

## Sodium Perfluoroalkane Carboxylates as Sources of Perfluoroalkyl Groups

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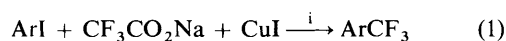
Sodium trifluoroacetate, in the presence of copper(I) iodide, is used as a source of trifluoromethyl to replace halogen by trifluoromethyl in benzenoid and heterocyclic aromatic systems, as well as in alkenyl and alkyl halogen compounds. The mechanism of this interesting copper-assisted process has been explored and an intermediate of the form  $[\text{CF}_3\text{CuI}]^-$  is proposed. Introduction of higher perfluoroalkyl groups from their respective sodium perfluoroalkane carboxylates has been demonstrated and the mechanistic features are compared with those of the trifluoromethylation process.

Methods for the introduction of a perfluoroalkyl group into aromatic systems have become especially significant because of the increasing importance of various plant protection products containing trifluoromethyl. Approaches which are now classical include Swarts reactions ( $\text{CCl}_3 \longrightarrow \text{CF}_3$ ),<sup>1</sup> modification of the carboxylate group using sulphur tetrafluoride,<sup>2</sup> and the use of trifluoroiodomethane as a source of trifluoromethyl *via* a radical  $(\text{CF}_3\cdot)$ <sup>3</sup> or the use of fluoroiodoalkanes or other halogeno fluoroalkanes as sources of organocopper intermediates.<sup>4</sup> Russian workers have also introduced  $\text{CF}_3$  *via*  $(\text{CF}_3)_2\text{Hg}$ .<sup>5</sup> All of these processes have their limitations.

Recently Japanese workers briefly described<sup>6</sup> an attractive approach to the introduction of trifluoromethyl which involves the decarboxylation of sodium trifluoroacetate in a copper-assisted process. This method has the obvious advantage of a readily accessible and easily handled starting material. We have further investigated the application of this route and attempted to obtain some mechanistic understanding of the process, which is especially interesting since mechanisms of copper-assisted reactions are notoriously difficult to determine.

### Results

*Development of Preparative Procedure.*—The reaction described previously is summarised in equation (1)<sup>6</sup> and an alternative procedure has also been described using hexamethylphosphoramide as solvent.<sup>7</sup> We have used the former



i. *N*-methylpyrrolidin-2-one,  $\text{N}_2$ , 160 °C, 4 h

method to introduce trifluoromethyl into a wider range of iodo- and bromo-benzene derivatives than has previously been attempted. The results are shown in Table 1 where yields were determined accurately by g.l.c. analysis; isolation procedures were developed separately and are described in the Experimental section. The yields demonstrate the order of reactivity to be  $\text{ArI} > \text{ArBr} \gg \text{ArCl}$ , although the use of bromo derivatives is still quite efficient, and up to three trifluoromethyl groups have been introduced into a benzene nucleus using this one-step procedure. Pentafluoroiodobenzene, the most electron-deficient benzene derivative used, gave no trifluoromethylated products but was completely converted by coupling and reductive dehalogenation into decafluorobiphenyl (44%) and pentafluorobenzene (46%), respectively. This is almost certainly due

to formation of a pentafluorophenylcopper derivative<sup>8</sup> which could then either couple or undergo reductive elimination at reaction temperature.

Using the same procedure we have also demonstrated that the process can be applied successfully to certain heterocyclic systems (Table 2), although the yields are generally lower than those obtained from benzene derivatives. This reduced reactivity probably results from partial co-ordination of the heterocycle to the copper(I) species and evidence for the adverse effects of potential co-ordinating agents such as quinoline will be discussed later. Such adverse effects on reactions of copper-assisted nucleophilic displacement of bromine and iodine have been noted earlier.<sup>9</sup> Likewise, no trifluoromethylated products were observed either for 2-iodo-*N*-methylimidazole, which is known to form copper complexes,<sup>10</sup> or aminoiodopyridines. In contrast, however, 2-chloro-5-iodopyridine reacted efficiently and, since the chlorine is sufficiently activated by the trifluoromethyl group introduced, a small amount of 2,5-bis(trifluoromethyl)pyridine was formed. Clearly, the presence of halogen atoms *ortho* to nitrogen in the pyridine system inhibits co-ordinating ability of the nitrogen.

The method can also be used to replace halogen in alkenyl and alkyl sites: styrene derivatives, (2-bromovinyl)benzene, and (2-bromo-2-fluorovinyl)benzene (kindly provided by Professor H. F. Koch), were converted into the corresponding trifluoromethylated derivatives in 53 and 59% yields, respectively, and iodopentane gave 1,1,1-trifluorohexane in 40% yield. However, bromophenylacetylene underwent a coupling reaction, giving a butadiene as the only product.

