

**173. Aromatic Polyfluoro-compounds. Part VIII.<sup>1</sup> Pentafluorobenzaldehyde and Related Pentafluorophenyl Ketones and Carboxylic Acids.**

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Pentafluorophenylmagnesium halides with *N*-methylformanilide or ethyl formate gave pentafluorobenzaldehyde. This was converted into 2,3,4,5,6-pentafluoro-benzoic, -mandelic, -cinnamic, and -phenylpropionic acid. Reduction gave 2,3,4,5,6-pentafluorobenzyl alcohol which was converted into 2,3,4,5,6-pentafluorobenzyl chloride and bromide. These were prepared also from 2,3,4,5,6-pentafluorotoluene, made both from pentafluorophenylmagnesium iodide and dimethyl sulphate, and from hexafluorobenzene and methyl-lithium. The benzyl halides gave the cyanide and thence pentafluorophenyl-acetic acid, -ethanol, and -ethylamine. 2,3,4,5,6-Pentafluorotoluene gave 2,3,5,6-tetrafluoro-*p*-xylene on further reaction with methyl-lithium. From pentafluorophenylmagnesium halides, dimethyl(pentafluorophenyl)methanol (and thence 2,3,4,5,6-pentafluoro- $\alpha$ -methylstyrene), bis-pentafluorophenylmethanol (and thence decafluorobenzophenone),  $\alpha$ -pentafluorophenylbenzyl alcohol (and thence 2,3,4,5,6-pentafluorobenzophenone), 2,3,4,5,6-pentafluoroacetophenone, and octafluoroacetophenone were made. Haloform cleavage of the last gave pentafluorobenzene and trifluoroacetic acid.

PREVIOUS preparations<sup>2</sup> of pentafluorobenzaldehyde from pentafluorophenylmagnesium bromide and ethyl orthoformate or 3,4-dihydro-6-methyl-3-*p*-tolylquinazoline methiodide gave poor yields. Better routes have now been found in the reactions of this or the analogous iodo-Grignard reagent with an excess of ethyl formate<sup>3</sup> or of *N*-methylformanilide.<sup>4</sup> From the former, pentafluorobenzaldehyde was prepared in about 40% yield, bispentafluorophenylmethanol being formed as well (see below). By the latter route, yields of aldehyde were about 60%, and there was no evidence of amine formation as is the case with phenylmagnesium bromide.<sup>4</sup> Pentafluorobenzaldehyde, a low-melting solid, did not give a hydrate very readily but formed derivatives, *e.g.*, *N*-(2,3,4,5,6-pentafluorobenzylidene)aniline and 2,3,4,5,6-pentafluorobenzylidene diacetate in the normal way. The aldehyde did not appear to undergo atmospheric oxidation particularly rapidly, though, when oxygen was bubbled through it at 110°, pentafluorobenzoic acid<sup>2,5</sup> was formed. This oxidation was also done with sodium dichromate, the acid being characterised by conversion into its acid chloride and then into amides. The reaction of the aldehyde bisulphite compound with potassium cyanide has been repeated and ( $\pm$ )-2,3,4,5,6-pentafluoromandelic acid obtained by hydrolysis of the nitrile<sup>2</sup> *in situ*.

Application of the Perkin and the Knoevenagel reaction to pentafluorobenzaldehyde gave 2,3,4,5,6-pentafluorocinnamic acid. In the former process a lower temperature (130°) than that usually recommended gave a larger yield. The use of piperidine in the Knoevenagel reaction was not necessary. However, the initial product of the reaction, a viscous liquid, appeared to consist largely of a hydroxy-acid, which nevertheless gave the cinnamic acid on treatment with concentrated sulphuric acid. Presumably, the strongly electron-withdrawing pentafluorophenyl group stabilizes the hydroxyl group on C<sub>(2)</sub> of the side chain (cf. *p*-nitrobenzaldehyde and hydantoin,<sup>6</sup> and aliphatic fluoro-aldehydes<sup>7</sup>). The strong selective ultraviolet absorption suggests that the acid obtained is very largely

<sup>1</sup> Part VII, Brooke, Burdon, and Tatlow, preceding paper.

<sup>2</sup> Nield, Stephens, and Tatlow, *J.*, 1959, 166.

<sup>3</sup> Gattermann and Maffezzoli, *Ber.*, 1903, **36**, 4152.

<sup>4</sup> Smith, and Bayliss, *J. Org. Chem.*, 1941, **6**, 437.

<sup>5</sup> McBee and Rapkin, *J. Amer. Chem. Soc.*, 1951, **73**, 1366.

<sup>6</sup> Phillips, and Murphy, *J. Org. Chem.*, 1951, **16**, 954.

<sup>7</sup> McBee, Roberts, and Wilson, *J. Amer. Chem. Soc.*, 1957, **79**, 2323.

the *trans*-isomer.<sup>8</sup> This acid was hydrogenated smoothly over Raney nickel to give  $\beta$ -(2,3,4,5,6-pentafluorophenyl)propionic acid.

As expected, pentafluorobenzaldehyde did not undergo a Cannizzaro reaction with aqueous alkali. Instead, a haloform cleavage, typical of fluoro-carbonyl compounds, occurred to give pentafluorobenzene and formic acid.

Pentafluorobenzaldehyde was readily reduced by lithium aluminium hydride in diethyl ether at 20°, to 2,3,4,5,6-pentafluorobenzyl alcohol, which formed esters in the usual way. This alcohol, which has already been reported<sup>5</sup> in crude form as the reduction product of pentafluorobenzoic acid, was made also by treatment of 2,3,4,5,6-pentafluorobenzyl chloride (see below) with potassium carbonate solution. It was converted into 2,3,4,5,6-pentafluorobenzyl bromide with hydrogen bromide and into the corresponding chloride by phosphorus pentachloride. The derived *S*-(2,3,4,5,6-pentafluorobenzyl)thiourom chloride did not give a water-insoluble salt with a fluorinated dibasic acid.

Since these compounds were of potential use as intermediates, routes to them through pentafluorotoluene were investigated. Small yields of impure 2,3,4,5,6-pentafluorotoluene had been reported<sup>9</sup> from the reaction of hexafluorobenzene with methylmagnesium iodide. We first made it (yield 53%) from pentafluorophenylmagnesium iodide and dimethyl sulphate in ether. Better yields (70%) were obtained on reaction of hexafluorobenzene with methyl-lithium in diethyl ether, a process used also by Dr. Wall.<sup>10</sup> It was best to add the methyl-lithium solution to the hexafluorobenzene, but even so some 2,3,5,6-tetrafluoroxylene was formed. This compound was also obtained when 2,3,4,5,6-pentafluorotoluene was treated with methyl-lithium in ether. The orientation was established by bromination to the xylylene dibromide and oxidation of this to tetrafluoroterephthalic acid,<sup>11</sup> also made by hydrolysis of the side chains of perfluoro-*p*-xylene.<sup>12</sup> The nuclear magnetic resonance spectrum of the xylene supported this structure since four equivalent fluorine atoms were present. This is another example of nucleophilic replacement in the fluoro-aromatic field giving a *para*-product.

