Aromatic Polyfluoro-compounds. Part LV.[1] Preparation and Reactions of Some Polyfluoro(alkylbenzenes)

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Perfluoro-n-butyl-, -n-octyl-, and ω-*H*-n-pentyl-benzenes have been prepared from pentafluorophenylmagnesium bromide by reaction with the corresponding aldehyde, followed by oxidation of the resulting alcohol to the ketone, which in turn has been treated with sulphur tetrafluoride. Some nucleophilic substitution reactions of these compounds and perfluoro-n-propylbenzene are described. The possibility of the use of some of the products as surfactants is discussed.

In earlier papers the reactions of perfluoro-toluene[2] and -ethylbenzene[3] have been described. These compounds were prepared by the defluorination of the corresponding perfluoroalkylcyclohexanes. Defluorination of polyfluoroalkylcyclohexanes with larger alkyl groups than propyl is impracticable since the yields of the desired benzenes become vanishingly small as the chain length increases.[4] We therefore now describe an alternative chemical synthesis of some members of the homologous series. There are a number of

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methods available for the introduction of polyfluoroalkyl groups into aromatic systems.[5-8] Of these the reaction of ketones with sulphur tetrafluoride appeared to be the most suitable for our purposes. Subsequent to the completion of this work a similar reaction of perfluoroacetophenone with sulphur tetrafluoride to yield perfluoroethylbenzene[3] has been reported.[9]

The reactions of pentafluorophenylmagnesium bromide with aldehydes and acid halides are well known.[10] In the former case secondary alcohols result and in the latter ketones are formed directly. However, in terms of overall yield, the two step process of alcohol formation and oxidation is often better. Thus, we found that reaction of the Grignard reagent with perfluoro-n-butyraldehyde yielded heptafluoro-n-propyl(pentafluorophenyl)methanol (I) in good yield. This alcohol was readily oxidised by chromium trioxide in acetic acid to perfluorobutyrylbenzene (II) in almost quantitative yield. Heating the ketone (II) alone with excess of sulphur tetrafluoride gave only poor yields of the desired compound with a low conversion of ketone; however, addition of aluminium fluoride increased the yield of perfluorobutylbenzene (III) dramatically. This is in keeping with the proposed mechanism of SF_4 reaction involving the two step process,[11] the Lewis acid acting as a fluoride ion transfer agent. The overall yield from bromopentafluorobenzene was *ca.* 54%.

In the same way perfluoro-n-octylbenzene (VI) was prepared *via* the methanol (IV) and the ketone (V), and ω-*H*-perfluoro-n-pentylbenzene (IX) was obtained *via* the methanol (VII) and the ketone (VIII).

$C_6F_5CH(R)\cdot OH$	$C_6F_5\cdot CO\cdot R$	$C_6F_5\cdot CF_2\cdot R$
(I) $R = C_3F_7$	(II) $R = C_3F_7$	(III) $R = C_3F_7$
(IV) $R = C_7H_{15}$	(V) $R = C_7H_{15}$	(VI) $R = C_7H_{15}$
(VII) $R = [CF_2]_3\text{-}CHF_2$	(VIII) $R = [CF_2]_3\text{-}CHF_2$	(IX) $R = [CF_2]_3\text{-}CHF_2$

In order to prepare potential surfactants from the benzenes (III), (VI), and (IX), we have investigated some of their nucleophilic substitution reactions.

It was reported[3] that attempts to make the phenol from perfluoroethylbenzene by standard methods yielded only tars, probably resulting from hydrolysis of the alkyl side chain. With this in mind, perfluoropropylbenzene was treated with potassium hydroxide in pyridine at 0° for 1 h to give the expected phenol (X) in reasonable yield. ^1H and ^{19}F N.m.r. spectra indicated the absence of significant amounts of any isomer but the 4-substituted compound. This is in accord with the results obtained for nucleophilic displacement reactions with perfluoro-toluene[2] and -ethylbenzene[3] when only the 4-isomer was isolated. This is the expected result, and follows from the suggestion[12] that the perfluoroalkyl group readily stabilises the negative charge in the intermediate complex. In similar reactions using lithium, methyl, and sodium hydrogen sulphide as nucleophiles, the expected 4-substituted derivatives (XI) and (XII) were obtained, again with no evidence for other isomers being present in significant amounts. Further, little decomposition of the side chain was indicated. Thus, it seemed likely that we could prepare derivatives of polyfluoro(alkylbenzenes) with longer side chains which might have some useful detergent properties. In particular, we wished to prepare the sulphonic acids of perfluoro-n-butyl- and -n-octyl-benzenes.