The suitability of other solvents has been investigated and we have found that dimethylformamide is a useful alternative to *N*-methylpyrrolidin-2-one but no trifluoromethylated products were observed using sulpholane or diphenyl sulphone. It has also been established that  $\text{Cu}^0$  and  $\text{Cu}^{\text{II}}$  will promote the reaction but substantially less effectively than  $\text{Cu}^{\text{I}}$ . Copper(I) iodide is more effective than copper(I) bromide but must be present in stoichiometric quantities in order to obtain the maximum yield.

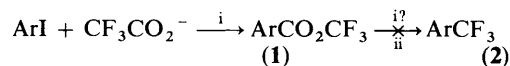
*Halogen Exchange.*—Remarkably, we observed that exchange of bromine for iodine occurs as an accompanying process in the trifluoromethylation reaction with bromobenzene and becomes the main process, giving a 37% yield of iodobenzene, when the initial amount of sodium trifluoroacetate is substantially reduced. This exchange process is unusual since it opposes the observed order of reactivity,  $\text{ArI} > \text{ArBr}$ , and we are only

aware of one other report of this potentially useful process,<sup>11</sup> in which 1-bromonaphthalene is converted into 1-iodonaphthalene in 30% yield using pyridine and copper(I) iodide. We have found that a 22% yield of iodobenzene can be obtained simply by heating bromobenzene and copper(I) iodide in *N*-methylpyrrolidin-2-one at 160 °C and this can be slightly increased to 28% by the addition of an equivalent amount of sodium iodide.

**Mechanism.**—We have addressed the question of mechanism in this process for introduction of trifluoromethyl and considered a number of possibilities, as outlined below:

(i) *Initial formation of an aryl-copper species.* This seems most likely for the reaction of pentafluoroiodobenzene, since only in this case was a significant amount of biaryl formed. Also, coupling of bromophenylacetylene indicates the preferential formation of an organocopper intermediate.<sup>12</sup>

(ii) *Initial formation of a phenyl ester.* A feasible process involves copper-assisted nucleophilic displacement of iodine by trifluoroacetate to yield an ester (1) followed by decarboxylation to the trifluoroaryl compound (2). However, we have

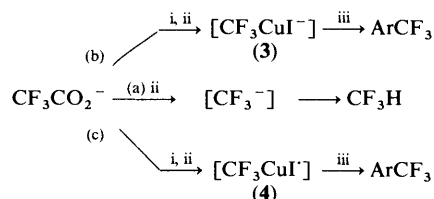


i, CuI; ii, -CO<sub>2</sub>

prepared phenyl trifluoroacetate and demonstrated that it is not decarboxylated under standard reaction conditions described in the Experimental section which indicates that esters are not intermediates in the trifluoromethylation process.

(iii) *Copper-assisted decarboxylation of trifluoroacetate.* We have shown that sodium trifluoroacetate is decarboxylated, forming fluoroform, when heated alone in aqueous *N*-methylpyrrolidin-2-one and that the addition of copper(I) iodide increases the rate of decarboxylation dramatically.

A four-fold excess of sodium trifluoroacetate was used in the trifluoromethylation since significant amounts of fluoroform are produced as a by-product. We envisage that copper-assisted substitution of the aryl halide occurs according to one of the routes, (b) or (c), shown in Scheme 1, whereas fluoroform can be formed by (b), (c), and the competing unassisted process (a).



Scheme 1. i, CuI; ii, -CO<sub>2</sub>; iii, ArI

In our view the crucial distinction between the two assisted processes (b) and (c) lies in the fact that a trifluoromethyl radical and corresponding complex (4) would be *electrophilic* and therefore reaction with ArI would be inhibited by electron-withdrawing substituents, whereas the anion (3) would be nucleophilic and therefore trifluoromethylation would be facilitated by electron withdrawal. We have constructed a crude Hammett plot using substituted iodobenzenes. *p*-XC<sub>6</sub>H<sub>4</sub>I (X = Me, MeO, H, F, Cl, I, CF<sub>3</sub>, and NO<sub>2</sub>) to synthesize the corresponding *p*-trifluoromethyl derivatives. A plot of log(*K*<sub>X</sub>/*K*<sub>H</sub>) against σ gave a ρ-value of +0.46, which clearly shows that the reactive species is nucleophilic in character and so is only consistent with a reaction scheme approximating to (b). The ρ-value obtained is in agreement with those recorded by other workers<sup>13</sup> for copper-assisted nucleophilic aromatic substitution.