Bromination of 2,3,4,5,6-pentafluorotoluene to give the benzyl bromide was readily effected in ultraviolet light, and was more easily controlled than chlorination. This gave mainly 2,3,4,5,6-pentafluorobenzyl chloride but also some of the analogous benzylidene chloride and benzotrichloride. The last was hydrolysed with sulphuric acid to give pentafluorobenzoic acid. In aqueous-ethanolic solution the bromine and the chlorine in the pentafluorobenzyl halides were more susceptible than the nuclear fluorine atoms to replacement by cyanide ions (cf. sodium pentafluorobenzenesulphonate and sodium cyanide<sup>2</sup>). The amount of fluoride ion liberated, however, was much greater when ethanol was used as solvent. Accordingly, only sufficient ethanol was added to homogenise the system. The liquid so obtained, 2,3,4,5,6-pentafluorobenzyl cyanide, was hydrolysed by aqueous acid to give 2,3,4,5,6-pentafluorophenylacetic acid, which formed esters in the usual way. Partial hydrolysis of the nitrile gave the amide which was made also from the acid *via* the acid chloride. Reduction of ethyl 2,3,4,5,6-pentafluorophenylacetate with lithium aluminium hydride gave 2-(pentafluorophenyl)ethanol, whilst an analogous reduction of 2,3,4,5,6-pentafluorobenzyl cyanide gave pentafluorophenethylamine. The free amine decomposed on being kept, with liberation of fluoride ions, but its hydrochloride and benzoyl derivative were both stable.

With equimolar proportions of ethyl formate, or with pentafluorobenzaldehyde, pentafluorophenylmagnesium iodide gave bis(pentafluorophenyl)methanol. Oxidation of this was difficult, but by using chromium trioxide in acetic acid there was obtained decafluorobenzophenone, the first aromatic perfluoro-ketone to be synthesised. It did not form a

<sup>8</sup> Braude, *Ann. Reports*, 1945, **42**, 126.

<sup>9</sup> Pummer and Wall, *Science*, 1958, **127**, 643.

<sup>10</sup> Wall, personal communication.

<sup>11</sup> Gething, Patrick, and Tatlow, unpublished work.

<sup>12</sup> Gething, Patrick, Stacey, and Tatlow, *Nature*, 1959, **183**, 588.

hydrate readily and did not display normal carbonyl properties, for example, no oxime, semicarbazone, or 2,4-dinitrophenylhydrazone could be made. This is due presumably to steric factors (cf. 2,2',4,4'-tetramethylbenzophenone<sup>13</sup>). Pentafluorophenylmagnesium bromide and benzaldehyde afforded  $\alpha$ -pentafluorophenylbenzyl alcohol. Both this and bispentafluorophenylmethanol appeared to undergo esterification with 3,5-dinitrobenzoyl chloride in the normal manner. Presumably the presence of the pentafluorophenyl groups suppressed the tendency for alkyl-oxygen fission, a type of reaction observed<sup>14</sup> for diphenylmethanol and some of its substituted analogues. Oxidation of  $\alpha$ -pentafluorophenylbenzyl alcohol with chromium trioxide in acetic acid gave 2,3,4,5,6-pentafluorobenzophenone; this was prepared also from pentafluorophenylmagnesium bromide and benzoyl chloride. This ketone formed, rather sluggishly, a 2,4-dinitrophenylhydrazone. It appeared to form an oxime also, but this decomposed rapidly, presumably by an elimination involving an *o*-fluorine atom, to give a 1,2-benzisoxazole as occurs with the oxime of 2-bromo-5-nitroacetophenone.<sup>15</sup>

With lithium trifluoroacetate,<sup>16</sup> or in poorer yield with trifluoroacetic anhydride, pentafluorophenylmagnesium iodide gave octafluoroacetophenone. This perfluoro-ketone also gave no derivatives and on its treatment with aqueous potassium hydroxide a haloform reaction occurred to give pentafluorobenzene and trifluoroacetic acid. The preferential cleavage of the aryl-carbon bond indicates a greater stability for a pentafluorophenyl than for a trifluoromethyl anion, if the reaction involves an anionic intermediate.

Pentafluorophenylmagnesium bromide and acetone gave 2,3,4,5,6-pentafluoro- $\alpha$ -dimethylbenzyl alcohol, which was dehydrated easily to 2,3,4,5,6-pentafluoro- $\alpha$ -methylstyrene. Oxidation of this was unsuccessful, but the desired product, 2,3,4,5,6-pentafluoroacetophenone, was made from the Grignard reagent and acetyl chloride.

#### EXPERIMENTAL

*Pentafluoroiodobenzene.*—A mixture of penta- and hexa-fluorobenzene (84.0 g.), prepared by the defluorination of a mixture of 1*H*- and 2*H*-heptafluorocyclohexa-1,3-diene and heptafluorocyclohexa-1,4-diene,<sup>17</sup> was added to a stirred solution of iodine (60 g.) in sulphuric acid (20% SO<sub>3</sub>; 100 g.) at 65–70°. After being stirred for 4½ hr. the mixture was poured on ice and decolorised with sodium hydrogen sulphite solution, and the product fractionally distilled through a 6'' vacuum-jacketed column packed with glass helices to give: (i) hexafluorobenzene (29.5 g.), b. p. 80°, (ii) a mixture of fractions (i) and (iii) (8.5 g.), and (iii) pentafluoroiodobenzene (40 g.), b. p. 162–163°.

*Pentafluorobenzaldehyde.*—(a) *By use of ethyl formate.* Pentafluoroiodobenzene (5.0 g.) was added to magnesium turnings (0.5 g.) in diethyl ether (25 c.c.). After reaction had been started by gentle warming, spontaneous refluxing ensued and when this ceased heat was applied for 3 hr. The solution was then added to stirred ethyl formate (10.0 g.) at 0°. After 1 hr. 5*N*-hydrochloric acid (100 c.c.) was added and the ether layer separated, combined with the ether extracts (2 × 50 c.c.) of the aqueous phase, dried (MgSO<sub>4</sub>), filtered, and evaporated. The residual liquid was shaken with sodium hydrogen sulphite solution, and the resulting precipitate collected and decomposed by refluxing dilute sulphuric acid. The crude pentafluorobenzaldehyde so obtained was steam-distilled and the ether extract of the distillate dried, filtered, and evaporated. The liquid residue was distilled to give pentafluorobenzaldehyde (1.0 g.), m. p. 20°, b. p. 168–170°. The 2,4-dinitrophenylhydrazone<sup>2</sup> had m. p. and mixed m. p. 229–230°. During the steam-distillation a small amount of crystals, m. p. 74–75°, was deposited in the condenser; this was bispentafluorophenylmethanol (see below).

(b) *By use of N-methylformanilide.* Bromopentafluorobenzene (99.0 g.), dissolved in dry ether (50 c.c.), was added during 90 min. to magnesium turnings (10.6 g.) in dry ether (100 c.c.).

