BB′X system), δ_F (same soln.) +31·0br (s, 4′-F), +76·5 (m, 2- and 6-F), +80·0 (m, 4-F), and +90·0 (m, 3- and 5-F) p.p.m. (rel. int. 1 : 2 : 1 : 2), m/e 290 (M⁺, 61%), 167 ($C_6F_5^+$, 26), 123 ($C_6H_4FN_2^+$, 42), and 95 ($C_6H_4F^+$, 100); elution with chloroform–light petroleum (b.p. 60—80 °C) (1 : 9 v/v), followed by recrystallisation from aqueous ethanol, provided red needles of 3,4,4′,5,6-pentafluoro-2-(p-fluoroanilino)azobenzene (0·07 g, 0·18 mmol, 2·5%) (Found: C, 56·3; H, 2·3; N, 10·8. $C_{18}H_9F_6N_3$ requires C, 56·6; H, 2·4; N, 11·0%), m.p. 155—156 °C, δ_F (ca. 2% soln. in Me_2SO; 94·1 MHz spectrum, p-$CF_3 \cdot S \cdot C_6H_4Cl$ lock, observed shifts converted to the ext. $CF_3 \cdot CO_2H$ scale by subtracting 35·5 p.p.m.) +28·7 (m, 4′-F), +36·1 (m, p-$FC_6H_4 \cdot NH$), +67·5 (m, 6- or 3-F), +71·0 (m, 3- or 6-F), +73·5 (m, 4-F), and +89·8 (m, 5-F) p.p.m., m/e 381 (M⁺, 38%), 123 ($C_6H_4FN_2^+$, 42), and 95 ($C_6H_4F^+$, 100).

(k) With pentafluoroaniline. The azide (2·0 g, 9·6 mmol) was added dropwise during 1 h to hot (130 °C) pentafluoroaniline in an atmosphere of nitrogen. The mixture was kept at 130 °C for 4 h then cooled to 20 °C. Fractional sublimation of the solid product at 2 mmHg gave pentafluoroaniline (collected with a bath temp. of 30 °C) and an orange solid (bath temp. 100 °C). The latter was subjected to column chromatography (silica gel). Elution with light petroleum (b.p. 60—80 °C) provided perfluoroazobenzene (0·3 g, 0·96 mmol, 10%) (Found: C, 40·1; F, 52·5; N, 7·7%; M⁺, 362. Calc. for $C_{12}F_{10}N_2$: C, 39·8; F, 52·5; N, 7·7%; M, 362), m.p. 138—140 °C (lit.,[21] 143 °C), identified by ¹⁹F n.m.r. spectroscopy and by direct comparison of its i.r. spectrum with that of an authentic sample.[21] Subsequent elution with chloroform–light petroleum (b.p. 60—80 °C) (1 : 1 v/v) gave yellow needles of octafluorophenazine (0·01 g), m.p. 230—231 °C (lit., 230—232,[21] 234,[20] 239 °C [21]), identified by mass spectrometry, m/e 324 ($C_{12}F_8N_2^+$, 100%), 305 ($C_{12}F_7N_2^+$, 17), 162 ($C_6F_4N^+$, 12·5), and 148 ($C_6F_4^+$, 32·5).

(l) Flow pyrolysis. Perfluoroazidobenzene (7·0 g, 33·5 mmol) was dripped slowly (ca. 1 g h⁻¹) into the mouth of a hot (280—300 °C) platinum tube (100 × 1 cm; heated length 56 cm) through which a slow stream of nitrogen was passing. Nothing collected in cold traps (−196 °C) connected to the exit from the tube, and the product took the form of a carbonaceous mass adhering to the walls of the tube between the exit and heated zone. This material was washed out of the tube with acetone and, after evaporation of the acetone, subjected to vacuum sublimation to provide (bath temp. 90—100 °C; pressure 0·3 mmHg) orange needles, m.p. 118—120 °C, possibly perfluoro-bi-(2-azacyclohepta-2,4,6-trien-1-ylidene) (0·6 g, 1·65 mmol, 10%) (Found: C, 40·1; F, 52·3; N, 7·7%; M⁺, 362. Calc. for $C_{12}F_{10}N_2$: C, 39·8; F, 52·5; N, 7·7%; M, 362), $\lambda_{max.}$ (mull) 5·85, 5·93 (d) and 6·13 μm (C=C and/or C=N str.; cf.[27] perfluoro-N-cyanoazepine, CF=CF str. 5·80 μm), δ_F (ca. 20% soln. in Me_2CO) −21·5br (m, CF:N), +38·3 (m), +56·3 (m), +70·5 (m), and +73·7 (m) p.p.m. (rel. int. 1 : 1 : 1 : 1 : 1).

