31. *Aromatic Polyfluoro-compounds. Part I. The Synthesis of Aromatic Polyfluoro-compounds from Pentafluorobenzene.*

By E. Nield, R. Stephens, and J. C. Tatlow.

Pentafluorobenzene has been prepared by dehydrofluorination of 1*H* : 4*H*/2*H* : 5*H*-, 1*H* : 5*H*/2*H* : 4*H*-, 1*H* : 2*H*/4*H* : 5*H*-, and 1*H* : 2*H* : 4*H*/5*H*-octafluoro*cyclo*hexane. Three general types of reaction are undergone by this new compound: addition to the unsaturated ring system (for example, of chlorine), attack on the fluorine atoms by nucleophilic reagents (*e.g.*, sodium methoxide), and replacement of the hydrogen atom by electrophilic reagents. Fuming sulphuric acid gave pentafluorobenzenesulphonic acid; bromine or iodine in sulphuric acid gave respectively bromopentafluoro- or pentafluoroiodo-benzene. From these a general route to pentafluorophenyl derivatives has been provided since they give, fairly readily, Grignard reagents which react normally, *e.g.*, to give 1-(pentafluorophenyl)ethanol. The bromo-compound also gave decafluorodiphenyl by an Ullmann reaction.

Some aromatic fluoro-compounds have been known for a considerable time and fluorobenzene derivatives were amongst the first organic fluoro-compounds to be investigated systematically. Aromatic fluoro-compounds have usually been prepared by the Balz–Schiemann reaction,[1] *i.e.*, thermal decomposition of diazonium fluoroborates, most of which are insoluble in water. In this way, *o*-, *m*-, and *p*-difluorobenzene,[2] 1 : 2 : 4-[3] and

---

[1] Balz and Schiemann, *Ber.*, 1927, **60**, 1186; Booth and Martin, " Boron Trifluoride and its Derivatives," John Wiley and Sons, 1949; Roe, *Organic Reactions*, 1949, **5**, 193.

[2] Schiemann and Pillarsky, *Ber.*, 1929, **62**, 3035.

[3] Schiemann, *J. prakt. Chem.*, 1934, **140**, 97.

1 : 3 : 5-trifluorobenzene,[4] and 1 : 2 : 4 : 5-[5] and 1 : 2 : 3 : 5-tetrafluorobenzene[6] have been synthesised, the last by stepwise nitration, reduction, diazotisation, and fluorination. However, extension of this method to give pentafluorobenzene broke down owing to the expulsion of two *para*-fluorine atoms, to give 2 : 5-difluorobenzoquinone, during the attempted nitration of the tetrafluorobenzene.[5]

Though pentafluorobenzene was unknown until the present work, hexafluorobenzene, the simplest fluorocarbon of the aromatic series, had been prepared by three methods. First, a small yield was obtained from hexachlorobenzene by saturation of the ring with fluorine and then dehalogenation.[7] A novel method, involving pyrolysis of tribromofluoromethane, was reported recently[8] and under optimum conditions good yields can be obtained;[9] the formation of bromopentafluorobenzene in small yield in this pyrolysis was mentioned but no constants were given. The third method was developed in this Department[10] and consists of dehydrofluorination with aqueous alkali of two nonafluoro*cyclo*hexanes[11] obtained from the partial fluorination of benzene with cobaltic fluoride It has been extended[12] to the preparation of the hitherto unknown pentafluorobenzene from four octafluoro*cyclo*hexanes[13] isolated later from the same polyfluoro*cyclo*hexane mixture. Pentafluorobenzene has been prepared[11] also by dehydrofluorination of 1*H*,4*H*/5*H*-heptafluoro*cyclo*hexene which was obtained from 4*H*/5*H*-octafluoro*cyclo*hexene (a dehydrofluorination product of the nonafluoro*cyclo*hexanes) by reaction with lithium aluminium hydride in diethyl ether.