<sup>13</sup> Böeseken, *Rec. Trav. chim.*, 1907, **26**, 285; Cohen, *ibid.*, 1919, **38**, 119.

<sup>14</sup> Meisenheimer and Schmidt, *Annalen*, 1929, **475**, 177.

<sup>15</sup> Meisenheimer, Zimmermann, and Kummer, *Annalen*, 1925, **446**, 205.

<sup>16</sup> Rausch, Lovelace, and Coleman, *J. Org. Chem.*, 1956, **21**, 1328.

<sup>17</sup> Gething, Patrick, Tatlow, Banks, Barbour, and Tipping, *Nature*, 1959, **183**, 586.

Further dry ether (100 c.c.) was added during the reaction. The mixture was kept at 20—25° for 16 hr., then *N*-methylformanilide (109.0 g.) was added during 100 min. The mixture was refluxed for 4 hr., then an excess of 50% v/v sulphuric acid was added, the ether distilled off, and the residue steam-distilled. The steam-distillate was extracted with ether, and the dried (MgSO<sub>4</sub>) extract was filtered and evaporated. Further distillation under reduced pressure gave pentafluorobenzaldehyde (46.3 g.), b. p. 67—70°/15 mm., 168—170°/760 mm., m. p. 20° (Found: C, 42.4; H, 0.6. Calc. for C<sub>7</sub>H<sub>2</sub>F<sub>5</sub>O: C, 42.9; H, 0.5%). There were infrared bands at 1715 and 1515 cm.<sup>-1</sup> attributable to carbonyl and an aromatic ring vibration, respectively.

(c) *Derivatives*. The aldehyde (1.43 g.) and aniline (0.74 g.) formed a paste. After 10 minutes' heating at 100° the solid product was collected and recrystallised from ethanol, to give *N*-(2,3,4,5,6-pentafluorobenzylidene)aniline (1.45 g.), m. p. 117° (Found: C, 57.7; H, 2.4; F, 34.6. C<sub>13</sub>H<sub>6</sub>F<sub>5</sub>N requires C, 57.6; H, 2.2; F, 35.0%).

Pentafluorobenzaldehyde (0.2 g.), acetic anhydride (3 c.c.), and concentrated sulphuric acid (0.1 c.c.) were kept together at 15° for 15 min. and then poured into water to give an oil which solidified (0.25 g.; m. p. 64—65°). Recrystallisation from aqueous ethanol gave 2,3,4,5,6-pentafluorobenzylidene diacetate (0.19 g.), m. p. 64—65° (Found: C, 44.4; H, 2.3. C<sub>11</sub>H<sub>2</sub>F<sub>5</sub>O<sub>4</sub> requires C, 44.5; H, 2.0%).

Pentafluorobenzaldehyde (2.70 g.) was shaken with an excess of saturated sodium metabisulphite solution, and the precipitated bisulphite compound (4.07 g.) collected and heated with 10% v/v sulphuric acid (40 c.c.) for 20 min. The cold solution was then extracted with ether (2 × 50 c.c.), the dried (MgSO<sub>4</sub>) ether extract evaporated, and the liquid residue distilled to give pentafluorobenzaldehyde (1.42 g.), m. p. 20°, b. p. 168—170°.

*Pentafluorobenzoic Acid* (with L. J. BELF).—(a) A fine stream of oxygen was bubbled through pentafluorobenzaldehyde (30.6 g.) at 110° for 20 hr. Ether was added and the ethereal solution washed with an excess of sodium carbonate solution. Evaporation of the ethereal solution gave pentafluorobenzaldehyde (5.9 g.). The aqueous layer was acidified with hydrochloric acid and ether-extracted. Evaporation of the ether afforded pentafluorobenzoic acid<sup>2</sup> (21.1 g.), m. p. and mixed m. p. 99°.

(b) A mixture of pentafluorobenzaldehyde (25.3 g.), concentrated sulphuric acid (20.5 g.), sodium dichromate (15.0 g.), and water (15 c.c.) was heated at 100° for 2½ hr., then extracted with ether, and the extract was shaken with an excess of 10% sodium carbonate solution. Acidification of the aqueous layer with hydrochloric acid and extraction with ether afforded pentafluorobenzoic acid (19.8 g.), m. p. and mixed m. p. 103—104°.

2,3,4,5,6-Pentafluorobenzamide.—A mixture of 2,3,4,5,6-pentafluorobenzoic acid (8.4 g.) and phosphorus pentachloride (9.3 g.) was heated at 100° for 1 hr., then distilled to give 2,3,4,5,6-pentafluorobenzoyl chloride (5.5 g.), b. p. 60—67°/23 mm. The acid chloride (5.5 g.) in dry ether (50 c.c.), cooled in ice, was treated with an excess of gaseous ammonia. Water was added, and the ether layer, combined with ether-extracts of the aqueous phase, was washed with water, dried (MgSO<sub>4</sub>), filtered, and evaporated to give 2,3,4,5,6-pentafluorobenzamide (4.7 g.), m. p. 150° (from benzene) (Found: C, 39.7; H, 0.9. C<sub>7</sub>H<sub>2</sub>F<sub>5</sub>ON requires C, 39.8; H, 0.95%).

2,3,4,5,6-Pentafluorobenzoyl chloride (3.4 g.), dissolved in dry ether (50 c.c.), was cooled in ice and treated with diethylamine (2.1 g.). Water (20 c.c.) was added, and the ether layer was combined with ether extracts of the aqueous phase, washed with water, dried (MgSO<sub>4</sub>), filtered, and distilled to give *NN*-diethyl-2,3,4,5,6-pentafluorobenzamide (3.4 g.), b. p. 128—135°/14 mm. (Found: C, 48.7; H, 3.7; F, 35.4. C<sub>11</sub>H<sub>10</sub>F<sub>5</sub>NO requires C, 49.4; H, 3.8; F, 35.55%).

(±)-2,3,4,5,6-Pentafluoromandelic Acid.—A cooled solution of potassium cyanide (1.0 g.) in water (5 c.c.) was added slowly with stirring to pentafluorobenzaldehyde sodium bisulphite compound (3.4 g.) in water (25 c.c.). After 8 hours' stirring at 15° a yellow precipitate separated and this was extracted with ether. The dried (MgSO<sub>4</sub>) extract was evaporated to leave a sticky colourless gum which was kept at 100° with concentrated hydrochloric acid (50 c.c.) for 4 hr. The resulting clear solution was diluted with water and extracted continuously with ether. The ether layer was dried (MgSO<sub>4</sub>), decolorised with charcoal, filtered, and evaporated to leave a white solid (1.2 g.), m. p. 141—142°, which was recrystallised twice from benzene and sublimed (90°/12 mm.) to give (±)-2,3,4,5,6-pentafluoromandelic acid (0.6 g.), m. p. 141—142° (Found: C, 39.8; H, 1.1. C<sub>8</sub>H<sub>2</sub>F<sub>5</sub>O<sub>3</sub> requires C, 39.7; H, 1.2%),  $\nu_{\max}$  3500 and 1750 (CO<sub>2</sub>H) and 1525 and 1515 cm.<sup>-1</sup> (fluorinated benzene ring). The acid (0.2 g.) and *S*-benzylthiouronium chloride gave, after two recrystallisations from water, *S*-benzylthiouronium (±)-pentafluoromandelate (0.1 g.), m. p. 168—169° (Found: C, 46.9; H, 2.9. C<sub>16</sub>H<sub>13</sub>F<sub>5</sub>N<sub>2</sub>O<sub>3</sub>S requires C, 47.0; H, 3.2%).