Copper-promoted reactions are susceptible to spectacular solvent and ligand effects,<sup>9</sup> and the initial formation of a complex between the aryl halide and a copper species appears to be important, in that the copper should be co-ordinatively unsaturated or can easily be made so.<sup>13</sup> It is clear that the co-ordinating ability of copper is vital in trifluoromethylation because the addition of excess quantities of quinoline and iodide ions (both good ligands for copper) to the reaction involving iodobenzene resulted in formation of complexes of the type [CuL<sub>4</sub>]<sup>+</sup> and, consequently, significant inhibition of the reaction. Addition of the co-ordinating ligand inhibited decarboxylation of sodium trifluoroacetate indicating that copper-assisted decarboxylation requires initial formation of a copper carboxylate complex. We have also shown that silver(I) iodide, whilst promoting decarboxylation, does not transfer trifluoromethyl to the aryl iodide and it is probable that silver(I), which prefers bis co-ordination, is less able to accommodate both trifluoromethyl and aryl iodide as ligands thus enabling substitution to occur.

Table 1. Trifluoromethylation of substituted halogeno benzenes

Arene (mmol)	CF <sub>3</sub> CO <sub>2</sub> Na (equiv.)	Product	Yield (%)
PhI	1	PhCF <sub>3</sub>	87
PhBr	1	PhCF <sub>3</sub>	68
PhCl	1		
<i>p</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> I	1	<i>p</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CF <sub>3</sub>	64
<i>p</i> -C <sub>6</sub> H <sub>4</sub> I <sub>2</sub>	2	<i>p</i> -C <sub>6</sub> H <sub>4</sub> (CF <sub>3</sub> ) <sub>2</sub>	93
<i>p</i> -C <sub>6</sub> H <sub>4</sub> I <sub>2</sub>	1	<i>p</i> -C <sub>6</sub> H <sub>4</sub> (CF <sub>3</sub> ) <sub>2</sub>	24
		<i>p</i> -IC <sub>6</sub> H <sub>4</sub> CF <sub>3</sub>	24
<i>p</i> -CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub> I		<i>p</i> -C <sub>6</sub> H <sub>4</sub> (CF <sub>3</sub> ) <sub>2</sub>	73
<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> I	1	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> CF <sub>3</sub>	98
<i>o</i> -ClC <sub>6</sub> H <sub>4</sub> I	1	<i>o</i> -ClC <sub>6</sub> H <sub>4</sub> CF <sub>3</sub>	87
C <sub>6</sub> Me <sub>5</sub> I	1	C <sub>6</sub> Me <sub>5</sub> CF <sub>3</sub>	60
<i>m</i> -MeC <sub>6</sub> H <sub>4</sub> Br	1	<i>m</i> -MeC <sub>6</sub> H <sub>4</sub> CF <sub>3</sub>	78
<i>p</i> -CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub> Br	1	<i>p</i> -C <sub>6</sub> H <sub>4</sub> (CF <sub>3</sub> ) <sub>2</sub>	62
1,3,5-Br <sub>3</sub> C <sub>6</sub> H <sub>3</sub>	3	1,3,5-(CF <sub>3</sub> ) <sub>3</sub> C <sub>6</sub> H <sub>3</sub>	48
		1,3-(CF <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	41

Table 2. Trifluoromethylation of heterocyclic halogen compounds

Heterocycle	Product	Yield (%)
2-Amino-5-iodopyridine		
2-Acetamido-5-iodopyridine		
2-Chloro-5-iodopyridine	2-Chloro-5-trifluoromethylpyridine + 2,5-Bis(trifluoromethyl)pyridine	85 7
2-Chloro-5-trifluoromethylpyridine	2,5-Bis(trifluoromethyl)pyridine	27
2-Iodothiophene	2-Trifluoromethylthiophene	46
2-Bromopyrimidine	2-Trifluoromethylpyrimidine	34
1-Methyl-5-iodoimidazolium		

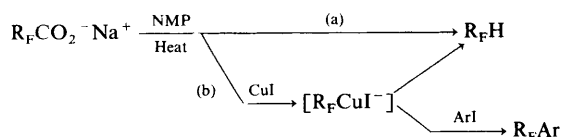
**Table 3.** Introduction of the pentafluoroethyl group

Arene (mmol)		Product	Yield (%) <sup>a</sup>
PhI	(7.5)	PhC <sub>2</sub> H <sub>5</sub>	86 (53)
C <sub>6</sub> H <sub>4</sub> I <sub>2</sub>	(3.8)	C <sub>6</sub> H <sub>4</sub> (C <sub>2</sub> F <sub>5</sub> ) <sub>2</sub>	83
<i>p</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> I	(7.5)	<i>p</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> C <sub>2</sub> F <sub>5</sub>	51
<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> I	(7.5)	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> C <sub>2</sub> F <sub>5</sub>	75 (54)
<i>o</i> -ClC <sub>6</sub> H <sub>4</sub> I	(7.5)	<i>o</i> -ClC <sub>6</sub> H <sub>4</sub> C <sub>2</sub> F <sub>5</sub>	62 (14)
<i>p</i> -CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub> Br	(7.5)	<i>p</i> -CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub> C <sub>2</sub> F <sub>5</sub>	71 (19)
		<i>p</i> -CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub> I	5
1,3,5-Br <sub>3</sub> C <sub>6</sub> H <sub>3</sub>	(2.5)	1,3,5-(C <sub>2</sub> F <sub>5</sub> ) <sub>3</sub> C <sub>6</sub> H <sub>3</sub>	(31)
2-Iodothiophene	(7.5)	2-Pentafluoroethylthiophene	28
		Thiophene	31
2-Chloro-5-iodo-pyridine	(7.5)	2-Chloro-5-pentafluoroethylpyridine	30
PhCH=CHBr		PhCH=CHC <sub>2</sub> F <sub>5</sub>	53
C <sub>5</sub> H <sub>11</sub> I		C <sub>5</sub> H <sub>11</sub> C <sub>2</sub> F <sub>5</sub>	(22)