$p\text{-}RC_6F_4\cdot OH$	$p\text{-}RC_6F_4\cdot Me$	$p\text{-}RC_6F_4\cdot SH$
(X) $R = C_3F_7$	(XI) $R = C_3F_7$	(XII) $R = C_3F_7$ (XIII) $R = C_4F_9$ (XV) $R = C_8F_{17}$

$p\text{-}RC_6F_4\cdot SO_2Cl$
(XIV) $R = C_4F_9$

Treatment of perfluoro-n-butylbenzene with sodium hydrogen sulphide in ethylene glycol–pyridine at 0° afforded the thiophenol (XIII) in moderate yield. Oxidation of the thiophenol with chlorine and hydrogen peroxide by the method previously described for the oxidation of pentafluorothiophenol[13] yielded the expected sulphonyl chloride (XIV), treatment of which with potassium hydroxide in water gave the potassium salt of the sulphonic acid. In the same way perfluoro-n-octylbenzene gave the potassium salt of the corresponding sulphonic acid *via* the thiophenol (XV).

The phenol (X) and the two potassium salts of the sulphonic acids show considerable detergent properties which are particularly useful in their oxidative stability, and this enables their use as spray suppressant agents on chromium plating baths.[14]

EXPERIMENTAL

Heptafluoro-n-propyl(pentafluorophenyl)methanol.— Perfluorobutyraldehyde (2·7 g) in ether (20 cm³) was added to pentafluorophenylmagnesium bromide [from C_6F_5Br (5·0 g)] in ether (30 cm³). The mixture was stirred at 20° for 20 h, and then dilute sulphuric acid (20 cm³) was added. The ether layer was separated and combined with the ether extracts (2 × 50 cm³) of the aqueous layer. The combined extracts were dried ($MgSO_4$) and the ether distilled off to yield a viscous oil which was distilled *in vacuo* to yield *heptafluoro-n-propyl(pentafluorophenyl)methanol* (I) (5·0 g), b.p. 76° at 12 mmHg (Found: C, 33·1; H, 0·6; F, 62·2. $C_{10}H_2F_{12}O$ requires C, 32·8; H, 0·6; F, 62·3%).

In the usual way the alcohol (6·0 g) afforded on reaction with toluene-p-sulphonyl chloride (3·3 g) *heptafluoro-n-propyl(pentafluorophenyl)methyl toluene-p-sulphonate* (3·9 g), m.p. 64—65° (Found: C, 39·5; H, 1·5. $C_{17}H_8F_{12}O_3S$ requires C, 39·2; H, 1·5%).

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Perfluorobutyrylbenzene.—(a) The alcohol (I) (11·0 g) in glacial acetic acid (150 cm^3) and chromium trioxide (30 g) were shaken together at room temperature for 12 h. The mixture was poured into water (200 cm^3). The fluorocarbon layer was separated, washed with water, and distilled *in vacuo* from phosphoric oxide to yield *perfluorobutyrylbenzene* (II) (10·0 g), b.p. 62—64° at 19 mmHg (Found: C, 33·0; H, 0. $C_{10}F_{12}O$ requires C, 33·0; H, 0%).

(b) Pentafluorophenylmagnesium bromide [from C_6F_5Br (5 g)] in ether (20 cm^3) was added to a solution of perfluorobutyryl chloride (5 g) in ether (20 cm^3). The mixture was stirred at 20° for 20 h and worked up in the usual way to give perfluorobutyrylbenzene (5·2 g, 66%).