**2,3,4,5,6-Pentafluorocinnamic Acid.**—Pentafluorobenzaldehyde (5.0 g.), acetic anhydride (4.2 g.), and fused potassium acetate (1.5 g.) were kept at 130° for 3 hr., then poured into water and the solution was made alkaline with sodium carbonate. Any unchanged aldehyde was removed by steam-distillation, and the residual liquid filtered and acidified with 16*N*-hydrochloric acid. The precipitate was filtered off, washed with water, dried (2.2 g.), and recrystallised from ethanol–light petroleum (b. p. 80–100°) to give 2,3,4,5,6-*pentafluorocinnamic acid*, m. p. 152.5° (Found: C, 45.3; H, 1.2.  $C_9H_3F_5O_2$  requires C, 45.4; H, 1.3%),  $\lambda_{max}$  (in EtOH) 2570 Å ( $\epsilon$  42,000),  $\nu_{max}$  3100–2500 and 1900 (CO<sub>2</sub>H) and 1510 and 1530 cm.<sup>-1</sup> (aromatic ring). The acid (0.1 g.) and *S*-benzylthiuronium chloride gave *S*-benzylthiuronium 2,3,4,5,6-*pentafluorocinnamate* (0.07 g.), m. p. 175–176° (Found: C, 50.5; H, 3.5.  $C_{17}H_{13}F_5N_2O_2S$  requires C, 50.5; H, 3.2%).

A solution of pentafluorobenzaldehyde (4.5 g.) and malonic acid (7.2 g.) in dry pyridine (10 c.c.) was kept at 100° for 90 min., then poured into 16*N*-hydrochloric acid at 0° and the solution extracted continuously with ether. The residual gum from the dried ether extract was kept in concentrated sulphuric acid (10 c.c.) at 100° for 10 min. and then poured on ice. The precipitate was filtered off and taken up in 5% sodium carbonate solution, and the solution was filtered and acidified to give 2,3,4,5,6-*pentafluorocinnamic acid* (2.4 g.), m. p. and mixed m. p. 152°.

Addition of small amounts of piperidine to the reaction mixture gave no apparent improvement. The acid (0.5 g.), neutralised with 5% sodium hydroxide solution and treated with a solution of 4-bromophenacyl bromide (0.6 g.) in ethanol at 100° for 1 hr., gave 4-*bromophenacyl* 2,3,4,5,6-*pentafluorocinnamate* (0.4 g.; from aqueous ethanol), m. p. 126.5° (Found: C, 46.7; H, 1.9.  $C_{17}H_8BrF_5O_3$  requires C, 46.9; H, 1.85%).

$\beta$ -(2,3,4,5,6-*Pentafluorophenyl*)*propionic Acid.*—2,3,4,5,6-*Pentafluorocinnamic acid* (2.2 g.) in absolute ethanol (25 c.c.), and Raney nickel (approx. 0.1 g.), were shaken in hydrogen at 20–25°/1 atm. The calculated amount was absorbed in 3 hr. The solution was filtered and the filtrate evaporated to give  $\beta$ -(2,3,4,5,6-*pentafluorophenyl*)*propionic acid* (1.3 g.; from water), m. p. 95–96° (Found: C, 44.8; H, 2.1.  $C_9H_5F_5O_2$  requires C, 45.0; H, 2.1%).

Treated as described above, the acid (0.7 g.) afforded 4-*bromophenacyl*  $\beta$ -(2,3,4,5,6-*pentafluorophenyl*)*propionate* (0.6 g.; from aqueous ethanol), m. p. 111° (Found: C, 46.9; H, 2.4; F, 21.9.  $C_{17}H_{10}BrF_5O$  requires C, 46.7; H, 2.3; F, 21.7%).

**Reaction of Pentafluorobenzaldehyde with Aqueous Potassium Hydroxide.**—Pentafluorobenzaldehyde (1.0 g.), potassium hydroxide (0.5 g.), and water (1 c.c.) were kept at 15° for 16 hr., then ether (5 c.c.) was added followed by water (5 c.c.). The aqueous layer was separated and extracted with ether. The ether was dried (MgSO<sub>4</sub>) and shown by gas chromatography to contain pentafluorobenzene (0.4 g.) which was separated and found to have a correct infrared spectrum. The pH of the aqueous phase was adjusted to 4, and *S*-benzylthiuronium chloride added to give *S*-benzylthiuronium formate, m. p. and mixed m. p. 149–150°.

**2,3,4,5,6-Pentafluorobenzyl Alcohol.**—(a) A solution of pentafluorobenzaldehyde (10.3 g.) in dry ether (20 c.c.) was slowly added to a stirred suspension of lithium aluminium hydride (0.75 g.) in dry ether (50 c.c.) in a nitrogen atmosphere. After 90 min. at 20°, water (10 c.c.) was added slowly followed by hydrochloric acid. The ether layer was separated, the aqueous phase was extracted with ether, the combined extracts were dried (MgSO<sub>4</sub>), filtered, and evaporated, and the residual liquid was distilled *in vacuo* to give 2,3,4,5,6-*pentafluorobenzyl alcohol* (9.7 g.), b. p. 114–115°/60 mm., 180–182°/1 atm., m. p. 30–32° (Found: C, 42.8; H, 1.8. Calc. for  $C_7H_5F_5O$ : C, 42.5; H, 1.6%). The alcohol (0.2 g.) and *p*-nitrobenzoyl chloride (0.2 g.) were kept together at 100° for 1 hr. and then poured into sodium hydrogen carbonate solution. The crystalline precipitate was washed with dilute hydrochloric acid and water and recrystallised from ethanol, to give 2,3,4,5,6-*pentafluorobenzyl p*-nitrobenzoate (0.3 g.), m. p. 122–123° (Found: C, 48.4; H, 1.9. Calc. for  $C_{14}H_6F_5NO_4$ : C, 48.4; H, 1.7%). A m. p. of 114–116° has been given<sup>5</sup> for this ester.

(b) 2,3,4,5,6-*Pentafluorobenzyl chloride* (3.0 g.) was boiled with potassium carbonate (5.0 g.) and water (25 c.c.) for 17 hr. The organic layer was extracted with ether, dried (MgSO<sub>4</sub>), filtered, and distilled to give 2,3,4,5,6-*pentafluorobenzyl alcohol* (1.4 g.), b. p. 110–116°/52 mm. The alcohol (0.6 g.) in the usual way gave 2,3,4,5,6-*pentafluorobenzyl 3,5-dinitrobenzoate* (0.4 g.; from aqueous ethanol), m. p. 121.5° (Found: C, 42.9; H, 1.4; F, 24.2.  $C_{14}H_5F_5N_2O_8$  requires C, 42.9; H, 1.3; F, 24.2%).