<sup>a</sup> Figures in parentheses represent isolated yields.

**Higher Perfluoroalkyl Groups.**—The use of sodium pentafluoropropionate and heptafluorobutyrate has been investigated in analogous processes for the transfer of pentafluoroethyl and heptafluoropropyl groups, respectively. Pentafluoroethylation (see Table 3) is even more successful than trifluoromethylation in that a greater proportion of the pentafluoropropionate was converted into the pentafluoroethyl derivative, but transfer of the heptafluoropropyl group was very inefficient and only a 30% yield of heptafluoropropylbenzene could be obtained from iodobenzene.

The surprising difference in reactivity between sodium pentafluoropropionate and heptafluorobutyrate can be explained by considering the relative rates of unassisted and copper-promoted decarboxylation. Sodium pentafluoropropionate is decarboxylated more readily in the presence of copper(I) iodide; decarboxylation begins at 160 °C when the salt alone is heated in *N*-methylpyrrolidin-2-one as compared with 140 °C when copper(I) iodide is added. In contrast, decarboxylation of sodium heptafluorobutyrate occurs at 140 °C whether or not copper(I) iodide is present. In perfluoroalkylation, as outlined in Scheme 2, the assisted

**Scheme 2.**

process (b) is clearly important for sodium pentafluoropropionate, but it is obvious that much more of the sodium heptafluorobutyrate reacts *via* the unassisted process (a) and consequently leads to a lower yield of perfluoroalkylbenzene than that obtained from sodium pentafluoropropionate.

## Experimental

Spectroscopic data were obtained using the following spectrometers: i.r., Perkin-Elmer 457; u.v., Pye-Unicam S18-100; mass, VG 7070E or V.G. Micromass 12B linked with g.l.c.; n.m.r., Varian EM 360L. Trichlorofluoromethane was used as an external standard and upfield shifts (p.p.m.) are recorded as negative. G.l.c. was carried out using a Varian Aerograph instrument fitted with a gas-density balance detector. Three columns were used: Column 0, 10% silicon gum rubber; Column 1, 5% polyethylene glycol (20 m); and Column 2, 10%

polyethylene glycol (20 m). *N*-Methylpyrrolidin-2-one (NMP) was distilled under reduced pressure (87 °C, 10 mmHg) onto a molecular sieve (4A) and stored under dried nitrogen. Sodium perfluoroalkancarboxylates were prepared by treatment of sodium hydroxide with perfluoroalkancarboxylic acids and dried *in vacuo* before storage under nitrogen. Iodo and bromo compounds were prepared by literature methods or obtained from commercial sources.

**Trifluoromethylation Reactions.**—(a) *Benzenoid and heterocyclic aromatic compounds: general procedure.* A mixture containing sodium trifluoroacetate (2.72 g, 20 mmol), copper(I) iodide (1.91 g, 10 mmol), halogen compound (1.7–5 mmol), and NMP (40 ml) was stirred under nitrogen at 160 °C (4 h). Products in the resulting mixture were identified by a combination of m.s.–g.l.c. (Column 2) and n.m.r. spectroscopy using mass and <sup>19</sup>F n.m.r. spectra of authentic materials. The yields were calculated from g.l.c. of the reaction mixture by incorporating an internal standard and the results are given in Tables 1 and 2.

(b) *2-Bromovinylbenzene.* A mixture containing sodium trifluoroacetate (2.72 g, 20 mmol), copper(I) iodide (1.91 g, 10 mmol), 2-bromovinylbenzene (0.92 g, 5 mmol), and NMP (40 ml) was stirred under nitrogen at 160 °C (4 h). The resultant mixture was analysed by g.l.c. (Column 2) and <sup>19</sup>F n.m.r., and the product yield calculated by g.l.c. after addition of an internal standard and identified as (3,3,3-trifluoroprop-1-enyl)benzene<sup>14</sup> (54%); δ<sub>F</sub> – 63.4; *m/z* 172 (*M*<sup>+</sup>).

