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A ROUTE TO FLUOROALKYL-SUBSTITUTED AROMATIC COMPOUNDS INVOLVING FLUOROALKYLCOPPER INTERMEDIATES[1]

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Abstract—Interaction of iodofluoroalkanes, iodoaromatic compounds and copper in polar aprotic solvents at 110–130° leads to good yields of (fluoroalkyl)aromatic compounds. The iodofluoroalkanes and iodoaromatic compounds can bear a wide variety of substituents (carboxyl, nitro, amino, hydroxyl, etc). The reactions proceed *via* fluoroalkylcopper compounds which are markedly more stable than their non-fluorinated analogues.

THERE are a number of routes to fluoroalkyl-substituted aromatic compounds. Thus good results have been obtained[2–4] by free-radical processes when aromatic compounds are heated with iodofluoroalkanes. High yields also result from the reaction of polyfluoroacyl chlorides with aromatic compounds in the presence of nickel carbonyl.[5] The main alternative to these direct methods is the fluorination of fluoroalkyl aryl ketones, either with sulphur tetrafluoride,[6] or by the phosphorus pentachloride/antimony trifluoride sequence.[7]

We now report another direct preparative route to a wide range of fluoroalkyl-substituted aromatic compounds of both benzenoid and heterocyclic types. Iodofluoroalkanes and iodoaromatic compounds react with copper in polar aprotic solvents to give good yields of such compounds: $R_FI + ArI \xrightarrow{Cu} R_FAr + CuI$. Substitution in the aromatic ring occurs exclusively at the iodine site, and ^{19}F NMR spectroscopy[8] indicates that the structure of the fluoroalkyl group remains unchanged. Biaryls, from Ullmann coupling, are usually absent.

This synthesis is applicable to a range of monoiodofluoroalkanes (Table 1) and the two classes most frequently employed have been 1-iodoperfluoroalkanes and α-iodo-ω*H*-perfluoroalkanes. 2-Iodoheptafluoropropane is an example of a secondary fluoroalkyl iodide that has been used. Other groups such as phenyl, carboxylic ester or even a free carboxyl group may be present in the iodofluoroalkane. Yields of over 60% are usual and even when bromofluoroalkanes are employed, yields of 40% are obtainable. In general, the use of a bromofluoroalkane in place of the corresponding iodofluoroalkane requires more vigorous reaction conditions, and lower yields are obtained. The partially fluorinated alkyl iodide CF_3CH_2I gave (2,2,2-trifluoroethyl)benzene, albeit in low yield (ca. 10%). However, iodoalkanes do not undergo any comparable condensation with iodobenzene: 1-iodobutane gave a mixture of butane and but-1-ene.

The reaction is also applicable to α,ω-di-iodoperfluoroalkanes, yielding α,ω-diarylperfluoroalkanes (Tables 2 and 3). The preparations of 1,3-diarylhexafluoropropanes have been investigated extensively (Table 2) and 1,3-diphenylhexafluoropropane has been prepared in 60–90% yield in several solvents. 1,7-Di-iodotetra-