**2,3,4,5,6-Pentafluorobenzyl Bromide and Chloride.**—2,3,4,5,6-*Pentafluorobenzyl alcohol*

(1.9 g.), 48% aqueous hydrogen bromide (6 g.) and concentrated sulphuric acid (2 c.c.) were kept together at 70° for 2 hr., then poured into water (20 c.c.) and extracted with ether. The dried (MgSO<sub>4</sub>) ether extract was filtered and evaporated and the residual liquid distilled to give the extremely lachrymatory 2,3,4,5,6-pentafluorobenzyl bromide (0.9 g.), b. p. 174—175° (Found: C, 31.5; H, 0.8. C<sub>7</sub>H<sub>2</sub>BrF<sub>5</sub> requires C, 32.2; H, 0.8%).

Refluxing of the alcohol (1.5 g.) with phosphorus pentachloride (2 g.) in carbon tetrachloride (5 c.c.) for 2 hr. gave the slightly lachrymatory 2,3,4,5,6-pentafluorobenzyl chloride (1.1 g.), b. p. 160—163°. The chloride (0.5 g.) and thiourea (0.2 g.) were kept together in refluxing ethanol (10 c.c.) for 30 min. Removal of the solvent gave crystals which recrystallised from 10% hydrochloric acid gave S-(2,3,4,5,6-pentafluorobenzyl)thiourenium chloride (0.4 g.), m. p. 200—201° (Found: C, 32.6; H, 2.2. C<sub>8</sub>H<sub>6</sub>ClF<sub>5</sub>N<sub>2</sub>S requires C, 32.8; H, 2.1%).

**2,3,4,5,6-Pentafluorotoluene.**—(a) *From the Grignard reagent.* To a stirred ethereal solution of pentafluorophenylmagnesium iodide at 0°, prepared in the usual way from pentafluoriodobenzene (10.0 g.), was added dimethyl sulphate (8.6 g.) in dry ether (10 c.c.). When the initial reaction was complete the mixture was stirred at the b. p. for 16 hr. 5N-Hydrochloric acid (100 c.c.) was then added and the aqueous phase extracted with ether. The combined extracts were dried (MgSO<sub>4</sub>) and most of the ether was distilled through a 6" vacuum-jacketed column packed with glass helices. The residual liquid was separated by gas chromatography (column 488 × 7.5 cm.; packing dinonyl phthalate-kieselguhr 1 : 2; temp. 100°; N<sub>2</sub> flow-rate 52 l./hr.) to give ether, pentafluorobenzene (0.7 g.) (correct infrared spectrum), and 2,3,4,5,6-pentafluorotoluene (3.3 g.), b. p. 115—118° (Found: C, 46.4; H, 1.7. C<sub>7</sub>H<sub>3</sub>F<sub>5</sub> requires C, 46.2; H, 1.7%), which had infrared bands at 2950, 2900, 1450, and 1380 (Me), and 1520 cm.<sup>-1</sup> (aromatic ring).

(b) *From hexafluorobenzene.* An ethereal solution of methyl-lithium (70 c.c., containing 2.1 g. of methyl-lithium) was added to a stirred solution of hexafluorobenzene (20 g.) in dry ether (20 c.c.) at a rate sufficient to maintain gentle refluxing. Stirring was maintained for ½ hr. after the addition was complete and water (100 c.c.) then added. The ether layer was dried (MgSO<sub>4</sub>) and filtered, most of the ether distilled through a 6" column, and the residual liquid (17 g.) separated by gas chromatography (column 488 × 7.5 cm.; packing silicone gum-kieselguhr 1 : 3; temp. 100°; N<sub>2</sub> flow-rate 45 l./hr.) to give ether and hexafluorobenzene (1.2 g.), 2,3,4,5,6-pentafluorotoluene (13.8 g.) (both displaying correct infrared spectra), and a fraction (2.5 g.) which was distilled to give 2,3,5,6-tetrafluoroxylene (2.0 g.), b. p. 143—144° (Found: C, 53.7; H, 3.5. C<sub>8</sub>H<sub>6</sub>F<sub>4</sub> requires C, 53.9; H, 3.4%). The nuclear magnetic resonance spectrum indicated the presence of four equivalent fluorine atoms; there were infrared bands at 2980, 2940, 2860, and 1380 (Me) and 1495 cm.<sup>-1</sup> (aromatic ring).

Irradiation of the tetrafluoro-*p*-xylene (1.5 g.) and bromine (1.5 g.) with ultraviolet light at 15° for 16 hr. gave 1,4-bisbromomethyl-2,3,5,6-tetrafluoroxylene (2.3 g.), m. p. 68—70° (Found: C, 28.8; H, 1.0. C<sub>8</sub>H<sub>4</sub>Br<sub>2</sub>F<sub>4</sub> requires C, 28.6; H, 1.2%).

Oxidation of the tetrafluoroxylene dibromide (2.0 g.) with potassium permanganate (2 g.) in the presence of sodium carbonate (2 g.) in water (50 c.c.) gave tetrafluoroterephthalic acid (0.45 g.), m. p. 283—284° alone and in admixture with an authentic specimen.<sup>11</sup>

**2,3,5,6-Tetrafluoroxylene from 2,3,4,5,6-Pentafluorotoluene.**—An ethereal solution of methyl-lithium (45 c.c.; containing 1.3 g. of methyl-lithium) was slowly added to a stirred solution of 2,3,4,5,6-pentafluorotoluene (3 g.) in ether (10 c.c.) at a rate sufficient to maintain gentle refluxing. The reaction was completed by refluxing for a further 3 hr., and the aforementioned isolation procedure gave 2,3,5,6-tetrafluoroxylene (2.5 g.) with a correct infrared spectrum.

**Bromination of 2,3,4,5,6-Pentafluorotoluene.**—This compound (9.0 g.), mixed with bromine (8.1 g.), was irradiated with ultraviolet light at 15° for 12 hr., after which most of the bromine had reacted. The lachrymatory liquid residue was distilled from phosphorus pentoxide to give 2,3,4,5,6-pentafluorobenzyl bromide (12.0 g.), b. p. 174—175°; the infrared spectrum was identical with that of the product from the reaction of pentafluorobenzyl alcohol and hydrogen bromide [bands at 3000 (methylene) and 1510 cm.<sup>-1</sup> (aromatic ring)].