(c) *Phenylbromoacetylene.* A mixture containing sodium trifluoroacetate (1.32 g, 10 mmol), copper(I) iodide (0.96 g, 5 mmol), phenylbromoacetylene (0.45 g, 2.5 mmol), and NMP (20 ml) was stirred under nitrogen at 160 °C (4 h). The product mixture was diluted with water, extracted with diethyl ether, and the ethereal layer washed with water and dried (MgSO<sub>4</sub>) before evaporation to leave a brown solid. This was sublimed (60 °C) and recrystallised (ethanol–water 1:1) to give white crystals, identified by comparison with literature data, as 1,4-diphenylbuta-1,3-diyne, m.p. 82–84 °C (lit.,<sup>15</sup> 87 °C); ν<sub>max</sub> (KBr disc) 915, 755, 680, and 520 cm<sup>-1</sup>; λ<sub>max</sub> (diethyl ether) 248, 258, 288, 305, and 326 nm [lit.,<sup>16</sup> (ethanol) 227, 247, 257, 287, 306, and 307 nm]; δ<sub>H</sub>(CCl<sub>4</sub>) 7.2; *m/z* 202 (*M*<sup>+</sup>).

(d) *Iodopentane.* A mixture containing sodium trifluoroacetate (2.72 g, 2 mmol), copper(I) iodide (1.91 g, 10 mmol), iodopentane (0.99 g, 5 mmol), and NMP (20 ml) was stirred under nitrogen at 160 °C (4 h). The volatile components were separated *in vacuo*, and shown by capillary m.s.–g.l.c. and <sup>19</sup>F n.m.r., to contain NMP, pentane, and 1,1,1-trifluorohexane;<sup>16</sup> *m/z* 71 (C<sub>5</sub>H<sub>11</sub><sup>+</sup>), 70 (C<sub>5</sub>H<sub>10</sub><sup>+</sup>), 55 (C<sub>4</sub>H<sub>7</sub><sup>+</sup>), 43 (C<sub>3</sub>H<sub>7</sub><sup>+</sup>), and 69 (CF<sub>3</sub><sup>+</sup>); δ<sub>F</sub> – 76 (CF<sub>3</sub>).

**Isolation of Products.**—(a) *Volatile materials: 1,3,5-tris(trifluoromethyl)benzene.* A mixture containing sodium trifluoroacetate (1.36 g, 10 mmol), copper(I) iodide (0.96 g, 5 mmol), 1,3,5-tribromobenzene (0.25 g, 0.8 mmol), and NMP (20 ml) was stirred under nitrogen at 160 °C (4 h). The resulting mixture, with added internal standard, was found by m.s.–g.l.c. (Column 2, 150 °C) to contain 1,3,5-tris(trifluoromethyl)benzene (48%) [*m/z* 282 (*M*<sup>+</sup>)] and 1,3-bis(trifluoromethyl)benzene (41%) [*m/z* 214 (*M*<sup>+</sup>)]. Products were isolated by dropping the mixture onto heated glass-wool and carrying the volatile material in a stream of nitrogen into a trap immersed in liquid air. A small quantity of colourless liquid was obtained and shown by g.l.c. (Column 2) to contain NMP (1.7 g), 1,3,5-tris(trifluoromethyl)benzene (0.09 g, 82% recovery of compound available in the mixture), and 1,3-bis(trifluoromethyl)benzene (0.07 g, 100% recovery). Further separation was achieved by preparative-scale g.l.c.

(b) *Less volatile materials: p-chloropentafluoroethylbenzene.*

**Table 4.** Oxidation state of copper

Copper compound	Mass (g)	PhCF <sub>3</sub> (%)	PhI (%)	PhCl (%)
Copper(0)	0.16	10	88	
Copper(I) iodide	0.48	68	34	
Copper(II) chloride	0.34	12	60	21

**Table 5.** Halogen exchange

CuI (mmol)	NaI (mmol)	PhI/PhBr		
		1 h	2 h	4 h
10		0.30		0.27
20		0.14	0.14	0.13
10	10		0.38	0.41
20	10		0.39	
10	20		v. small	

A mixture containing sodium pentafluoropropionate (0.37 g, 2 mmol), copper(I) iodide (0.38 g, 2 mmol), *p*-chloriodobenzene (0.32 g, 1.34 mmol), *p*-chloriodo[<sup>14</sup>C]benzene (0.04 g, 0.16 mmol, 250 μCi), and NMP (4 ml) was stirred under nitrogen at 170 °C (3 h). The resulting mixture was found by radio-g.l.c. (Column 2) to contain *p*-chloriodobenzene (24%) and *p*-chloropentafluoroethylbenzene (62%). The mixture was added to water and the organic products extracted with aliquots of pentane (5 ml) until the activity, as measured by Geiger Counter, was no longer reduced on extraction. The pentane solution was washed with water to remove any NMP and dried (MgSO<sub>4</sub>). The solution was found by scintillation counting to contain 168 μCi (69% recovery) of active material which, by g.l.c. (Column 2), was distributed as *p*-chloropentafluoroethylbenzene (71%) and *p*-chloriodobenzene (24%).

