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Polyfluoroarenes. Part XII.[1] Some Azoxy-compounds and Benzotriazoles

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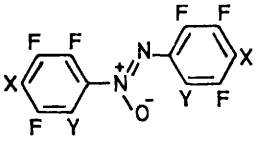
Polyfluoroazoxyarenes [$RC_6F_4{\cdot}N(O){:}N{\cdot}C_6F_4R$; R = F, *p*-H, or *o*-H] are obtained in high yield (>90%) by oxidation of the corresponding azo-compounds with trifluoroperacetic acid. Decafluoroazoxybenzene is substituted at the 2- or 4-position in the ring adjacent to the $\overset{+}{N}{-}\overset{-}{O}$ group when treated with aqueous ethanolic ammonia, and the azoxy-compounds undergo reductive cleavage to amines and/or diamines on treatment with hydriodic acid. The reactions of azoxypolyfluoroarenes with hydrazine hydrate yield 1-anilinobenzotriazoles. Tetrafluorobenzotriazole itself may be obtained by reduction of the 1-pentafluoroanilino-compound or of tetrafluorobenzotriazol-1-ol with hydriodic acid, or by treatment of tetrafluoro-*o*-phenylenediamine with nitrous acid. Tetrafluorobenzotriazol-1-ol is obtained by the reaction of nitropentafluorobenzene with hydrazine hydrate.

DECAFLUOROAZOXYBENZENE (I) was first prepared, in 22% yield, by Wall and his co-workers[2] from pentafluoroaniline and peracetic acid. Burdon, Morton, and Thomas have described its formation as a by-product during the preparation of pentafluoronitrosobenzene and during the pyrolysis or reduction (with triethyl phosphite) of the nitroso-compound.[3] The azoxy-compound (I) reacts with methoxide ion to give octafluoro-4,4′-dimethoxyazoxybenzene, which may also be prepared by the oxidation of the corresponding azo-compound with trifluoroperacetic acid; 4*H*,4′*H*-octafluoroazobenzene may also be oxidised in this way, but decafluoroazobenzene was apparently unaffected by the peroxy-acid and a number of other oxidising agents.[3]

Azoxy-compounds.—It has now been found that decafluoroazoxybenzene is obtained in 94% yield by the oxidation of decafluoroazobenzene with trifluoroperacetic acid, prepared in the usual way from hydrogen peroxide and trifluoroacetic anhydride, in dichloromethane. An improved yield (98%) of 4*H*,4′*H*-octafluoroazoxybenzene (II) and a quantitative yield of the



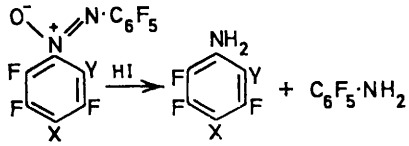
(I) X = F, Y = F
(II) X = H, Y = F
(III) X = F, Y = H

new 2*H*,2′*H*-octafluoroazoxybenzene (III) are also obtained by similar oxidations of the corresponding azo-compounds. The success of these reactions, particularly the oxidation of decafluoroazobenzene, is dependent on the concentrations of the reagents. If too much hydrogen peroxide is used, or if the peroxide solution is too dilute, an aqueous phase containing most of the oxidising power (perhaps as H_2O_2 rather than $CF_3{\cdot}CO_3H$) separates, whereas the oxidations proceed readily in homogeneous solutions.

2*H*,2′*H*-Octafluoroazoxybenzene (III) is pale orange and has a u.v. spectrum similar to that of azoxybenzene itself. However, decafluoroazoxybenzene (I) and the 4*H*,4′*H*-compound (II) are colourless; their u.v. spectra are similar to each other, but both compounds absorb more weakly and at shorter wavelengths than does azoxybenzene. These spectral differences are attributed to steric hindrance, suggested by molecular models to involve the oxygen atom and one of the *ortho*-fluorine atoms on the ring further from the $\overset{+}{N}{-}\overset{-}{O}$ group. Such effects have been noted before in azoxy-compounds containing two bulky *ortho*-substituents (*e.g.* Me or Br)[4,5] in different rings, but it is evident that fluorine atoms must occupy *both ortho*-positions in a single ring in order to provide significant hindrance to coplanarity.