The dehydrofluorination of the four octafluoro*cyclo*hexanes[13] obtained from the product of partial fluorination of benzene gave reasonable yields of pentafluorobenzene in three cases. Preparative-scale gas chromatography was used for separation of the aromatic from the other dehydrofluorination products in the early work, but 300 g. or more of the mixtures can be separated efficiently by fractional distillation controlled by analytical gas chromatography.

A detailed study of the general chemistry of both hexafluoro- and pentafluoro-benzene is now in progress in this Department. The former undergoes nucleophilic attack without difficulty, giving pentafluoroaniline[14] with sodamide and pentafluoroanisole[10,15] with methoxide ion, the anisole being attacked in turn by methoxide ion to give a dimethoxy-derivative. Recently,[15] pyridine has been suggested as a useful solvent in which to carry out these reactions. It has of course been observed before that, when negative groups are present, aromatic fluorine is susceptible to nucleophilic attack, *e.g.*, notably in 2 : 4-fluorodinitrobenzene,[16] and another example[17] is the replacement of fluorine already present in the nucleus of an aryldiazonium fluoroborate by chloride ions present in the salt as impurity.

With pentafluorobenzene the effect has been demonstrated in the reaction with sodium methoxide in methanol. A tetrafluoroanisole was obtained in good yield, and analytical gas chromatography indicated the presence of one isomer only, though the orientation has not yet been completed. The reactions of hexa- and penta-fluorobenzene with negative ions show that the fluorine substituents do not impair the aromatic character of the ring. The reactions of such ions with perfluoro-olefins and -diolefins are qualitatively faster and

---

[4] Finger, Reed, and Finerty, *J. Amer. Chem. Soc.*, 1951, **73**, 153.
[5] Finger, Reed, Burness, Fort, and Blough, *ibid.*, p. 145.
[6] Finger, Reed, and Oesterling, *ibid.*, p. 152.
[7] McBee, Lindgren, and Ligett, *Ind. Eng. Chem.*, 1947, **39**, 378.
[8] Désirant, *Bull. Classe Sci. Acad. roy. Belg.*, 1955, **41**, 759.
[9] Hellmann, Peters, Pummer, and Wall, *J. Amer. Chem. Soc.*, 1957, **79**, 5654.
[10] Godsell, Stacey, and Tatlow, *Nature*, 1956, **178**, 199.
[11] *Idem, Tetrahedron*, 1958, **2**, 193.
[12] Stephens and Tatlow, *Chem. and Ind.*, 1957, 821.
[13] Nield, Stephens, and Tatlow, preceding paper.
[14] Forbes, Richardson, and Tatlow, *Chem. and Ind.*, 1958, 630.
[15] Pummer and Wall, *Science*, 1958, **127**, 643.
[16] Sanger, *Biochem. J.*, 1945, **39**, 507.
[17] Finger and Oesterling, *J. Amer. Chem. Soc.*, 1956, **78**, 2593.

often take the form of progressive addition–elimination stages. However, addition to the unsaturated ring of pentafluorobenzene can be accomplished under different conditions. As with hexafluorobenzene,[10] addition of chlorine was promoted by ultraviolet irradiation, presumably owing to a radical process. The product was a hexachloropentafluoro*cyclo*hexane, saturation of the ring being completed before replacement of the hydrogen under these conditions.

The usual type of aromatic substitution, that of electrophilic replacement of the hydrogen atom, has also been studied with pentafluorobenzene. It is of considerable value since it has provided the route to several new pentafluorophenyl derivatives and thus opened the way to a study of the effect of this strongly electron-attracting system on various functional groups.

Sulphonation with oleum (20% sulphur trioxide) or with stabilised sulphur trioxide at room temperature readily gave a high yield of the hygroscopic, crystalline pentafluorobenzenesulphonic acid, which was characterised as the anilinium and the *S*-benzylthiuronium salt. It was of interest to observe evidence of slight surface activity in the sodium salt. Unfortunately, the susceptibility of the nuclear fluorine atoms to attack by anions rendered the acid of little apparent use for the preparation of other substituted pentafluorobenzenes. Thus, when a dry finely divided mixture of sodium cyanide and sodium pentafluorobenzenesulphonate was heated to about 80° a violent reaction occurred, with evolution of a large volume of gas, to leave a carbonaceous residue. Possibly substitution of cyanide for fluorine occurred and the highly cyanogenated sulphonic acid then decomposed with the evolution of nitrogen.