**Copper Source.**—(a) *Copper(I) bromide.* A mixture containing sodium trifluoroacetate (1.32 g, 10 mmol), copper(I) bromide (0.72 g, 5 mmol), iodobenzene (0.51 g, 2.5 mmol), and NMP (20 ml) was stirred under nitrogen at 160 °C (4 h). The product mixture was shown by g.l.c. (Column 1, 140 °C) and by comparison with standard solutions to contain trifluoromethylbenzene (45%) and bromobenzene (48%).

(b) *Reduced amount (× 0.1) of copper(I) iodide.* A mixture containing sodium trifluoroacetate (0.27 g, 2 mmol), copper(I) iodide (0.02 g, 0.1 mmol), bromobenzene (11.5 μl)–[<sup>14</sup>C]–PhBr [(40 μl) in diethyl ether (0.5 mmol)], and NMP (4 ml) was stirred under nitrogen at 155 °C (4 h). The product mixture was shown by radio-g.l.c. (Column 2, 80–180 °C) to contain trifluoromethylbenzene (12%), bromobenzene (79%), and iodobenzene (9%).

(c) *Oxidation state of copper.* Three mixtures containing sodium trifluoroacetate (0.65 g, 5 mmol), iodobenzene (0.25 g, 1.25 mmol), and copper (2.5 mmol) in oxidation state 0, I, or II, and NMP (10 ml) were stirred under nitrogen at 160 °C (4 h). The resulting mixtures were analysed by g.l.c. (Column 2, 140 °C) and the yields calculated after incorporation of an internal standard. Chlorobenzene was identified by comparison of its mass spectrum with that of the authentic material. The results are shown in Table 4.

**Halogen Exchange.**—(a) *Trifluoromethylation of bromobenzene.* A mixture containing sodium trifluoroacetate (1.36 g, 10 mmol), copper(I) iodide (1.91 g, 10 mmol), bromobenzene (0.78 g, 5 mmol), and NMP (20 ml) was stirred under nitrogen at 160 °C (4 h). The product reaction mixture was shown by m.s.–g.l.c. (Column 1, 150 °C), and, by comparison with authentic

**Table 6.** Decarboxylation of sodium trifluoroacetate

Time (h)	[CF <sub>3</sub> CO <sub>2</sub> <sup>-</sup> ]	
	with CuI (cm)	without CuI (cm)
0	5.8	3.0
1	3.1	2.3
2	2.8	2.2
3	1.7	1.9
4	0.5	1.7

**Table 7.** Hammett plot

<i>para</i> -Substituent	σ-Value	ArI (g)	lg(K <sub>t</sub> /K <sub>tH</sub> )
H	0.00	0.2506	0.00
Cl	+0.23	0.2981	0.13
NO <sub>2</sub>	+0.78	0.3122	0.29
H	0.00	0.2506	0.00
Me	-0.17	0.2709	-0.12
H	0.00	0.2507	0.00
MeO	-0.27	0.2982	-0.13
H	0.00	0.2556	0.00
I	+0.18	0.4188	0.22
H	0.00	0.2506	0.00
F	+0.06	0.2773	0.05
H	0.00	0.1279	0.00
CF <sub>3</sub>	+0.54	0.1692	0.19

materials, to contain NMP, trifluoromethylbenzene, bromobenzene, and iodobenzene.

This procedure was repeated with half the amount of sodium trifluoroacetate and the yield of iodobenzene was found to be 37%.

(b) *Maximisation of halogen exchange.* Mixtures containing bromobenzene (0.79 g, 5 mmol), copper(I) iodide (10–20 mmol), sodium iodide (10–20 mmol), and NMP (20 ml) were stirred under nitrogen at 160 °C (4 h).

Samples were removed at intervals and analysed by g.l.c. (Column 2, 150 °C). The results are shown in Table 5.

**Mechanism.**—(a) *Decarboxylation of sodium trifluoroacetate.* Two mixtures of sodium trifluoroacetate (2.72 g, 10 mmol) and NMP (40 ml) were made and copper(I) iodide (1.91 g, 10 mmol) was added to one. Both solutions were stirred under nitrogen at 160 °C (4 h) in the same oil-bath. Samples were removed by syringe, through a rubber septum, at hourly intervals and the concentration of sodium trifluoroacetate was calculated from <sup>19</sup>F n.m.r. integration. The results are shown in Table 6 where (cm) refers to the heights of the integration steps in the <sup>19</sup>F n.m.r. spectra.