Like decafluoroazobenzene and the hydrazo-compound,[6] decafluoroazoxybenzene (I) is cleaved by refluxing hydriodic acid to give pentafluoroaniline. The azoxy-compound also reacts with aqueous ethanolic ammonia under reflux to yield tetrafluoro-2-(pentafluorophenylazoxy)aniline (IV) (65% yield) and the corresponding 4-substituted compound (V) (33%). Both aminoazoxy-compounds are yellow and reveal additional bands in their u.v. spectra at *ca.* 360 nm., presumably owing to conjugation of the amino-groups with the benzenoid system.

Cleavage of each of the amino-compounds [(IV) and (V)] with hydriodic acid yields pentafluoroaniline together with the corresponding known *ortho*- or *para*-diamine, respectively, thus revealing the relative positions of the amino- and azoxy-groups. The fact that



(IV) X = F, Y = NH_2
(V) X = NH_2, Y = F

ammonia attacks decafluoroazoxybenzene at the ring adjacent to the $\overset{+}{N}{-}\overset{-}{O}$ group is deduced from the reactions

[1] Part XI, J. M. Birchall, R. N. Haszeldine, and J. O. Morley, *J. Chem. Soc.* (*C*), 1970, 456.
[2] L. A. Wall, W. J. Pummer, J. E. Fearn, and J. M. Antonucci, *J. Res. Nat. Bur. Stand.*, 1963, **67***A*, 481.
[3] J. Burdon, C. J. Morton, and D. F. Thomas, *J. Chem. Soc.*, 1965, 2621.
[4] M. P. Grammaticakis, *Bull. Soc. chim. France*, 1951, 951.
[5] P. H. Gore and O. H. Wheeler, *J. Amer. Chem. Soc.*, 1956, **78**, 2160.
[6] J. M. Birchall, R. N. Haszeldine, and J. E. G. Kemp, *J. Chem. Soc.* (*C*), 1970, 449.

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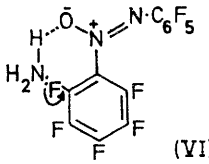
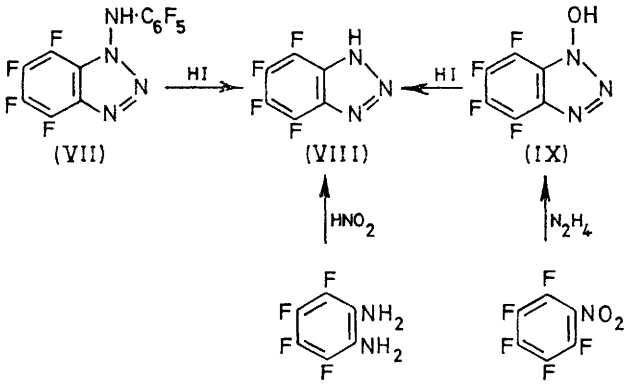
of compounds (IV) and (V) with hydrazine, described later, and is confirmed by the n.m.r. spectra of the aminoazoxy-compounds which show the predicted changes from the spectrum of decafluoroazoxybenzene itself. The quaternary nitrogen atom is probably mainly responsible for the greater reactivity shown by the ring to which it is attached, and the predominance of substitution by ammonia at the 2-position in decafluoroazoxybenzene, which contrasts with attack by methoxide ion at the 4-position,[3] may be attributed to hydrogen bonding (VI). A similar explanation has been advanced for the behaviour of pentafluoronitrobenzene towards nucleophiles of different types,[7] and its applicability to the azoxy-compound has been predicted.[3]

Benzotriazoles.—Decafluoroazoxybenzene reacts with hydrazine hydrate in refluxing ethanol to give tetrafluoro-1-pentafluoroanilinobenzotriazole (VII) in 28% yield. This compound was identified spectroscopically and by its reductive cleavage with hydriodic acid, which



(VI)

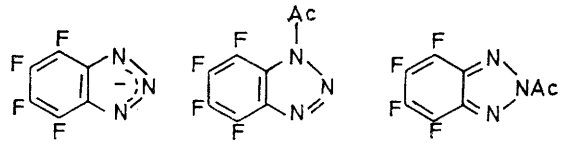
gives pentafluoroaniline (54%) and 4,5,6,7-tetrafluorobenzotriazole (VIII). The low yield of the triazole (VIII) (4%) obtained from this reduction may be attributed to the lengthy period of reflux (72 hr.) required; it seems likely that further reduction occurred. The same triazole (VIII) is obtained in 84% yield from the reaction of tetrafluoro-*o*-phenylenediamine with nitrous acid or, quantitatively, by reduction of tetra-



fluorobenzotriazol-1-ol (IX). The last compound is prepared in low yield (14%) by treatment of pentafluoronitrobenzene with hydrazine hydrate in ethanol, a reaction analogous to the preparation of benzotriazol-1-ol itself from 2-chloronitrobenzene.[8]