Reactions of Perfluoro-4-azidotoluene.—Where no experimental details are given, the method employed was that used in the corresponding reaction with perfluoroazidobenzene.

(a) With dimethyl sulphoxide. Perfluoro-4-azidotoluene (0·6 g, 2·3 mmol) and dimethyl sulphoxide (2 cm³) gave, after 4 h at 160 °C, nitrogen (2·3 mmol) and SS-dimethyl-N-(perfluoro-p-tolyl)sulphoximide (0·45 g, 1·5 mmol, 65%) (Found: C, 35·3; H, 2·1; F, 43·1; N, 4·4. $C_9H_6F_7NOS$ requires C, 35·0; H, 1·9; F, 43·0; N, 4·5%), isolated by vacuum sublimation (120—125 °C at 0·1 mmHg) as white crystals, m.p. 160 °C, δ_H (ca. 5% soln. in Me_2CO) +3·65 (s) δ_F (same soln.) −23·0 (t, $J_{CF_3,3-(5-)F}$ 21 Hz, CF_3), +70·0 (m, 2- and 6-F), and +74·5 (m, 3- and 5-F) p.p.m. (rel. int. 3 : 2 : 2).

(b) With cyclohexane. A solution of the azide (1·1 g, 4·2 mmol) in cyclohexane (15 cm³) was heated at 160 °C for 40 h in a Pyrex ampoule (250 cm³) in the absence of air. The product was filtered to remove a black solid that failed to yield a sublimate when heated to 200 °C at ca. 0·1 mmHg; the filtrate was distilled to remove cyclohexane, leaving a brown oil that was shown by i.r. and n.m.r. spectroscopy to contain much 1-cyclohexylamino-2,3,5,6-tetrafluoro-4-trifluoromethylbenzene (0·4 g, 1·3 mmol, 30%).

An authentic sample of the cyclohexylamino-compound (Found: C, 49·4; H, 4·1; F, 42·1; N, 4·7. $C_{13}H_{12}F_7N$ requires C, 49·5; H, 3·8; F, 42·2; N, 4·5%), m.p. 24—25 °C, b.p. 75—77 °C at ca. 0·1 mmHg, $\lambda_{max.}$ (melt) 2·92 μm (N–H str.), δ_F (neat liq.) −23·0 (t, $J_{CF_3,3-(5-)F}$ 21 Hz, CF_3), +68·8 (m, 2- and 6-F), and +86·4 (m, 3- and 5-F) p.p.m. rel. int. 3 : 2 : 2), was obtained in 70% yield (3·8 g, 12 mmol) by adding cyclohexylamine (3·3 g, 33 mmol) to a stirred solution of perfluorotoluene (4·0 g, 17 mmol) in acetonitrile (15 cm³), followed by a conventional work-up [pour product into water; extract with ether; distil the dried ($MgSO_4$) extract].

(c) With undecafluorocyclohexane. Only a black intractable tar was obtained by heating perfluoro-4-azidotoluene (1·0 g) with an excess of undecafluorocyclohexane (5·0 g) at 150 °C for 20 h in a Pyrex ampoule (250 cm³) in the absence of air.