(b) *Analysis of gaseous products.* A solution of sodium trifluoroacetate (2.66 g, 19 mmol) in NMP (20 ml) was sealed in a Carius tube with a 150 mm × 5-mm diameter neck and heated at 150 °C in a rocking autoclave (4 h). The gaseous product was condensed using a vacuum system into a gas bulb of known volume through a tube containing Carbosorb–magnesium perchlorate to absorb the carbon dioxide. After warming to room temperature, the yield was calculated from the pressure exerted. Analysis by m.s. and i.r. showed that the gas was fluoroform (50%);  $v_{\max}$  3 040, 2 280, 1 370, and 1 150 cm<sup>-1</sup> (lit.,<sup>17</sup> 3 055, 1 352vs, 1 209, 1 152vs, and 509 cm<sup>-1</sup>);  $m/z$  70 ( $M^+$ ) and 69 ( $M^+ - 1$ ).

The reaction was repeated with the addition of copper(I) iodide, the Carbosorb–Mg(ClO<sub>4</sub>)<sub>2</sub> was weighed before and after the absorption of carbon dioxide and about 75% decarboxylation observed.

(c) *Hammett plot.* Copper(I) iodide (0.4761 g, 2.5 mmol) and

Table 8. Decarboxylation temperatures

Sodium salt	Decarboxylation temperature (°C)	
	without CuI	with CuI
C <sub>2</sub> F <sub>5</sub> CO <sub>2</sub> <sup>-</sup> Na <sup>+</sup>	160	140
C <sub>3</sub> F <sub>7</sub> CO <sub>2</sub> <sup>-</sup> Na <sup>+</sup>	145	145

sodium trifluoroacetate (1.72 g, 12.5 mmol) were added to each of two solutions, one containing iodobenzene (1.25 mmol) and the other a *para*-substituted iodobenzene derivative (1.25 mmol) in NMP (10 ml). The mixtures were immersed in an oil-bath at 150 °C and stirred under nitrogen (1 h) before cooling in an ice-salt bath. The concentration of iodobenzene derivative remaining was then calculated by g.l.c. (Column 2) after addition of an internal standard. This procedure was repeated for a range of *para*-substituted iodobenzene derivatives and from the results a pseudo-first-order rate constant was calculated and used to produce a Hammett plot. The values are given in Table 7.

**Higher Perfluoroalkyl Groups.**—(a) *Decarboxylation temperatures.* The sodium perfluoroalkane carboxylate (5 mmol) was placed in a side-arm of a flask containing NMP (20 ml) and the flask attached to a vacuum line through a reflux condenser and evacuated. After the solvent had been degassed, the system was decreased to 0.5 atm of nitrogen and the sodium salt added. The solution was stirred whilst the temperature was slowly raised until a steady pressure increase was noted on the manometer.

The procedure was repeated with added copper(I) iodide (0.48 g, 2.5 mmol) which was added to the NMP before degassing. The results are given in Table 8.

(b) *Pentafluoroethylation. General procedure.* A mixture containing sodium pentafluoropropionate (1.86 g, 10 mmol), copper(I) iodide (1.96 g, 10 mmol), halogen compound (2.5–7.5 mmol), and NMP (20 ml) was stirred under nitrogen at 170 °C (3 h). The reaction mixture was analysed by m.s.–g.l.c. (Column 2) and the products identified from the molecular ion peak and, where possible, by comparison with the <sup>19</sup>F n.m.r. and mass spectra of authentic materials. The yields were calculated by g.l.c. analysis after addition of an internal standard and are given in Table 3.

Some products, including all new compounds, were isolated as described.

(i) *p*-Bromotrifluoromethylbenzene. The volatile material was removed from the reaction mixture *in vacuo* and added to its own volume of water. The mixture was shaken so as to dissolve any NMP in the aqueous layer which was removed with a syringe. The remaining liquid was dried (MgSO<sub>4</sub>) and transferred *in vacuo*. G.l.c. (Column 2) showed one component, identified as *p*-pentafluoroethyltrifluoromethylbenzene (0.37 g, 19%) (Found: C, 40.6; H, 1.9; F, 57.2. Calc. for C<sub>9</sub>H<sub>4</sub>F<sub>8</sub>: C, 40.91; H, 1.52; F, 57.58%); δ<sub>F</sub> – 64 (3 F, CF<sub>3</sub>), –85.8 (3 F, CF<sub>3</sub>CF<sub>2</sub><sup>-</sup>), and –115.7 (2 F, CF<sub>3</sub>CF<sub>2</sub><sup>-</sup>); ν<sub>max</sub>. 1 410, 1 320, 1 285, 1 210, and 1 000 cm<sup>-1</sup>; m/z 264 (M<sup>+</sup>) and 195 (100%).

(ii) 1,3,5-Tribromobenzene. The volatile material was isolated *in vacuo*, as described above, yielding a colourless liquid identified as 1,3,5-tri(pentafluoroethyl)benzene (0.27 g, 20%) (Found: C, 33.6; F, 65.5. C<sub>12</sub>H<sub>3</sub>F<sub>15</sub> requires C, 33.30; F, 65.97%); δ<sub>F</sub> – 85 (3 F, CF<sub>3</sub>CF<sub>2</sub>) and –115 (2 F, CF<sub>3</sub>CF<sub>2</sub>); ν<sub>max</sub>. 1 330, 1 200, 1 160, 1 100, and 1 030 cm<sup>-1</sup>; m/z 432 (M<sup>+</sup>) and 363 (100%).