Tetrafluoro-1-pentafluoroanilinobenzotriazole (VII) gives a ^{19}F n.m.r. spectrum which, by comparison with the spectra of the simpler triazoles reported here, may be satisfactorily assigned to the AGPX system of the fused benzene ring (δ_4 78·0, δ_5 85·3, δ_6 75·7, and δ_7 84·0 p.p.m.) and to the pentafluorophenyl group ($\delta_{2'} = \delta_{6'} =$ 79·9 and $\delta_{3'} = \delta_{4'} = \delta_{5'} \approx$ 87·2 p.p.m.). Its u.v. spectrum resembles closely a predicted spectrum, compiled by addition of half the intensities from the spectrum of decafluorohydrazobenzene[3,6] to the spectrum of the triazolol (IX), and its i.r. spectrum shows sharp N–H absorption at 3·11 μm. The structure of the tetrafluorotriazolol (IX) is confirmed by the presence of strong, hydrogen-bonded OH absorption in the 3·0—4·5 μm. region and by the similarity of its u.v. spectrum to that of the hydrocarbon analogue; its ^{19}F n.m.r. spectrum is analysable as an AGPX system, and the chemical shifts (δ_4 80·1, δ_5 85·6, δ_6 76·9, and δ_7 84·0 p.p.m.) and coupling constants are completely consistent with the proposed structure. Treatment of the triazolol with toluene-*p*-sulphonyl chloride yields the expected *O*-tosyl derivative, from which the triazolol is quantitatively recovered (along with toluene-*p*-sulphonamide) by reaction with aqueous ethanolic ammonia.

Tetrafluorobenzotriazole (VIII) shows N–H absorption at 3·34 and 3·62 μm. (broad, hydrogen-bonded) and similar u.v. absorption to that of benzotriazole itself. The ^{19}F n.m.r. spectrum of the tetrafluorotriazole in tetrahydrofuran was poorly resolved, but the spectrum obtained when the compound is dissolved in aqueous sodium hydroxide, presumably that of the ion (X), is clearly defined and of the required AA′XX′ type ($\delta_4 = \delta_7 =$ 77·4 and $\delta_5 = \delta_6 =$ 88·5 p.p.m.). Like benzo-



(X) (XI) (XII)

triazole,[9] the tetrafluoro-compound (VIII) reacts with boiling acetic anhydride to give the 1-acetyl compound (XI), readily distinguished from the alternative, symmetrical, 2-isomer (XII) by n.m.r. spectroscopy (AGPX system). The acetyl compound (XI) is very readily hydrolysed, even in neutral solution, a fact which explains the low yield of this compound (5%) isolated after treatment of the tetrafluorobenzotriazole–acetic anhydride mixture with water.

2*H*,2′*H*-Octafluoroazoxybenzene (III) and the 4*H*,4′*H*-compound (II) give the corresponding trifluoro-1-tetrafluoroanilinobenzotriazoles (XIII) (34% yield) and (XIV) (37%), respectively, on treatment with hydrazine hydrate; similar treatment of the aminoazoxy-compounds [(IV) and (V)] gives the aminotrifluoro-1-pentafluoroanilinobenzotriazoles [(XV) and (XVI), respectively]. Identification of these four triazoles is based on analogy with the tetrafluoro-1-pentafluoroanilino-compound

[7] J. G. Allen, J. Burdon, and J. C. Tatlow, *J. Chem. Soc.*, 1965, 1045; J. Burdon, J. C. Tatlow, D. Fisher, and D. King, *Chem. Comm.*, 1965, 65.

[8] W. Borsche, *Ber.*, 1923, **56**, 1488.

[9] L. F. Fieser and E. L. Martin, *J. Amer. Chem. Soc.*, 1935, **57**, 1835.