Application to pentafluorobenzene of the bromination conditions successfully employed earlier[18] for the preparation of *p*-dibromotetrafluorobenzene from 1 : 2 : 4 : 5-tetrafluorobenzene (bromine in the presence of oleum) gave a good yield of bromopentafluorobenzene. Likewise with iodine and oleum pentafluoroiodobenzene was obtained. When heated with copper bronze in a sealed tube pentafluorobromobenzene underwent a classical Ullmann reaction and gave in excellent yield the new aromatic fluorocarbon, decafluorodiphenyl. Both the bromo- and the iodo-compound reacted fairly easily with magnesium in dry ether, to produce the corresponding Grignard reagent. The reactions did not seem to be so difficult and the reagents were apparently more stable than in the perfluoroalkyl series,[19] nor was the use of very pure magnesium necessary. Pentafluorophenylmagnesium bromide underwent several typical reactions. With water, pentafluorobenzene was regenerated, and analogously, with deuterium oxide, deuteropentafluorobenzene was prepared for spectroscopic purposes, material of high purity being obtained. However, reaction of the iodo-Grignard reagent with carbon dioxide gave a very poor yield of the known pentafluorobenzoic acid.[20] With acetaldehyde, a smooth reaction occurred to give 1-(pentafluorophenyl)ethanol, characterised as its 3 : 5-dinitrobenzoate. This alcohol with phosphoric oxide gave pentafluorophenylethylene, characterised as its dibromo-addition compound and readily polymerised by benzoyl peroxide or ultraviolet irradiation. Attempts to hydrate the double bond of pentafluorostyrene in sulphuric acid were unsuccessful: under mild conditions no reaction occurred, and more drastic ones led to polymer formation. The styrene was oxidised[21] by permanganate in acetone to pentafluorobenzoic acid, characterised as its *S*-benzylthiuronium salt.

Attempted preparations of pentafluorobenzaldehyde from the Grignard reagent by reaction with ethyl orthoformate or 3 : 4-dihydro-6-methyl-3-*p*-tolylquinazoline methiodide[22] gave rather poor yields. The sodium bisulphite compound was, therefore, prepared directly to facilitate purification and was subsequently decomposed with dilute sulphuric acid to regenerate the slightly water-soluble aldehyde. This was identified as its

---

[18] Hellmann and Bilbo, *J. Amer. Chem. Soc.*, 1953, **75**, 4590.

[19] Henne and Francis, *J. Amer. Chem. Soc.*, 1951, **73**, 3518; Haszeldine, *J.*, 1952, 3423; 1954, 1273.

[20] McBee and Rapkin, *J. Amer. Chem. Soc.*, 1951, **73**, 1366.

[21] Burdon and Tatlow, *J. Appl. Chem.*, 1958, **8**, 293.

[22] Fales, *J. Amer. Chem. Soc.*, 1955, **77**, 5118.

2 : 4-dinitrophenylhydrazone but rather poor elemental analyses were obtained for the free aldehyde. The aldehyde bisulphite compound was converted in poor yield into 2 : 3 : 4 : 5 : 6-pentafluoromandelonitrile by sodium cyanide in water.

EXPERIMENTAL

Preparation of Pentafluorobenzene.—In a typical experiment, the 1*H* : 4*H*/2*H* : 5*H*-octafluoro*cyclo*hexane (58·0 g.; b. p. 118°) was dehydrofluorinated with potassium hydroxide (116 g.) and water (116 c.c.) as described before.[13] The mixture of four products was separated by gas chromatography to give pentafluorobenzene (24·0 g.), b. p. 85°. It had infrared absorptions associated with the benzene ring at 1535 and 1512 cm.$^{-1}$. The three other octafluoro*cyclo*hexanes,[13] b. p. 125°, 133°, and 136°, also gave pentafluorobenzene on dehydrofluorination.