TABLE 1. FLUOROALKYLATION REACTIONS INVOLVING MONOIODOFLUOROALKANES

Iodofluoro-alkane mmole	Halogenoaromatic mmole	Copper mmole	Solvent ml	Products	Yield %	Reaction conditions		
						Method	Time (min)	Temp (°C)
CF_3I 25	C_6H_5I 35	95	DMF 25	$CF_3 \cdot C_6H_5$[a]	45	C	720	150
C_3F_7I 15	C_6H_5I 30	30	DMSO 25	$C_3F_7 \cdot C_6H_5$[b]	65	A	(i) 60 (ii) 60	120 120
C_3F_7I 32	$m\text{-}AcO \cdot C_6H_4I$ 61	130	DMF 60	$m\text{-}C_3F_7 \cdot C_6H_4 \cdot OAc$[b]	65	D	(i) 60 (ii) 50	135 125–135
C_3F_7I 30	$o\text{-}O_2N \cdot C_6H_4Cl$ 175	90	DMF 15	$o\text{-}C_3F_7 \cdot C_6H_4 \cdot NO_2$[b]	17[c]	C	840	175
$(CF_3)_2CFI$ 38	C_6H_5I 75	270	DMF 50	$(CF_3)_2CF \cdot C_6H_5$[b]	40	D	(i) 15 (ii) 90	125 125
$C_5F_{11}I$ 11	$p\text{-}HO_2C \cdot C_6H_4I$ 10	50	DMSO 20	$p\text{-}C_5F_{11} \cdot C_6H_4 \cdot CO_2H$	65	B	210	105–120
$C_7F_{15}I$ 100	C_6H_5I 100	240	DMSO 110	$C_7F_{15} \cdot C_6H_5$[b]	70	D	(i) 60 (ii) 120	110–120 110
$C_7F_{15}Br$ 18	C_6H_5I 80	160	DMF 60	$C_7F_{15} \cdot C_6H_5$[b] C_6H_5Br[a] $C_6H_5 \cdot C_6H_5$[a]	40[c] 25[c] 25[c]	C	3000	188
$C_7F_{15}I$ 10	C_6F_5Br 10	20	DMSO 25	$C_6F_5 \cdot C_6F_5$ $C_7F_{15} \cdot C_6F_5$	80[c] 12[c]	A	(i) 85 (ii) 90	120 120
$C_7F_{15}I$ 10	$p\text{-}MeO_2C \cdot C_6H_4I$ 10	40	DMF 25	$p\text{-}C_7F_{15} \cdot C_6H_4 \cdot CO_2H$[d]	70[c]	D	(i) 15 (ii) 180	125 125

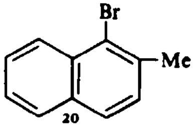
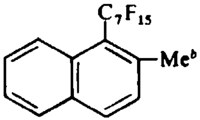
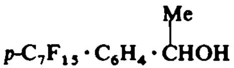
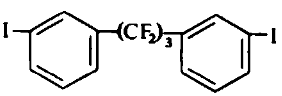
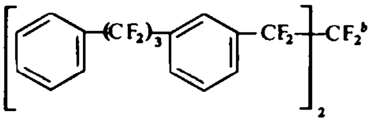
$C_7F_{15}I$ 44	p-$MeO_3S \cdot C_6H_4I$ 40	160	DMF 100	p-$C_7F_{15} \cdot C_6H_4 \cdot SO_2Cl^{b,e}$	14	D	(i) 60 (ii) 290	110–120 115–120
$C_7F_{15}I$ 20	 20	120	HMPA 30		17^c	D	(i) 15 (ii) 40	156–162 155–160
$C_7F_{15}I$ 40	p-$HO\overset{Me}{C}H \cdot C_6H_4Br$ 40	160	DMSO 60	p-$C_7F_{15} \cdot C_6H_4 \cdot \overset{Me}{C}HOH$	65	D	(i) 30 (ii) 720	125 125
$C_9F_{19}I$ 21	m-$H_2N \cdot C_6H_4I$ 20	80	DMSO 25	m-$C_9F_{19} \cdot C_6H_4 \cdot NH_2{}^b$	45	B	210	105–120
$H(CF_2)_6I$ 63	p-BrC_6H_4I 60	140	DMSO 50	p-$H(CF_2)_6C_6H_4Br^b$ p-$H(CF_2)_6C_6H_4I^b$ p-$H(CF_2)_6C_6H_4(CF_2)_6H^b$	50 10^c 4^c	D	(i) 15 (ii) 180	104–110 110–114
$H(CF_2)_{10}I$ 1·2	C_6H_5I 2·4	2·4	DMSO 2·0	$H(CF_2)_{10}C_6H_5$	65^c	A	(i) 10 (ii) 90	120–140 120
$C_6H_5(CF_2)_3I$ 3·3	C_6H_5I 3·3	7·0	DMSO 5·0	$C_6H_5(CF_2)_3C_6H_5{}^b$	60	A	(i) 25 (ii) 10	120 120
$C_6H_5(CF_2)_3I$ 10	 4·0	40	DMF 11		70	B	180	110–120
$HO_2C(CF_2)_3I$ 5·0	C_6H_5I 5·0	16	DMSO 5·0	$C_6H_5(CF_2)_3CO_2H$	60	B	70	110–130

TABLE 1—*continued*

Iodofluoro-alkane mmole	Halogenoaromatic mmole	Copper mmole	Solvent ml	Products	Yield	Reaction conditions		
						Method	Time (min)	Temp (°C)
$EtO_2C(CF_2)_3I$ 250	C_6H_5I 1250	1500	DMF 275	$C_6H_5(CF_2)_3CO_2Et$[b]	70	B	95	135–140
CF_3CH_2I 52	C_6H_5I 120	160	DMF 35	$CF_3CH_2 \cdot C_6H_5$[b]	15[c]	C	1200	190