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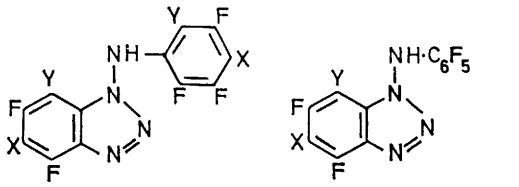
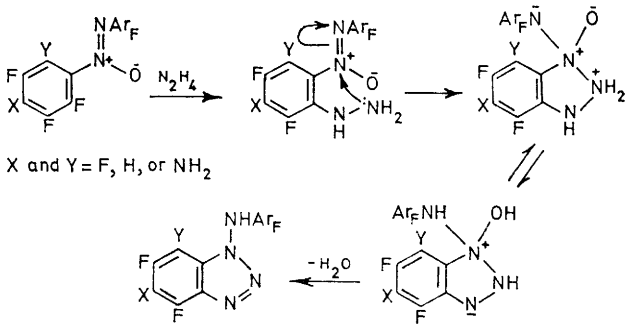


(XIII) X = F, Y = H
(XIV) X = H, Y = F

(XV) X = F, Y = NH_2
(XVI) X = NH_2, Y = F

(VII) and on ^{19}F n.m.r. spectroscopy [the n.m.r. spectrum of triazole (XIII) provides the key to the assignment of the ^{19}F bands given by all the triazoles described here [10]]. In addition, the u.v. spectra of both the trifluoro(tetrafluoroanilino)benzotriazoles [(XIII) and (XIV)] resemble closely that of the completely fluorinated compound (VII), but the u.v. spectra of the aminobenzotriazoles [(XV) and (XVI)] are complicated by the appearance of additional bands [(XV), at 220 nm.; (XVI), at 225 nm.] and of medium-intensity bands (at 310—330 nm.), probably arising from conjugation involving the amino-group. However, the aminobenzotriazoles give pentafluoroaniline in good yield following reductive cleavage with hydriodic acid, thus affording further proof of the presence of the pentafluorophenyl group; the product from the triazole part of the molecule was not isolated from either of these reactions.

The reaction of *ortho*-halogenoazoxy-compounds with hydrazine to give anilinobenzotriazoles is new and is likely to be of general applicability. The reactions described here presumably involve initial nucleophilic displacement of fluorine from a position *ortho* to the $\overset{+}{N}-\overset{-}{O}$ group followed by cyclisation, possibly *via* the route shown or a variation of it. The deactivating influence of the amino-group in the aminoazoxy-compounds (X or



Y = NH_2) is apparently insufficient to prevent attack by the hydrazine molecule on the same ring. However, some substitution in the second ring (and/or at the position *para* to the $\overset{+}{N}-\overset{-}{O}$ group when X = F) may also have occurred, since the yields in all the hydrazine reactions were far from quantitative and the by-products were not investigated in detail.

EXPERIMENTAL

Spectroscopic methods and the preparation of starting materials have been described earlier.[6] U.v. spectra were measured for solutions in ethanol, and log ε values are shown in parentheses. ^{19}F N.m.r. spectra were measured for solutions in tetrahydrofuran at 54·46 MHz; chemical shifts are to high field of an external trifluoroacetic acid reference; subscripts associated with values of δ refer to the systematic position number of the fluorine atom to which the band is assigned. Known compounds were identified by i.r. spectroscopy and (where applicable) m.p. and mixed m.p. determination.

Decafluoroazoxybenzene.—Decafluoroazobenzene (5·00 g., 13·8 mmoles), aqueous 85% hydrogen peroxide (2·5 ml.), trifluoroacetic anhydride (25 ml.), and dry dichloromethane (100 ml.) were heated under reflux for 4 hr. in an apparatus protected from atmospheric moisture. More trifluoroacetic anhydride (20 ml.) and hydrogen peroxide (8 ml.) were added in small portions during the reaction, at the end of which the yellow solution was diluted with water (100 ml.). The organic layer was washed with water, dried ($MgSO_4$), and evaporated to give decafluoroazoxybenzene (4·90 g., 94%) (Found: C, 38·1. Calc. for $C_{12}F_{10}N_2O$: C, 38·1%), m.p. 54—55° [from light petroleum (b.p. 30—40°)] [$\lambda_{max.}$ 224 (4·05) and 292 (3·76) nm., $\lambda_{infl.}$ 232 (3·99) nm.] [lit.,[2] m.p. 53—54°; lit.,[3] $\lambda_{max.}$ 228 (3·9) and 293 (3·7) nm.].