Extraction by the flash separation technique described earlier led to a more efficient (31%) recovery.

(iii) *p*-Chloriodobenzene. The product was separated from the bulk of the reaction mixture by the flash separation

technique, washed with a small amount of water, dried (MgSO<sub>4</sub>), and the solvent removed under reduced pressure to yield a colourless liquid identified as *p*-chloropentafluoroethylbenzene (1.09 g, 54%) (Found: C, 41.9; H, 1.7. C<sub>8</sub>H<sub>4</sub>ClF<sub>5</sub> requires C, 41.6; H, 1.7%); δ<sub>F</sub> – 85.5 (3 F, CF<sub>3</sub>CF<sub>2</sub>) and –115.3 (2 F, CF<sub>3</sub>CF<sub>2</sub>); ν<sub>max</sub>. 1 340, 1 290, 1 210, 1 150, 1 100, 980 and 830 cm<sup>-1</sup>; m/z 232/230 (M<sup>+</sup>) and 161/163 (M – CF<sub>3</sub>).

(iv) *o*-Chloriodobenzene. The product was isolated by the flash separation technique and an analytical sample was obtained by preparative-scale g.l.c. A colourless liquid was obtained and identified as *o*-chloropentafluoroethylbenzene (0.24 g, 14%) (Found: C, 41.8; H, 2.0. C<sub>8</sub>H<sub>4</sub>ClF<sub>5</sub> requires C, 41.6; H, 1.7%); δ<sub>F</sub> – 83.8 (3 F, CF<sub>3</sub>CF<sub>2</sub>) and –111.3 (2 F, CF<sub>3</sub>CF<sub>2</sub>); ν<sub>max</sub>. 1 340, 1 290, 1 210, 1 110, 1 120, 1 060, 970, 730, and 760 cm<sup>-1</sup>; m/z 232/230 (M<sup>+</sup>) and 161/163 (M – CF<sub>3</sub>).

(v) Iodopentane. The volatile material was isolated *in vacuo* and shown by g.l.c. (Column 2, 100 °C) to contain one major component. A small sample was obtained by preparative-scale g.l.c. (Column '0') and identified from <sup>19</sup>F n.m.r. and mass spectra as 1,1,1,2,2-pentafluoroheptane (0.08 g, 22%); δ<sub>F</sub> – 83.7 (3 F, CF<sub>3</sub>CF<sub>2</sub>) and –122.6 (2 F, CF<sub>3</sub>CF<sub>2</sub>); m/z 119 (C<sub>2</sub>F<sub>5</sub><sup>+</sup>), 69 (CF<sub>3</sub><sup>+</sup>), 71 (C<sub>5</sub>H<sub>11</sub><sup>+</sup>), and 43 (C<sub>3</sub>H<sub>7</sub><sup>+</sup>).

(c) *Heptafluoropropylbenzene.* A mixture containing sodium heptafluorobutyrate (2.36 g, 10 mmol), copper(I) iodide (0.96 g, 5 mmol), iodobenzene (0.51 g, 2.5 mmol), and NMP (20 ml) was stirred under nitrogen at 132 °C (3 h). Samples were taken at intervals and the amounts of iodobenzene remaining were calculated by g.l.c. (Column 1). During the first hour, the concentration of iodobenzene fell to 70% of the original value and thereafter remained constant. Analysis of the reaction mixture by m.s.–g.l.c. (Column 1) and <sup>19</sup>F n.m.r. showed two products, identified from molecular ion peaks as heptafluoropropane, δ<sub>F</sub> – 76 (CF<sub>3</sub>CF<sub>2</sub>CF<sub>2</sub>H), –114 (CF<sub>3</sub>CF<sub>2</sub>CF<sub>2</sub>H), and –124 (CF<sub>3</sub>CF<sub>2</sub>CF<sub>2</sub>H); m/z 151 (M<sup>+</sup> – 19); and heptafluoropropylbenzene,<sup>18</sup> δ<sub>F</sub> – 81 (CF<sub>3</sub>CF<sub>2</sub>CF<sub>2</sub>), –112 (CF<sub>3</sub>CF<sub>2</sub>CF<sub>2</sub>), and –127 (CF<sub>3</sub>CF<sub>2</sub>CF<sub>2</sub>); m/z 246 (M<sup>+</sup>).

This was the highest conversion of iodobenzene achieved in several reactions carried out at various temperatures from 100 °C, at which little decarboxylation took place, to 170 °C where vigorous bubbling occurred immediately after the solution was placed in the oil-bath.

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