[a] By IR

[b] Identified by MS

[c] By GLC

[d] Reaction product, $p\text{-}C_7F_{15} \cdot C_6H_4 \cdot CO_2Me$, was not characterised but converted into the acid by hydrolysis

[e] Reaction product, $p\text{-}C_7F_{15} \cdot C_6H_4 \cdot SO_3Cu$, was not characterised but converted, *via* the free acid, into the acid chloride with PCl_5

decafluoroheptane[9] with copper bronze and dimethyl 4-iodophthalate in DMSO gives the required 1,7-diaryltetradecafluoroheptane in 85% yield. 1,4-Di-iodo-octafluorobutane gave a less than 10% yield of 1,4-diphenyloctafluorobutane in a reaction with iodobenzene in DMF, while in reactions with dimethyl 4-iodophthalate in DMSO, 25% yields of 1,4-bis-(3,4-dimethoxycarbonylphenyl)octafluorobutane were obtained.[10] 1,2-Di-iodotetrafluoroethane, 1,2-dibromotetrafluoroethane, and dibromodifluoromethane react with copper in the presence of iodobenzene in polar aprotic solvents to give tetrafluoroethylene by dehalogenation directly in the first two cases and probably *via* difluorocarbene in the last.

A representative range of aromatic compounds has been examined and some examples are given in Tables 1, 2 and 3; in the majority of reactions iodobenzene or a substituted iodobenzene has been used. Reactions involving various halogenobenzenes are in accord with the expected ease of replacement of halogens. Thus, there was no replacement of fluorine or chlorine in reactions involving bromopentafluorobenzene, chloropentafluorobenzene, and *p*-chloroiodobenzene, although *o*-chloronitrobenzene has been fluoroalkylated. Using bromobenzene in place of iodobenzene in preparations of 1,3-diphenylhexafluoropropane, reaction was slower and gave only a 20% yield. In reactions of *p*-bromoiodobenzene and iodofluoroalkanes, 10–15% yields of products arising from bromine replacement were obtained, compared with 50–60% yields from iodine replacement. Some heterocyclic halides have also been examined (Table 2).

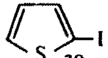
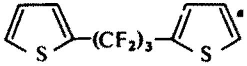
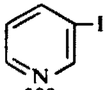
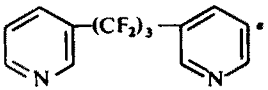
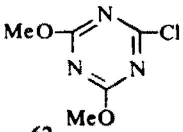
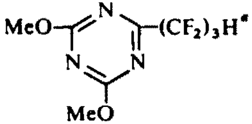
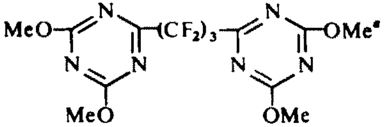
A wide variety of substituents on the halogenoaromatics are inert in this reaction: besides fluorine and chlorine, alkyl, alkoxy, carboxylic ester and nitro groups may be present without adversely affecting the yield. Even groups containing a readily protonisable hydrogen do not interfere with the fluoroalkylation process; thus, free carboxyl, amino, and hydroxyl groups may be present. However, aromatic sulphonate esters undergo a secondary reaction, probably with cuprous iodide, to give copper sulphonates: $C_7F_{15}I + Cu + p\text{-}IC_6H_4\cdot SO_3Me \rightarrow p\text{-}C_7F_{15}\cdot C_6H_4\cdot SO_3Cu$. Some substituents enhance the yields obtained, especially acetoxy and alkoxycarbonyl. The speed of reaction, however, does not appear to be influenced in the same way by such substituents: dimethyl iodophthalates as a class give very good yields (70–90%) even though reaction times are longer than average (5–15 hr).

Of all the suitable aprotic solvents, DMSO and DMF have been most used and DMSO is generally preferred. Pyridine, pyridine-N-oxide, 2,6-lutidine, hexamethylphosphoramide (HMPA), dimethylacetamide (DMAC) and sulpholane have also been successfully employed, but no reaction occurred in diethylene glycol dimethyl ether. Although one of the effective solvents is necessary for the fluoroalkylation to take place, only a small amount is required: dilute solutions of pyridine or DMSO in benzotrifluoride or hexafluorobenzene promoted reactions in high yield, whereas neither of the latter was effective alone.