Octafluoroazoxybenzenes.— 2*H*,2′*H*-Octafluoroazobenzene (1·50 g., 4·4 mmoles), aqueous 85% hydrogen peroxide (5 ml.), trifluoroacetic anhydride (15 ml.), and dichloromethane (15 ml.) were heated under reflux for 1 hr. The yellow mixture was washed with water (50 ml.) and the washings were extracted with dichloromethane (2 × 5 ml.). The organic layer was washed again with water (20 ml.), dried ($MgSO_4$), and evaporated, to give almost pure (i.r.) 2H,2′H-*octafluoroazoxybenzene* (1·59 g., 100%), m.p. 59—62°. Recrystallisation from aqueous methanol (charcoal) gave the pure compound (Found: C, 42·2; H, 0·8; N, 8·4. $C_{12}H_2F_8N_2O$ requires C, 42·1; H, 0·6; N, 8·2%) as pale orange needles, m.p. 62—63° [$\lambda_{max.}$ 228 (3·87), 250 (3·83), and 314 (4·05) nm.].

A similar procedure with 4*H*,4′*H*-octafluoroazobenzene (0·158 g., 0·485 mmoles), aqueous 85% hydrogen peroxide (0·52 ml.), trifluoroacetic anhydride (1·58 ml.), and dichloromethane (1·58 ml.) gave the 4*H*,4′*H*-azoxy-compound (0·162 g., 98%), obtained as white needles (Found: C, 42·2; H, 0·6; N, 8·2%), m.p. 55—55·5° (from methanol), $\lambda_{max.}$ 233 (3·95) and 287 (3·74) nm. [lit.,[3] m.p. 52°, $\lambda_{max.}$ 232 (3·9) and 288 (3·7) nm.].

Azoxyanilines.—Aqueous ammonia (*d* 0·88; 8·0 ml.) was added in 1 ml. portions at intervals of 30 min. to decafluoroazoxybenzene (4·25 g., 11·2 mmoles) in refluxing ethanol (30 ml.). After a total of 4 hr. under reflux, the mixture was poured into water (100 ml.) and extracted with ether (4 × 30 ml.); the resulting semi-solid (4·35 g.) was dissolved in 33% benzene–light petroleum (b.p. 60—80°) and chromatographed on alumina (Light, type A). The initial pale brown band yielded decafluoroazoxybenzene (0·46 g., 11% recovery). The second band (yellow) yielded crude *tetrafluoro-2-(pentafluorophenylazoxy)aniline* (2·42 g., 65% based on decafluoroazoxybenzene consumed), shown by i.r. spectroscopy to contain a little of the 4-isomer; the pure 2-isomer (Found: C, 38·6; H, 0·7; N, 11·2. $C_{12}H_2F_9N_3O$ requires C, 38·4; H, 0·5; N, 11·2%), m.p. 69·5°, was obtained as yellow needles after two recrystallisations from light petroleum (b.p. 40—60°) [$\lambda_{max.}$ 223 (4·28), 279 (3·79), and 368 (3·52) nm., $\lambda_{infl.}$ 238 (3·95) nm.]. The final band (off-white) gave *tetrafluoro-4-(pentafluorophenylazoxy)aniline*

[10] J. E. G. Kemp, Ph.D. Thesis, Manchester, 1966.

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(1·21 g., 33%) (Found: C, 38·8; H, 0·7; N, 11·4%) as pale yellow needles, m.p. 93° [from light petroleum (b.p. 60—80°)] [$\lambda_{max.}$ 228 (4·42), 283 (3·89), and 353 (3·95) nm., $\lambda_{infl.}$ 278 (3·86) and 310 (3·90) nm.].

Cleavage of the Azoxy-compounds.—(a) *Decafluoroazoxybenzene.* The azoxy-compound (1·00 g., 2·65 mmoles) and aqueous 55% hydriodic acid (10 ml.) were heated under reflux for 6·5 hr.; the mixture was then diluted with water (30 ml.), decolourised with solid sodium disulphite, and neutralised with solid sodium carbonate. Steam distillation gave pentafluoroaniline (0·32 g., 33%), m.p. and mixed m.p. 32—33° (lit.,[11] 33·5—35°).