**Chlorination of 2,3,4,5,6-Pentafluorotoluene.**—(a) A stream of chlorine was passed into boiling 2,3,4,5,6-pentafluorotoluene (50.6 g.) for 12 hr. in a silica reaction vessel irradiated with ultraviolet light. Fractional distillation of the product (57.8 g.) gave 2,3,4,5,6-pentafluorobenzyl chloride (29.3 g.), b. p. 80°/47 mm., *n*<sub>D</sub><sup>20</sup> 1.4435 (Found: C, 38.7; H, 1.1. C<sub>7</sub>H<sub>2</sub>ClF<sub>5</sub> requires C, 38.8; H, 0.9%), together with higher-boiling material (24.8 g.).

(b) From several experiments the last fractions were combined and fractionally distilled to

give 2,3,4,5,6-pentafluorobenzylidene dichloride, b. p. 84°/32 mm. This compound was prepared more conveniently by heating 2,3,4,5,6-pentafluorobenzaldehyde (10.6 g.) with phosphorus pentachloride (13.6 g.) at 100° for 30 min. The product was poured on ice and the organic layer dissolved in ether (50 c.c.). The ethereal solution was shaken with sodium metabisulphite solution, sodium carbonate solution, and water, and dried (MgSO<sub>4</sub>). Distillation afforded 2,3,4,5,6-pentafluorobenzylidene dichloride (10.8 g.), b. p. 82—84°/30 mm. (Found: C, 33.4; H, 0.5. C<sub>7</sub>HCl<sub>2</sub>F<sub>5</sub> requires C, 33.5; H, 0.4%).

(c) Prolonged action of chlorine on high-boiling products (23.3 g.) arising under (a) gave 2,3,4,5,6-pentafluorobenzotrichloride (12.3 g.), b. p. 109—116°/48 mm. (Found: C, 29.8. C<sub>7</sub>Cl<sub>3</sub>F<sub>5</sub> requires C, 29.5%), together with an unidentified solid product (1.4 g.), m. p. 165°, which may have been 1,1,2,2-tetrachloro-1,2-bis(pentafluorophenylethane).

*Hydrolysis of 2,3,4,5,6-Pentafluorobenzotrichloride.*—2,3,4,5,6-Pentafluorobenzotrichloride (19.1 g.) was stirred and heated at 100—110° with concentrated sulphuric acid (17 c.c.), which caused vigorous evolution of hydrogen chloride. After 2 hr. the mixture was cooled and poured on ice, and the resulting aqueous solution extracted with ether. The extracts were shaken with 5% sodium hydroxide solution (150 c.c.), and the aqueous layer was acidified with sulphuric acid and extracted with ether. Evaporation afforded pentafluorobenzoic acid (13.7 g.), m. p. and mixed m. p. 100—101.5°.

*2,3,4,5,6-Pentafluorobenzyl Cyanide.*—A mixture of 2,3,4,5,6-pentafluorobenzyl chloride (11.9 g.), potassium cyanide (4.5 g.), water (15 c.c.), and ethanol (35 c.c.) was stirred at 75° for 60 min. and then poured into water (250 c.c.). The organic layer and ether extracts of the aqueous phase were combined, washed with water, dried (CaCl<sub>2</sub>), filtered, and distilled to give 2,3,4,5,6-pentafluorobenzyl cyanide (9.0 g.), b. p. 107—111°/17 mm. (Found: C, 46.0; H, 0.9. C<sub>8</sub>H<sub>2</sub>F<sub>5</sub>N requires C, 46.4; H, 1.0%),  $\nu_{\max}$ . 2930 and 2900 (methylene), 2240 (cyanide), and 1515 cm.<sup>-1</sup> (aromatic ring). The same product (yield 52%) was obtained in a similar reaction with pentafluorobenzyl bromide. In both cases the aqueous phases contained fluoride ion.

*2,3,4,5,6-Pentafluorophenylacetic Acid.*—2,3,4,5,6-Pentafluorobenzyl cyanide (22.0 g.), concentrated sulphuric acid (22 c.c.), acetic acid (22 c.c.), and water (22 c.c.) were refluxed for 45 min., then poured into water. The precipitate was filtered off and taken up in sodium carbonate solution which was filtered. Acidification of the filtrate gave 2,3,4,5,6-pentafluorophenylacetic acid [21.0 g.; from light petroleum (b. p. 80—100°)], m. p. 109° (Found: C, 42.8; H, 1.4. C<sub>8</sub>H<sub>2</sub>F<sub>5</sub>O<sub>2</sub> requires C, 42.5; H, 1.3%),  $\nu_{\max}$ . 3200—2500 and 1720 (CO<sub>2</sub>H), and 1520 and 1530 cm.<sup>-1</sup> (aromatic ring).

2,3,4,5,6-Pentafluorophenylacetic acid (0.6 g.) with 4-bromophenacyl bromide gave 4-bromophenacyl 2,3,4,5,6-pentafluorophenyl acetate (0.7 g.; from aqueous ethanol), m. p. 104.5° (Found: C, 45.5; H, 2.0. C<sub>16</sub>H<sub>8</sub>BrF<sub>5</sub>O<sub>3</sub> requires C, 45.4; H, 1.9%).

2,3,4,5,6-Pentafluorophenylacetic acid (11.0 g.), absolute ethanol (4.5 g.), and fluorosulphonic acid (0.5 c.c.) were boiled together for 30 min., then cooled and poured into ice-water. The organic layer and an ether extract of the aqueous layer were washed with 5% sodium hydrogen carbonate solution (25 c.c.), dried (CaCl<sub>2</sub>), filtered, and distilled, finally under reduced pressure, to give ethyl 2,3,4,5,6-pentafluorophenylacetate (10.4 g.), b. p. 95—96°/14 mm. (Found: C, 47.1; H, 2.8; F, 36.9. C<sub>10</sub>H<sub>7</sub>F<sub>5</sub>O<sub>2</sub> requires C, 47.25; H, 2.8; F, 37.4%).

*2,3,4,5,6-Pentafluorophenylacetamide.*—(a) A mixture of 2,3,4,5,6-pentafluorobenzyl cyanide (5.3 g.) and concentrated sulphuric acid (10 c.c.) was stirred and heated at 100° for 20 min., then poured on ice. The precipitate was washed with 5% sodium carbonate solution and water and recrystallised from ethanol-benzene to give 2,3,4,5,6-pentafluorophenylacetamide (2.5 g.), m. p. 187—188° (Found: C, 42.8; H, 2.2; F, 41.9. C<sub>8</sub>H<sub>4</sub>F<sub>5</sub>NO requires C, 42.7; H, 1.8; F, 42.2%).

(b) 2,3,4,5,6-Pentafluorophenylacetic acid (5.7 g.) was added to phosphorus pentachloride (5.5 g.). The reaction, initially vigorous, was completed by heating the mixture at 100° for 30 min. Distillation gave somewhat impure 2,3,4,5,6-pentafluorophenylacetyl chloride (5.1 g.), b. p. 90—95°/29 mm. The acid chloride (1.2 g.), dissolved in dry ether (30 c.c.), was cooled in ice and treated with an excess of gaseous ammonia. Then water (20 c.c.) and ether (20 c.c.) were added and, after shaking, the ether layer was separated and combined with ether extracts of the aqueous phase. The dried (MgSO<sub>4</sub>) ether solution was filtered and evaporated to give 2,3,4,5,6-pentafluorophenylacetamide (1.0 g.), m. p. and mixed m. p. 187°.