1 : 2 : 3 : 4 : 5 : 6-*Hexachloro*-1 : 2 : 3 : 4 : 5-*pentafluoro*cyclo*hexane.*—Pentafluorobenzene (2·2 g.) and liquid chlorine (3·5 g.) were shaken together in a sealed tube which was irradiated with ultraviolet light at room temperature for 46 hr. The tube was then cooled in liquid oxygen and opened. Chlorine was allowed to evaporate and the residue was washed with sodium metabisulphite solution, to leave a viscous oil (4·3 g.), distillation of which *in vacuo* gave 1 : 2 : 3 : 4 : 5 : 6-*hexachloro*-1 : 2 : 3 : 4 : 5-*pentafluoro*cyclo*hexane,* b. p. 92°/0·5 mm. (Found: C, 19·0; H, 0·2; F, 25·2. $C_6HCl_6F_5$ requires C, 18·9; H, 0·3; F, 24·9%). An infrared absorption peak at *ca.* 2950 cm.$^{-1}$ was characteristic of a C–H bond. There were no C=C bands.

Pentafluorobenzenesulphonic Acid.—A mixture of pentafluorobenzene (6·8 g.) and fuming sulphuric acid (168 g.; 20% of sulphur trioxide) was kept at 15° for 48 hr., then poured on crushed ice, and the aqueous solution was extracted continuously with ether for 24 hr. The extract was dried ($MgSO_4$), filtered, and evaporated to leave a dark brown oil which was dissolved in a small volume of water and neutralised with barium carbonate. The hot solution was filtered and cooled, to give crystalline barium pentafluorobenzenesulphonate (11·2 g.). Small portions of the crude acid were converted into the S-*benzylthiuronium salt,* m. p. 176—178° (from water) (Found: C, 40·3; H, 2·5. $C_{14}H_{11}O_3N_2S_2F_5$ requires C, 40·6; H, 2·7%), and the *anilinium salt,* m. p. 298—300° (decomp.) (from acetone–chloroform) (Found: C, 42·3; H, 2·5. $C_{12}H_8O_3NSF_5$ requires C, 42·2; H, 2·4%). The free acid was prepared by precipitation of the barium as the sulphate with an equivalent amount of dilute sulphuric acid and evaporation of the aqueous solution. It formed low-melting (*ca.* 30°), extremely hygroscopic crystals which appeared to decompose at room temperature during a week. Evaporation of the aqueous solution of the sodium salt was rendered difficult by production of a foam; this, however, quickly collapsed.

Bromopentafluorobenzene.—Pentafluorobenzene (11·2 g.) was added to a stirred mixture of bromine (6·8 c.c.), 20% oleum (30 c.c.), and anhydrous aluminium tribromide (0·6 g.) at room temperature. The mixture was stirred and heated at 60—65° for 4 hr., then poured on ice (*ca.* 200 g.), and the lower layer was separated, washed with aqueous sodium carbonate, sodium metabisulphite, and water. Distillation from phosphoric oxide gave bromopentafluorobenzene (13·3 g.), b. p. 134—135°, n_D^{19} 1·4505 (Found: C, 29·2; F, 38·9. Calc. for C_6BrF_5: C, 29·2; F, 38·5%), $\lambda_{max.}$ 2430 Å (ε 887; concn. 0·1022 g./l. in ethanol).

Pentafluoroiodobenzene.—Pentafluorobenzene (11·2 g.) was iodinated, by the procedure described above, with iodine (24 g.) and 20% oleum (40 c.c.), to give *pentafluoroiodobenzene* (13·9 g.), b. p. 161—163°, n_D^{19} 1·4970 (Found: C, 24·6; F, 32·1. C_6F_5I requires C, 24·5; F, 32·3%), $\lambda_{max.}$ 2600 Å (ε 1081; concn. 0·1044 g./l. in ethanol).