(b) *Tetrafluoro-2-(pentafluorophenylazoxy)aniline.* The azoxy-compound (0·50 g., 1·3 mmole) and aqueous 55% hydriodic acid (5 ml.) were heated under reflux for 1 hr., and the mixture was then diluted with water, decolourised, and neutralised as before. Extraction with ether (5 × 10 ml.) gave a pink solid (0·43 g.), which was recrystallised from light petroleum (b.p. 80—100°; 10 ml.) to give tetrafluoro-*o*-phenylenediamine (0·13 g., 55%), m.p. 117—120° (lit.,[12] 131°), identified by i.r. spectroscopy. Extraction of the light petroleum mother liquor with concentrated hydrochloric acid (7 and 3 ml.), followed by neutralisation of the acid with solid sodium carbonate and extraction with ether (10 and 5 ml.), gave pentafluoroaniline (0·19 g., 80%), shown by i.r. spectroscopy to contain traces of the diamine. Treatment of the diamine with benzil in boiling glacial acetic acid for 1 hr. gave 5,6,7,8-*tetrafluoro*-2,3-*diphenylquinoxaline* (66%) (Found: C, 67·9; H, 2·9; N, 8·1. $C_{20}H_{10}F_4N_2$ requires C, 67·9; H, 2·8; N, 7·9%) as fine white needles, m.p. 182° (from ethanol).

(c) *Tetrafluoro-4-(pentafluorophenylazoxy)aniline.* The azoxy-compound (0·41 g., 1·1 mmole) and aqueous 55% hydriodic acid (4 ml.), heated under reflux for 90 min., similarly gave tetrafluoro-*p*-phenylenediamine (0·13 g., 66%), identical with the sample obtained by reductive cleavage of 4-aminononafluoroazobenzene,[6] and pentafluoroaniline (0·075 g., 38%).

Reactions of the Azoxy-compounds with Hydrazine Hydrate.—(a) *Decafluoroazoxybenzene.* The azoxy-compound (5·00 g., 13·2 mmoles), hydrazine hydrate (1·00 g., 20·0 mmoles), and ethanol (50 ml.) were heated under reflux for 30 min. The mixture was poured into water (100 ml.) and extracted with ether (3 × 50 ml.), and the resulting solid (4·5 g.) was recrystallised from 1,2-dichloroethane (charcoal) and light petroleum (b.p. 80—100:) to give white needles of *tetrafluoro-1-pentafluoroanilinobenzotriazole* (1·40 g., 28%) (Found: C, 38·9; H, 0·6; N, 15·3. $C_{12}HF_9N_4$ requires C, 38·7; H, 0·3; N, 15·0%), m.p. 158—159° [$\lambda_{max.}$ 281 (3·52) nm., $\lambda_{infl.}$ 216 (4·26) and 245 (3·78) nm.].

(b) 2H,2′H-*Octafluoroazoxybenzene.* The azoxy-compound (0·60 g., 1·8 mmole), hydrazine hydrate (0·15 g., 3·0 mmoles), and ethanol (6 ml.) were heated under reflux for 15 min. and then poured into water. Extraction with ether and recrystallisation of the product from light petroleum (b.p. 60—80°) gave white needles of 7H-*trifluoro-1-(2H-tetrafluoroanilino)benzotriazole* (0·20 g., 34%) (Found: C, 43·1; H, 1·2; N, 17·0. $C_{12}H_3F_7N_4$ requires C, 42·8; H, 0·9; N, 16·7%), m.p. 125—126° [$\lambda_{max.}$ 249 (3·89) and 275 (3·73) nm.].

(c) 4H, 4′H-*Octafluoroazoxybenzene.* Identical treatment of this azoxy-compound (0·40 g., 1·2 mmole) with hydrazine hydrate (0·10 g., 2·0 mmoles) in ethanol (4 ml.) gave 5H-*trifluoro-1-(4H-tetrafluoroanilino)benzotriazole* (0·15 g., 37%) (Found: C, 42·8; H, 0·8; N, 17·0%) as white needles, m.p. 162—164° (decomp.) [from light petroleum (b.p. 60—80°)] [$\lambda_{max.}$ 254 (3·76) nm., $\lambda_{infl.}$ 227 (4·20) and 276 (3·59) nm.].