The acid chloride (8.2 g.) and dry ether (100 c.c.) were cooled in ice and stirred while a solution of diethylamine (5.3 g.) in dry ether (5 c.c.) was added slowly. The mixture was

warmed to 20—25°, then water (20 c.c.) was added to dissolve the precipitate. The ether layer, combined with an ether extract of the aqueous layer, was washed with dilute hydrochloric acid (20 c.c.), dried (MgSO<sub>4</sub>), filtered, and distilled to give NN-diethyl-2,3,4,5,6-pentafluorophenylacetamide (6·3 g.), b. p. 126—128°/2 mm. (Found: C, 51·0; H, 4·4; F, 33·8. C<sub>12</sub>H<sub>12</sub>F<sub>5</sub>ON requires C, 51·25; H, 4·3; F, 33·8%).

2-(2,3,4,5,6-Pentafluorophenyl)ethanol.—A solution of ethyl 2,3,4,5,6-pentafluorophenyl acetate (9·8 g.) in dry ether (10 c.c.) was added during 30 min. to a stirred suspension of lithium aluminium hydride (1·75 g.) in dry ether (70 c.c.) under dry nitrogen. Stirring was continued for 3½ hr., then the mixture was cooled in ice while water (25 c.c.) and concentrated sulphuric acid (5 c.c.) were added. The ether layer and extracts were dried (MgSO<sub>4</sub>), filtered, and distilled, finally under reduced pressure, to give 2-(2,3,4,5,6-pentafluorophenyl)ethanol (7·7 g.), b. p. 104°/16 mm.

The alcohol (0·8 g.) and 3,5-dinitrobenzoyl chloride (0·8 g.) afforded 2-(2,3,4,5,6-pentafluorophenyl)ethyl 3,5-dinitrobenzoate (0·7 g.; from aqueous ethanol), m. p. 94—95° (Found: C, 44·8; H, 1·9; F, 22·8. C<sub>15</sub>H<sub>7</sub>F<sub>5</sub>O<sub>6</sub>N<sub>2</sub> requires C, 44·4; H, 1·7; F, 23·4%).

2,3,4,5,6-Pentafluorophenethylamine.—2,3,4,5,6-Pentafluorobenzyl cyanide (13·4 g.) in dry ether (20 c.c.) was added during 30 min. to a stirred suspension of lithium aluminium hydride (2·5 g.) in dry ether (100 c.c.) under dry nitrogen. The mixture was stirred for 1 hr. at 20° then for 1 hr. at 30—40°. Water (15 c.c.) and 20% aqueous sodium hydroxide (4 c.c.) were added, and the ether layer was separated, dried (NaOH), filtered, and evaporated. The residue was distilled to give a light brown liquid (4·4 g.), b. p. 80—90°/20 mm., with a strong ammoniacal odour. On being kept, it became red and partly solid and was then only partially soluble in ether. The ether-insoluble part was soluble in cold water and this solution gave a positive test for fluoride ion. The clear distillate (2·5 g.) in dry ether (40 c.c.) was cooled in ice and treated with an excess of hydrogen chloride. The precipitate (2·4 g.) was recrystallised from ethanol to give 2,3,4,5,6-pentafluorophenethylamine hydrochloride (1·9 g.), m. p. 281° (Found: C, 39·0; H, 3·0; F, 38·9; Cl, 14·3. C<sub>8</sub>H<sub>7</sub>ClF<sub>5</sub>N requires C, 38·8; H, 2·85; F, 38·4; Cl, 14·3%).

The distilled amine (1·0 g.) was shaken with 10% sodium hydroxide solution (3·5 c.c.) and benzoyl chloride (0·6 c.c.). The precipitated solid was washed with water and recrystallised from aqueous ethanol to give N-benzoyl-2,3,4,5,6-pentafluorophenethylamine (0·7 g.), m. p. 161—162° (Found: C, 57·3; H, 3·3; F, 30·4. C<sub>15</sub>H<sub>10</sub>F<sub>5</sub>NO requires C, 57·15; H, 3·2; F, 30·1%).

Bispentafluorophenylmethanol.—(a) Pentafluorophenylmagnesium iodide, from pentafluoriodobenzene (5 g.), was treated with ethyl formate (1·8 g., 1 mol.) in ether (10 c.c.) in the manner described previously. Two recrystallisations of the product from perfluoro-1,4-dimethylcyclohexane gave bispentafluorophenylmethanol (1·2 g.), m. p. 79—80° (Found: C, 42·9; H, 0·5; F, 52·4. C<sub>13</sub>H<sub>2</sub>F<sub>10</sub>O requires C, 42·9; H, 0·5; F, 52·2%),  $\nu_{\max}$ . 3400 (OH) and 1525 cm.<sup>-1</sup> (aromatic ring).

(b) Pentafluorophenylmagnesium bromide was prepared from bromopentafluorobenzene (10·0 g.) and magnesium (1·1 g.), in dry ether (30 c.c.). After being refluxed for 3 hr., the solution was treated with pentafluorobenzaldehyde (7·6 g.) in dry ether (9 c.c.). Refluxing for 1 hr., followed by isolation as above, afforded a solid which was distilled under reduced pressure to give bispentafluorophenylmethanol (11·6 g.), b. p. 108—110°/1·5 mm., m. p. 79—80°. This alcohol (0·2 g.) and 3,5-dinitrobenzoyl chloride (0·15 g.) were refluxed together in benzene (5 c.c.) for 4 hr.; isolation as usual gave bispentafluorophenylmethyl 3,5-dinitrobenzoate (0·2 g.; from ethanol), m. p. 186—187° (Found: C, 43·4; H, 0·6. C<sub>20</sub>H<sub>4</sub>F<sub>10</sub>N<sub>2</sub>O<sub>6</sub> requires C, 43·0; H, 0·7%).

Decafluorobenzophenone.—Bispentafluorophenylmethanol (0·5 g.), chromium trioxide (2 g.) and glacial acetic acid (10 c.c.) were refluxed together for 15 min. and then poured into water. A white powder (0·3 g.), m. p. 91—92°, was obtained which was recrystallised from perfluoro-1,4-dimethylcyclohexane to give decafluorobenzophenone (0·1 g.), m. p. 91—92° (Found: C, 43·4. C<sub>13</sub>F<sub>10</sub>O requires C, 43·1%),  $\lambda_{\max}$ . (in EtOH) 2500 Å ( $\epsilon$  13,000),  $\nu_{\max}$ . 1720 (C=O) and 1510 cm.<sup>-1</sup> (aromatic ring). The ketone was recovered after being refluxed for 8 hr. with 2,4-dinitrophenylhydrazine in ethanol.