Decafluorodiphenyl.—Bromopentafluorobenzene (2·00 g.) and activated copper bronze (2·00 g.) were heated together in a sealed tube at 200° for 42 hr. The product was extracted with ether, and the extracts were evaporated, to leave a white solid which, recrystallised from benzene, gave *decafluorodiphenyl* (1·15 g.), m. p. 68—69° (Found: C, 42·8; F, 56·9. $C_{12}F_{10}$ requires C, 43·1; F, 56·9%), $\lambda_{max.}$ 2690 Å (ε 2446; concn. 0·086 g./l. in ethanol).

This fluorocarbon was mentioned [23] in a patent, but no properties or constants were given.

Pentafluorophenylmagnesium Bromide.—Bromopentafluorobenzene (2·47 g.) was added to magnesium turnings (0·30 g.) in dry ether (5 c.c.) and a small crystal of iodine added. The reaction started on slight warming and was completed by 2 hours' refluxing. Water (5 c.c.) was then added to the dark solution, followed by dilute sulphuric acid (5 c.c.). The ether layer was

---

[23] McBee, Lindgren, and Ligett, U.S.P. 2,488,216; *Chem. Abs.*, 1950, **44**, 1628.

separated, dried ($MgSO_4$), and shown to contain pentafluorobenzene by analytical gas chromatography. Most of the ether was removed by distillation through a 6″ vacuum-jacketed fractionating column packed with Dixon gauze spirals (1/16″ × 1/16″), and the residue was separated by preparative-scale gas chromatography (column A;[13] temp. 108°; N_2 flow-rate 9·4—9·6 l./hr.), to give pentafluorobenzene (0·9 g.), n_{D}^{18} 1·3931. This had an infrared absorption spectrum identical over the range 3000—700 cm.$^{-1}$ with that of an authentic specimen. *Deuteropentafluorobenzene* (0·75 g.), n_{D}^{20} 1·3906, was prepared also by this method, from bromopentafluorobenzene (2·50 g.) and magnesium (0·30 g.) in ether, followed by the addition of deuterium oxide (2·0 g.). This compound displayed an infrared C–D stretching frequency of 2315 cm.$^{-1}$, and a purity of *ca.* 98% was indicated by the strength of the pentafluorobenzene peak at 837 cm.$^{-1}$.

Pentafluorobenzoic Acid from the Grignard Reagent.—Pentafluoroiodobenzene (2·9 g.) was added to a suspension of magnesium turnings (0·24 g.) in dry ether (20 c.c.), followed by a crystal of iodine. The Grignard appeared to be slowly formed and reaction was completed by 5 hours' refluxing. Dry carbon dioxide was bubbled through the Grignard solution for 8 hr. To the mixture was added 50% v/v sulphuric acid (50 c.c.), and the whole was extracted continuously with ether for several days. The ether extract was then dried ($MgSO_4$), filtered, and evaporated to give pentafluorobenzoic acid (0·046 g.), m. p. 102° alone and mixed with a specimen prepared by the oxidation of pentafluorophenylethylene.

1-(*Pentafluorophenyl*)*ethanol.*—Bromopentafluorobenzene (7·5 g.) was added to magnesium turnings (0·9 g.) in dry ether (100 c.c.). The Grignard reaction was started by addition of a crystal of iodine and gentle heat; it was completed by 1—2 hours' refluxing. Dry acetaldehyde (3·0 c.c.) in dry ether (30 c.c.) was added to the Grignard solution at 0°. The mixture was stirred for 16 hr. at 15°, then decomposed with dilute hydrochloric acid (50 c.c.). The aqueous layer was extracted several times with ether. The combined ethereal extracts were dried ($MgSO_4$) and distilled through a vacuum-jacketed column (6″ × ½″) packed with Dixon spirals, and the residue distilled under slightly reduced pressure. Redistillation of the product gave 1-(*pentafluorophenyl*)*ethanol* (4·4 g.), b. p. 68—70°/30 mm., n_{D}^{18} 1·4402 (Found: C, 45·6; H, 2·6. $C_8H_5OF_5$ requires C, 45·3; H, 2·4%). The alcohol (0·2 g.) and 3 : 5-dinitrobenzoyl chloride (0·5 g.) were kept at 100° for 1 hr. in pyridine (2 c.c.). Water (5 c.c.) was added and the mixture poured into sodium hydrogen carbonate solution and extracted with ether. The ethereal extract was washed with dilute hydrochloric acid, dried ($MgSO_4$), filtered, and evaporated and the residue recrystallised from ethanol, to give 1-(*pentafluorophenyl*)*ethyl* 3 : 5-*dinitrobenzoate* (0·16 g.), m. p. 83° (Found: C, 44·0; H, 1·9. $C_{15}H_7O_6N_2F_5$ requires C, 44·3; H, 1·7%).