(d) *Tetrafluoro-2-(pentafluorophenylazoxy)aniline.* The azoxy-compound (8·60 g., 22·9 mmoles), hydrazine hydrate (1·72 g., 34·5 mmoles), and ethanol (86 ml.) were heated under reflux for 30 min. Extraction of the product with ether, followed by recrystallisation from benzene–light petroleum (b.p. 60—80°) (charcoal) gave 7-*aminotrifluoro-1-pentafluoroanilinobenzotriazole* (1·44 g., 16%) (Found: C, 39·1; H, 1·0; F, 39·9; N, 19·6. $C_{12}H_3F_8N_5$ requires C, 39·0; H, 0·8; F, 41·2; N, 18·9%), m.p. (explodes) 147° [$\lambda_{max.}$ 220 (4·44) and 313 (3·60) nm., $\lambda_{infl.}$ 267 (3·42) nm.]. The ^{19}F n.m.r. spectrum showed no fluorine-containing impurity, but the elemental analysis suggested the presence of traces of material which had undergone further attack by hydrazine.

The triazole (0·50 g., 1·3 mmole) and aqueous 55% hydriodic acid (5 ml.) were heated under reflux for 90 min. The mixture was diluted to 50 ml. with water, decolourised with sodium disulphite, neutralised with sodium hydrogen carbonate, and extracted with ether (3 × 10 ml.) to give pentafluoroaniline (0·15 g., 60%).

(e) *Tetrafluoro-4-(pentafluorophenylazoxy)aniline.* This azoxy-compound (0·40 g., 1·1 mmole), hydrazine hydrate (0·10 g., 2·0 mmoles), and ethanol (4 ml.) similarly yielded 5-*aminotrifluoro-1-pentafluoroanilinobenzotriazole* (0·092 g., 23%) (Found: C, 39·2; H, 1·1; N, 19·2%), m.p. 152—153° (decomp.) [from benzene–light petroleum (b.p. 60—80°)] [$\lambda_{max.}$ 225 (4·63) and 326 (3·41) nm., $\lambda_{infl.}$ 259 (3·80) nm.].

The triazole (0·50 g., 1·3 mmole) was treated with refluxing aqueous 55% hydriodic acid (5 ml.) for 90 min. and yielded pentafluoroaniline (0·19 g., 77%).

Tetrafluorobenzotriazol-1-ol.—Hydrazine hydrate (2·2 g., 4·4 mmoles) in ethanol (50 ml.) was added dropwise during 10 min. to a stirred solution of pentafluoronitrobenzene (6·0 g., 28 mmoles) in ethanol (50 ml.) on a water-bath at 60°. Stirring was continued at 60° for a further 30 min., then the mixture was poured into water (100 ml.) and extracted with ether (5 × 40 ml.). The extracts were washed with saturated aqueous calcium chloride (10 ml.) and evaporated to dryness; 1,2-dichloroethane (50 ml.) was then added, and the mixture was carefully boiled down to about 10 ml. (note that, although experiments on this scale caused no difficulty, in an experiment on five times this scale the reaction mixture exploded at this stage). Light petroleum (b.p. 60—80°; 5 ml.) was added, and a brown powder (2·2 g.), shown by i.r. spectroscopy to consist largely of the triazolol, separated when the mixture was allowed to cool. The product from five such experiments (10·5 g.) was recrystallised from a mixture of 1,2-dichloroethane (200 ml.) and light petroleum (b.p. 60—80°; 100 ml.), and the purified material was boiled with water (100 ml.), leaving a black tarry residue. The aqueous phase was treated with charcoal, filtered, and extracted with ether (5 × 40 ml.), and the extract was dried ($MgSO_4$) and evaporated. The resulting solid was recrystallised from 50% 1,2-dichloroethane–light petroleum (b.p. 60—80°) to give *tetrafluorobenzotriazol-1-ol* (4·0 g., 14%) (Found: C, 34·7; H, 0·5; N, 20·5. $C_6HF_4N_3O$ requires C, 34·8; H, 0·5; N, 20·3%) as a white powder, exploding at 144° [$\lambda_{max.}$ 267 (3·70) and 287 (3·58) nm., $\lambda_{infl.}$ 259 (3·57) and 317 (3·10 nm.].