$\alpha$ -Pentafluorophenylbenzyl Alcohol.—A reaction similar to (b) above, but with bromopentafluorobenzene (10·0 g.) and benzaldehyde (4·3 g.), afforded a colourless syrup (9·3 g.), b. p. 115—117°/1·7 mm., which crystallised (m. p. 47°) (Found: C, 56·7; H, 2·6; F, 33·9. C<sub>13</sub>H<sub>7</sub>F<sub>5</sub>O requires C, 56·9; H, 2·6; F, 34·6%); infrared bands were at 3360 (OH) and 1510 and 1525 cm.<sup>-1</sup> (aromatic ring).



From 3,5-dinitrobenzoyl chloride (0.4 g.) and the alcohol (0.3 g.) in pyridine (5 c.c.) for 24 hr. at 15°, there was obtained  $\alpha$ -pentafluorophenylbenzyl 3,5-dinitrobenzoate [0.2 g.; from light petroleum (b. p. 100—120°)], m. p. 139—140° (Found: C, 51.2; H, 2.0.  $C_{20}H_9F_5N_2O_6$  requires C, 51.3; H, 1.9%).

2,3,4,5,6-Pentafluorobenzophenone.—(a)  $\alpha$ -Pentafluorophenylbenzyl alcohol (0.50 g.), chromium trioxide (0.15 g.), and glacial acetic acid (13 c.c.) were stirred together for 10 hr. The mixture was poured into water, the solution was extracted with ether, the extracts were dried ( $MgSO_4$ ) and evaporated, and the residue was distilled *in vacuo*, to give 2,3,4,5,6-pentafluorobenzophenone (0.30 g.), b. p. 93°/0.2 mm., m. p. 33—34° (Found: C, 57.1; H, 2.1.  $C_{15}H_5F_5O$  requires C, 57.3; H, 1.8%),  $\lambda_{max}$ . (in EtOH) 2560 Å ( $\epsilon$  19,000),  $\nu_{max}$ . 1704 (C=O) and 1515  $cm^{-1}$  (aromatic ring).

(b) Pentafluorophenylmagnesium bromide [from bromopentafluorobenzene (5 g.)] was added slowly at 0° to benzoyl chloride (3.0 g.) in ether (10 c.c.). After 15 hr. at 15°, isolation as before gave 2,3,4,5,6-pentafluorobenzophenone (3.4 g.).

The ketone (0.2 g.) was refluxed for 2 hr. in ethanol with 2,4-dinitrophenylhydrazine to give the 2,4-dinitrophenylhydrazone (0.2 g.), m. p. 204—205° (from ethanol) (Found: C, 50.9; H, 2.3.  $C_{19}H_9F_5N_4O_4$  requires C, 50.5; H, 2.0%).

The ketone (4.0 g.) was refluxed for 6 hr. with hydroxylamine hydrochloride (1.0 g.) and sodium acetate (1.5 g.) in ethanol (20 c.c.) and water (5 c.c.). By extraction in the usual way an oil was obtained which, on trituration with light petroleum (b. p. 60—80°) followed by recrystallisation from this solvent, gave a yellow solid (1.0 g.) which rapidly decomposed, particularly in the light.

Octafluoroacetophenone.—Pentafluorophenylmagnesium iodide (from pentafluoroiodobenzene, 5.0 g.) was added to lithium trifluoroacetate in ether [prepared by gradual addition of lithium hydride (0.136 g.) to trifluoroacetic acid (1.93 g.) in ether (10 c.c.)]. After 15 hr. at 15°, dilute sulphuric acid was added, the ether layer and ethereal extracts of the aqueous phase were dried ( $MgSO_4$ ), and most of the ether was distilled off through a 6" column. The residue was separated by gas chromatography [as for pentafluorotoluene (b)] to give ether, pentafluorobenzene (1.0 g.) and octafluoroacetophenone (3.2 g.), b. p. 130—131° (Found: C, 36.5.  $C_8F_8O$  requires C, 36.4%),  $\nu_{max}$ . 1760 (C=O) and 1520  $cm^{-1}$  (aromatic ring).

The same product, in smaller yield, was formed when pentafluorophenylmagnesium iodide was treated with trifluoroacetic anhydride.

No derivatives were formed when this ketone was treated with 2,4-dinitrophenylhydrazine and semicarbazide under similar conditions to those described above.

Haloform Reaction of Octafluoroacetophenone.—The ketone (1.0 g.) and 2N-aqueous potassium hydroxide (10 c.c.) were refluxed together for 4 hr. The organic layer was pure pentafluorobenzene (infrared spectroscopy). The pH of the aqueous phase was adjusted to 4 and, on addition of S-benzylthiuronium chloride, S-benzylthiuronium trifluoroacetate (0.4 g.), m. p. and mixed m. p. 174—175°, was precipitated.

2,3,4,5,6-Pentafluoroacetophenone.—Acetyl chloride (3.9 g.) in ether (20 c.c.) was added to pentafluorophenylmagnesium iodide (from pentafluoroiodobenzene, 5.0 g.). After 15 hr. at 15°, isolation as for the octafluorophenone afforded pentafluorobenzene (0.5 g.) and 2,3,4,5,6-pentafluoroacetophenone (1.0 g.) (Found: C, 45.5; H, 1.4.  $C_8H_3F_5O$  requires C, 45.8; H, 1.4%),  $\nu_{max}$ . 2960, 1325, 1370, and 1415 (Me), 1720 (C=O), and 1505 and 1530  $cm^{-1}$  (aromatic ring).

Pentafluoro- $\alpha$ -dimethylbenzyl Alcohol.—Acetone (3.0 g.) was added to pentafluorophenylmagnesium bromide (from bromopentafluorobenzene, 5.0 g.). After 15 hr. at 15°, the product was extracted as usual and the extracts were distilled *in vacuo* to give the alcohol (2.7 g.), b. p. 58°/0.25 mm. (Found: C, 48.0; H, 4.5.  $C_9H_7F_5O$  requires C, 47.8; H, 3.7%),  $\nu_{max}$ . 3400 (OH), 2960, 2920, 1450, and 1380 (Me), and 1525 and 1495  $cm^{-1}$  (aromatic ring).

The 3,5-dinitrobenzoate was made in benzene-pyridine (5:1) at 100° for  $\frac{1}{2}$  hr. It had m. p. 145—146° (from ethanol) (Found: C, 45.8; H, 2.4.  $C_{16}H_9F_5N_2O_6$  requires C, 45.7; H, 2.2%).

2,3,4,5,6-Pentafluoro- $\alpha$ -methylstyrene.—The last above-mentioned alcohol (1.0 g.), phosphoric oxide (3 g.), and quinol (0.1 g.) were heated together for  $\frac{1}{2}$  hr. at 150—160° (bath-temp.). The distillate, 2,3,4,5,6-pentafluoro- $\alpha$ -methylstyrene (0.8 g.), had b. p. 144—145° and infrared bands at 2980, 2940, 2880, 1446, and 1333 (Me and methylene), and 1528 and 1502  $cm^{-1}$  (aromatic ring) (Found: C, 51.4; H, 2.6.  $C_9H_5F_5$  requires C, 51.7; H, 2.9%).

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