Pentafluorophenylethylene.—1-(Pentafluorophenyl)ethanol (3·5 g.), phosphoric oxide (1·5 g.) and quinol (0·1 g.) were heated together at 160° for 1 hr. The product was distilled out under slightly reduced pressure and redistilled, to give *pentafluorophenylethylene* (2·0 g.), b. p. 139—140°, n_{D}^{22} 1·4444 (Found: C, 49·4; H, 1·6. $C_8H_3F_5$ requires C, 49·5; H, 1·6%), $\lambda_{\mathrm{max.}}$ 2340 and 2410 Å (ε 8364 and 9105, respectively; concn. 0·0078 g./l. in ethanol).

1 : 2-*Dibromo*-1-*pentafluorophenylethane.*—Bromine (0·4 c.c.) in dry ether (25 c.c.) was added to a solution of pentafluorophenylethylene (1·4 g.) in dry ether (25 c.c.) at 0°. The mixture was kept at 15° for 15 hr. and the excess of bromine then destroyed by sodium metabisulphite solution. The ether layer was separated, dried ($MgSO_4$), filtered, and evaporated to leave a liquid product which was distilled twice from phosphoric oxide to give 1 : 2-*dibromo*-1-*pentafluorophenylethane* (1·52 g.), b. p. 75—80°/0·5 mm. (Found: C, 27·2; H, 0·8. $C_8H_3Br_2F_5$ requires C, 27·1; H, 0·9%).

Attempted Addition of Water to Pentafluorophenylethylene.—No reaction was observed between pentafluorophenylethylene (0·9 g.) and 50% v/v sulphuric acid (18 c.c.) after 10 hours' refluxing. When shaken at 100° for 24 hr. in a sealed tube these reactants gave a polymeric material (0·4 g.) The aqueous phase was extracted continuously with ether but the extract left no residue on evaporation.

Pentafluorobenzoic Acid from Pentafluorophenylethylene.—Pentafluorophenylethylene (1·2 g.), potassium permanganate (3·0 g.), and dry acetone (50 c.c.) were shaken together at 15° for several hr. and then kept at 15° for 15 hr. Water was added and the acetone removed at reduced pressure. Unchanged permanganate and manganese dioxide were destroyed with sulphur dioxide, concentrated sulphuric acid (15 c.c.) was added, and the solution was extracted continuously with ether for 15 hr. The extract was dried ($MgSO_4$), filtered, and evaporated to leave a solid which recrystallised from toluene–light petroleum (b. p. 100—120°) as square plates of pentafluorobenzoic acid (0·52 g.), m. p. 103—104°, $\lambda_{max.}$ 2650 Å (ε 761; concn. 0·011 g./l. in water) (Found: C, 39·9; H, 0·5. Calc. for $C_7HO_2F_5$: C, 39·6; H, 0·5%).

The acid (0·09 g.) was dissolved in water and neutralised with sodium hydroxide, and the pH adjusted to 4 with hydrochloric acid. An aqueous solution of *S*-benzylthiuronium chloride was added, and the precipitate recrystallised from water, to give S-*benzylthiuronium pentafluorobenzoate* (0·13 g.), m. p. 178° (Found: C, 47·8; H, 3·2. $C_{15}H_{11}O_2N_2SF_5$ requires C, 47·6; H, 2·9%). An m. p. of 106—107° has been given [20] for the acid.