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The triazolol (0·200 g.), sodium hydrogen carbonate (1·0 g.), and toluene-*p*-sulphonyl chloride (1·0 g.), shaken in water (20 ml.) for 30 min. and then boiled for 5 min., gave *tetrafluorobenzotriazol*-1-*yl toluene*-p-*sulphonate* (0·146 g., 42%) (Found: C, 43·4; H, 1·9; N, 11·9. $C_{13}H_7F_4N_3O_3S$ requires C, 43·2; H, 1·9; N, 11·6%), m.p. 95—96° [from light petroleum (b.p. 60—80°) (charcoal)]. The tosyl derivative (0·200 g.) was heated under reflux for 5 min. with aqueous ammonia (*d* 0·88; 2 ml.) and ethanol (8 ml.) and the mixture was diluted with water (20 ml.) and extracted with ether (4 × 10 ml.), to give toluene-*p*-sulphonamide (0·103 g., 100%). Acidification of the aqueous phase, followed by extraction with ether (4 × 10 ml.), yielded tetrafluorobenzotriazol-1-ol (0·127 g., 100%). Both products were identified by i.r. spectroscopy.

Tetrafluorobenzotriazole.—(a) *From the triazolol.* Tetrafluorobenzotriazol-1-ol (0·250 g., 1·2 mmole) and aqueous 55% hydriodic acid (2·5 ml.) were heated under reflux for 30 min. The solution was decolourised with solid sodium disulphite, partly neutralised (to pH 6) with saturated aqueous sodium carbonate, and extracted with ether (5 × 10 ml.). The extracts were dried ($MgSO_4$) and evaporated to give almost pure (i.r.) *tetrafluorobenzotriazole* (0·241 g., 100%), m.p. 160—162°. Recrystallisation from benzene yielded the pure compound as colourless plates (Found: C, 37·8; H, 0·6; N, 21·9. $C_6HF_4N_3$ requires C, 37·7; H, 0·5; N, 22·0%), m.p. 162·5° [$\lambda_{max.}$ 223 (3·49), 258 (3·62), and 271 (3·60) nm.]. 1-*Acetyltetrafluorobenzotriazole* (30 mg., 5%) (Found: C, 41·4; H, 1·5; N, 18·2. $C_8H_3F_4N_3O$ requires C, 41·2; H, 1·3; N, 18·0%), m.p. 112—113° [white needles from light petroleum (b.p. 60—80°)], was obtained when tetrafluorobenzotriazole (0·50 g.) and acetic anhydride (5 ml.) were heated under reflux for 10 min. and the product was diluted with ice–water (50 ml.).

(b) *From tetrafluoro*-o-*phenylenediamine.* The diamine (21·0 mg., 0·117 mmole), sodium nitrite (10·5 mg., 0·15 mmole), and aqueous 70% sulphuric acid (1·0 g.) were heated to 75° in a water-bath. The mixture was diluted with water to 50 ml., partly neutralised (pH 6·5) with sodium carbonate, and extracted with ether (3 × 10 ml.), to give tetrafluorobenzotriazole (18·7 mg., 84%), identified by i.r. spectroscopy.

(c) *From tetrafluoro*-1-*pentafluoroanilinobenzotriazole.* The triazole (0·500 g., 1·34 mmole), aqueous 55% hydriodic acid (5 ml.) and *p*-xylene (5 ml.) were heated under reflux for 72 hr. The mixture was diluted with water to 100 ml., decolourised, partly neutralised to pH 6, and extracted with ether (100 and 5 × 20 ml.). The extracts were washed with water (25 ml.), benzene (25 ml.) was added, and the mixture was fractionally distilled until the volume had been reduced to 25 ml. This residual product was extracted with concentrated hydrochloric acid (5 and 2 × 2·5 ml.), and these extracts were neutralised with solid sodium carbonate and extracted with ether (5 × 5 ml.) to give pentafluoroaniline (0·132 g., 84% based on starting material consumed). The residual benzene solution was extracted with aqueous M-sodium hydroxide (3 × 10 ml.), and these extracts were neutralised with concentrated hydrochloric acid and extracted with ether (5 × 5 ml.), to give tetrafluorobenzotriazole (0·070 g., 4%). Tetrafluoro-1-pentafluoroanilinobenzotriazole (0·109 g., 22%) was recovered by evaporation of the remaining benzene *in vacuo*.

We thank Pennwalt Corporation for a grant and I. I. O. Allinson and M. G. Barlow for assistance with the interpretation of n.m.r. spectra.

[9/1718 *Received, October* 10*th*, 1969]