Perfluoro-n-butylbenzene.—A stainless steel autoclave (50 cm^3 capacity) was charged with perfluorobutyrylbenzene (5·0 g), sulphur tetrafluoride (8·0 g), and aluminium fluoride (1·5 g). After heating at 180° for 96 h the vessel was cooled to —78° and excess of sulphur tetrafluoride was vented off by gradually raising the temperature to 15°. The oily residue was distilled *in vacuo* to yield *perfluoro-n-butylbenzene* (III) (4·7 g), b.p. 103° (Found: C, 31·2; F, 69·2. $C_{10}F_{14}$ requires C, 31·1, F, 68·9%).

Perfluoro-n-octylbenzene.—In the same way as described above *perfluoro-n-octylbenzene* (VI), m.p. 24° (Found: C, 29·1; F, 71·8. $C_{14}F_{22}$ requires C, 28·7; F, 71·3%) was prepared *via pentadecafluoro-n-heptyl(pentafluorophenyl)-methanol* (IV), b.p. 140° at 18 mmHg (Found: C, 29·3; H, 0·4. $C_{14}H_2F_{20}O$ requires C, 29·7; H, 0·4%) and *perfluoro(n-heptyl phenyl ketone)* (V), b.p. 143° at 19 mmHg (Found: C, 29·7; H, 0·05. $C_{14}F_{20}O$ requires C, 29·8; H, 0%).

ω-H-*Pentadecafluoro-n-pentylbenzene*.—Similarly prepared was ω-H-*pentadecafluoro-n-pentylbenzene* (IX), b.p. 139° (Found: C, 36·3; H, 0·3. $C_{11}HF_{13}$ requires C, 36·2; H, 0·2%) *via* 4H-*octafluoro-n-butyl(pentafluorophenyl)methanol* (VII), b.p. 210° (Found: C, 32·4; H, 0·8. $C_{11}H_3F_5O$ requires C, 32·1; H, 0·8%) and 4H-*octafluoro-n-butyl pentafluorophenyl ketone* (VIII), b.p. 136—137° (Found: C, 31·8; H, 0·3. $C_{11}HF_{13}O$ requires C, 32·3; H, 0·3%).

2,3,5,6-*Tetrafluoro*-4-*heptafluoro-n-propylphenol*.—Perfluoro-n-propylbenzene (1·4 g) and potassium hydroxide pellets (0·6 g) in pyridine (10 cm^3) were kept at 0° for 1 h and then poured into water (20 cm^3), and the solution was made alkaline with 4N-sodium hydroxide and extracted with ether. The aqueous layer was acidified with 4N-sulphuric acid (15 cm^3) and extracted (3 × 50 cm^3) with ether. The combined, dried ($MgSO_4$) ether extracts were distilled to leave an oil which on distillation *in vacuo* gave the 4-*heptafluoro-n-propylphenol* (X) (1·2 g), b.p. 76° at 15 mmHg (Found: C, 32·6; H, 0·5. $C_9HF_{11}O$ requires C, 32·3; H, 0·3%).

2,3,5,6-*Tetrafluoro*-4-*heptafluoropropyl*-1-*methylbenzene*.—Methyl-lithium [from CH_3I (7·5 g) and Li (0·9 g)] in dry ether (20 cm^3) was added with stirring to perfluoro-n-propylbenzene (1·4 g) in ether (10 cm^3) at such a rate to maintain reflux. After the addition was complete the mixture was heated under reflux for 1 h, then cooled and 4N-sulphuric acid (4 cm^3) added. The dried ($MgSO_4$) ether layer was distilled and the residue separated by preparative scale g.l.c. to give starting material (0·6 g) and 2,3,5,6-*tetrafluoro*-4-*heptafluoropropyl*-1-*methylbenzene* (XI) (0·5 g), (Found: C, 36·5; H, 1·1. $C_{10}H_3F_{11}$ requires C, 36·1; H, 0·9%).

2,3,5,6-*Tetrafluoro*-4-*heptafluoro-n-propyl(thiophenol)*.—Sodium hydrogen sulphide (5·0 g) in ethylene glycol (30 cm^3) was added at 0° to a solution of perfluoro-n-propylbenzene (4·0 g) in pyridine (15 cm^3). The mixture was kept at 0° for 1 h, then heated at 50° for 1 h. 4N-Sulphuric acid (20 cm^3) was added to the cooled mixture and the solution continuously extracted with ether for 24 h. Distillation of the dried ($MgSO_4$) ether extract yielded a yellow solid which on recrystallisation from petroleum (b.p. 80—100°) yielded 2,3,5,6-*tetrafluoro*-4-*heptafluoro-n-propyl-(thiophenol)* (XII) (3·1 g), m.p. 63—64° (Found: C, 31·4; H, 0·5. $C_9HF_{11}S$ requires C, 30·9; H, 0·3%).