Pentafluorobenzaldehyde.—(*a*) Bromopentafluorobenzene (5·0 g.) was added to magnesium turnings (0·8 g.) in dry ether (100 c.c.), the reaction being initiated by iodine and completed by 2 hours' refluxing. Ethyl orthoformate (3·5 g.) was then added and the mixture heated under reflux with stirring for 10 hr. The ether was removed and dilute sulphuric acid (30 c.c.) was added with stirring, followed by concentrated sulphuric acid (25 c.c.). After being heated under reflux for 3 hr. the mixture was distilled in steam, and a saturated aqueous solution of sodium metabisulphite added to the organic layer of the distillate to give crystalline pentafluorobenzaldehyde sodium bisulphite compound (1·9 g.).

(*b*) Bromopentafluorobenzene (4·5 g.) was added to magnesium turnings (0·7 g.) in dry, peroxide-free tetrahydrofuran (30 c.c.). The reaction was started by iodine and completed by 1 hour's refluxing. 3 : 4-Dihydro-6-methyl-3-*p*-tolylquinazoline methiodide (7 g.) was then added and the suspension refluxed with stirring for 9 hr. Dilute hydrochloric acid (50 c.c.) was added and the mixture was steam-distilled. The aqueous phase remaining was extracted continuously with ether for 24 hr., the extracts were dried ($MgSO_4$), filtered, and evaporated, and the residue was combined with the steam-distillate. Saturated aqueous sodium metabisulphite was added, to give a precipitate of pentafluorobenzaldehyde sodium bisulphite compound (1·8 g.).

The above yields of bisulphite compound could not be improved by changes in reaction time, temperature, or solvent.

(*c*) The bisulphite compound (3·8 g.) was heated under reflux for 1 hr. with 10% v/v sulphuric acid (30 c.c.). The solution was steam-distilled and the distillate extracted several times with ether. The combined extracts were dried ($MgSO_4$), filtered, and evaporated and the residue was distilled, to give pentafluorobenzaldehyde (1·4 g.), b. p. 168—170°, n_D^{17} 1·4505, $\lambda_{max.}$ 2350, 2430 Å (ε 17,330, 14,780, respectively; concn. 0·0068 g./l. in *n*-hexane) (Found: C, 42·0; H, 0·7. Calc. for C_7HOF_5: C, 42·9; H, 0·5%).

The aldehyde was added to an alcoholic solution of 2 : 4-dinitrophenylhydrazine and after ½ hr. water was added. A yellow precipitate was obtained which was recrystallised from ethanol, to give *pentafluorobenzaldehyde* 2 : 4-*dinitrophenylhydrazone*, m. p. 229—230° (Found: C, 41·7; H, 1·6. $C_{13}H_5O_4N_4F_5$ requires C, 41·5; H, 1·3%).

2 : 3 : 4 : 5 : 6-*Pentafluoromandelonitrile*.—Sodium cyanide (2·0 g.) in water (5 c.c.) was added, dropwise, to a stirred suspension of pentafluorobenzaldehyde sodium bisulphite compound (3·2 g.) and sodium metabisulphite (0·9 g.) in water (20 c.c.) at 0°. The suspension was stirred for 8 hr. at 0°, then extracted continuously with ether for 48 hr. The ether extract was dried ($MgSO_4$), filtered, and evaporated, to leave a brown syrupy residue which crystallised from benzene–light petroleum (b. p. 60—80°) to give 2 : 3 : 4 : 5 : 6-*pentafluoromandelonitrile* (0·09 g.), m. p. 53—54° (Found: C, 42·9; H, 1·1. $C_8H_2ONF_5$ requires C, 43·1; H, 0·9%).

Infrared Spectra.—These have been deposited in the Documentation of Molecular Spectra issued by Butterworths.

The authors thank Professor M. Stacey, F.R.S., for his interest and the D.S.I.R. for a maintenance award (to E. N.).

THE CHEMISTRY DEPARTMENT, THE UNIVERSITY,
EDGBASTON, BIRMINGHAM, 15.

[*Received, July* 30*th*, 1958.]