(d) With pentafluoroaniline. The azide (2·5 g, 9·7 mmol) was added to hot (160 °C) pentafluoroaniline (10 g) during 4 h, under nitrogen, to give perfluoro-(4-methylazobenzene) (1·3 g, 3·15 mmol, 32%) (Found: C, 38·1; F, 53·6; N, 7·0. $C_{13}F_{12}N_2$ requires C, 37·9; F, 55·4; N, 6·8%), orange

²⁷ F. D. Marsh, U.S.P. 3,268,512/1966.

crystals (from aqueous ethanol), m.p. 97—98 °C, δ_F (ca. 3% soln. in Me_2SO; 94·1 MHz spectrum, p-CF_3·S·C_6H_4Cl lock, shifts converted to ext. CF_3·CO_2H by subtracting 35·5 p.p.m.) −23·1 (t, $J_{CF_3,3-(5-)F}$ 22 Hz, CF_3), +62·0 (m, 3- and 5-F), +68·1 (t showing much fine structure, $J_{4'F,3'(5')F}$ ca. 20 Hz, 4'-F), +69·4 (m, 2- and 6- or 2'- and 6'-F), +70·0 (m, 2'- and 6'- or 2- and 6-F), and +82·7 (m, 3'- and 5'-F), and yellow needles (0·01 g), m.p. 165—167 °C believed to be perfluoro-(2-methylphenazine) (Found: M^+, 374. Calc. for $C_{13}F_{10}N_2$: M, 374), m/e 374 ($C_{13}F_{10}N_2^+$, 100%), 355 ($C_{13}F_9N_2^+$, 44), 324 ($C_{12}F_8N_2^+$, 43), and 148 ($C_6F_4^+$, 21).

(e) *With aniline.* The azide (2·0 g, 7·7 mmol) was added during 3 h to hot (160 °C) aniline (5·0 g) under nitrogen, then the mixture was stirred at the same temperature for 2 h. Work-up gave orange-yellow needles, m.p. 123—124 °C, believed to be 2,3,5,6-tetrafluoro-4-(trifluoromethyl)azobenzene (0·01 g, 0·03 mmol, 0·4%) (eluted from a silica gel column with light petroleum), m/e 322 (M^+, 62%), 217 ($C_7F_7^+$, 13), 105 ($C_6H_5N_2^+$, 35), and 77

($C_6H_5^+$, 100), 2-*anilino*-3,5,6-*trifluoro*-4-(*trifluoromethyl*)*azo-benzene* (0·2 g, 0·5 mmol, 6·5%) [eluted with chloroform–light petroleum (b.p. 60—80 °C) (1 : 9 v/v)] (Found: C, 57·7; H, 2·8; F, 28·5; N, 10·7. $C_{19}H_{11}F_6N_3$ requires C, 57·7; H, 2·8; F, 28·9; N, 10·6%), red crystals (from aqueous ethanol), m.p. 135—136 °C, δ_H (ca. 3% soln. in Me_2SO) −2·3br (s, NH), and ca. −1·3 to −0·3 (aromatic CH), δ_F (same soln.; 94·1 MHz spectrum, p-CF_3·S·C_6H_4Cl lock, shifts converted to ext. CF_3·CO_2H by subtracting 35·5 p.p.m.) −23·5 (apparent t, $J_{CF_3,3-F}$ = $J_{CF_3,5-F}$ = 22 Hz, CF_3), +45·0 (m, 3-F), +68·2 (quint. of d, $J_{CF_3,5-F}$ = $J_{5-F,6-F}$ = 22, $J_{3-F,5-F}$ 6 Hz, 5-F), and +73·2 (dd, $J_{3-F,6-F}$ 12 Hz, 6-F) p.p.m., and brown crystals (eluted with chloroform; recrystallised from ethanol), m.p. 210—211° C, believed to be 2,6-*dianilino*-3,5-*difluoro*-4-(*trifluoromethyl*)-*azobenzene* (0·06 g, 0·13 mmol, 2%) (Found: C, 64·3; H, 3·7; N, 12·0%; M^+, 468. $C_{25}H_{17}F_5N_4$ requires C, 64·1; H, 3·6; N, 11·9%; M, 468).