2,3,5,6-*Tetrafluoro*-4-*nonafluoro-n-butyl(thiophenol)*.—An ice-cold solution of sodium hydrogen sulphide (2·5 g) in ethylene glycol (15 cm^3) was added to a cold solution of perfluoro-n-butylbenzene (2·0 g) in pyridine (8 cm^3). The solution was kept at 0° for 1 h and then water (20 cm^3) and 4N-hydrochloric acid (20 cm^3) were added to give a yellow precipitate. The solid was dissolved in ether and the aqueous layer extracted (3 × 25 cm^3) with ether. The combined, dried ($MgSO_4$) extracts were distilled to yield a yellow solid (1·9 g), recrystallisation of which from petroleum (b.p. 80—100°) gave 2,3,5,6-*tetrafluoro*-4-*nonafluoro-n-butyl(thiophenol)* (XIII) (1·2 g), m.p. 93—94° (Found: C, 33·4; H, 0·7. $C_{10}HF_{13}S$ requires C, 33·3; H, 0·3%).

2,3,5,6-*Tetrafluoro*-4-*nonafluoro-n-butylbenzenesulphonyl Chloride*.—Dry chlorine was bubbled through a mixture of (XIII) (1·9 g), glacial acetic acid (10 cm^3), and 20% (w/v) hydrogen peroxide (1·2 cm^3) for 2 h. The mixture was poured into water and extracted with ether (3 × 25 cm^3). The combined, dried ($MgSO_4$) extracts were distilled to leave a viscous liquid, distillation of which *in vacuo* afforded the *benzenesulphonyl chloride* (XIV) (0·8 g), m.p. 23—24° (Found: C, 26·3. $C_{10}ClF_3O_2S$ requires C, 25·7%).

Potassium 2,3,5,6-*Tetrafluoro*-4-*nonafluoro-n-butylbenzenesulphonate*.—The sulphonyl chloride (0·4 g), water (2·0 cm^3), and potassium hydroxide (0·1 g) were shaken together at 20° for 15 min. The precipitate (0·4 g) was recrystallised from water to give the *potassium sulphonate* (Found: C, 24·5. $C_{10}F_{13}KO_3S$ requires C, 24·7%).

2,3,5,6-*Tetrafluoro*-4-*heptadecafluoro-n-octyl(thiophenol)*.—Sodium hydrogen sulphide (0·8 g) in ethylene glycol (10 cm^3) was added to perfluoro-n-octylbenzene (1·08 g) in pyridine (10 cm^3) at 0°. The mixture was kept at 0° for 1 h and then warmed to 20° over 1 h, poured into water, and acidified with 4N-sulphuric acid (20 cm^3). The yellow precipitate was dissolved in ether and the aqueous layer extracted with ether (3 × 25 cm^3). The combined, dried ($MgSO_4$) extracts were distilled to give a yellow solid (0·6 g) which on recrystallisation gave 2,3,5,6-*tetrafluoro*-4-*heptadecafluoro-n-octyl(thiophenol)* (XV) (0·5 g), m.p. 80—81° (Found: C, 28·0; H, 0·1. $C_{14}HF_{21}S$ requires C, 28·0; H, 0·2%).

Potassium 2,3,5,6-*Tetrafluoro*-4-*heptadecafluoro-n-octylbenzenesulphonate*.—The thiophenol (XV) (0·2 g) was converted as above into the corresponding sulphonyl chloride (0·1 g) which after purification was shaken at 20° for 15 h with potassium hydroxide (0·1 g) in water (5 cm^3). The white solid formed (0·1 g) was recrystallised from water to give the *potassium sulphonate* (0·08 g) (Found: C, 24·8. $C_{14}F_{21}KO_3S$ requires C, 24·5%).

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