In preparative work, the reaction can be brought about by heating a mixture of the iodofluoroalkane, activated copper bronze, and the iodoaromatic compound in the solvent under an inert atmosphere at 110–130° (Method B). It is usually an advantage to employ an excess of copper and of iodoaromatic compound (Tables 1, 2 and 3), although when DMSO is the solvent, stoichiometric quantities of the three reactants can generally be used; attempts to do this in other solvents have often led to reduced yields. It is also often necessary to employ a large amount of most of the solvents:

TABLE 2. FLUOROALKYLATION REACTIONS INVOLVING 1,3-DI-IODOHEXAFLUOROPROPANE

Halogenoaromatic mmole	$I(CF_2)_3I$ mmole	Copper mmole	Solvent ml	Products	Yield %	Reaction conditions		
						Method	Time (min)	Temp (°C)
C_6H_5I 1990	330	2240	DMAC 1050	$C_6H_5(CF_2)_3C_6H_5$[a] $C_6H_5(CF_2)_3H$[a]	72 1	D	(i) 90 (ii) 195	115–120 115–120
C_6H_5I 33	15	95	Pyridine 30	$C_6H_5(CF_2)_3C_6H_5$[a]	40	A	(i) 30 (ii) 45	70–90 100
C_6H_5I 10	5·0	31	DMSO/C_6F_6 0·8 5·0	$C_6H_5(CF_2)_3C_6H_5$	95[b]	B	1320	80
C_6H_5I 23	7·5	35	DMSO/H_2O 10 5·0	$C_6H_5(CF_2)_3C_6H_5$	65	B	1440	100
C_6H_5I 200	230	400	DMSO 80	$C_6H_5(CF_2)_3I$ $C_6H_5(CF_2)_3C_6H_5$	60 10	E	(i) 90 (ii) 90	110–120 120
C_6H_5Br 100	13	160	DMF 22	$C_6H_5(CF_2)_3C_6H_5$	20[b]	B	1080	140
C_6F_5Br 100	15	160	DMF 20	$C_6F_5 \cdot C_6F_5$[c] $C_6F_5(CF_2)_3C_6F_5$	35 7	B	95	120–128
p-ClC_6H_4I 150	60	330	DMSO 120	$(p\text{-}ClC_6H_4 \cdot CF_2)_2CF_2$	80	D	(i) 60 (ii) 120	110–120 120
m-$HO \cdot C_6H_4I$ 7·0	3·5	20	DMSO 5·0	$(m\text{-}HO \cdot C_6H_4 \cdot CF_2)_2CF_2$	69	B	360	110–125
m-$Me \cdot C_6H_4I$ 160	25	240	DMF 40	$(m\text{-}Me \cdot C_6H_4 \cdot CF_2)_2CF_2$[a]	67	B	40	120

m-MeO $\cdot C_6H_4I$ 190	24	320	DMF 50	$(m\text{-MeO}\cdot C_6H_4\cdot CF_2)_2CF_2$[a]	55	B	120	140–150
m-$O_2N\cdot C_6H_4I$ 84	15	190	DMF 20	$(m\text{-}O_2N\cdot C_6H_4\cdot CF_2)_2CF_2$[a]	52	B	90	130–135
p-AcO $\cdot C_6H_4I$ 2420	495	3040	DMAC 2000	$p\text{-AcO}\cdot C_6H_4(CF_2)_3H$[a] $(p\text{-AcO}\cdot C_6H_4\cdot CF_2)_2CF_2$[a]	44 43	D	(i) 100 (ii) 145	110–124 122–127
m-AcO $\cdot C_6H_4I$ 630	111	833	DMF 300	$(m\text{-AcO}\cdot C_6H_4\cdot CF_2)_2CF_2$[a] $m\text{-AcO}\cdot C_6H_4(CF_2)_3H$[a]	82 1	B	120	120–130
 38	20	130	Pyridine 40		25[b]	A	(i) 40 (ii) 35	70–80 100
m-$EtO_2C\cdot C_6H_4I$ 1140	212	1825	DMF 350	$(m\text{-}EtO_2C\cdot C_6H_4\cdot CF_2)_2CF_2$[a]	76	D	(i) 82 (ii) 77	108–120 109–118
p-$MeO_2C\cdot C_6H_4I$ 1530	320	2580	DMF 1000	$(p\text{-}MeO_2C\cdot C_6H_4\cdot CF_2)_2CF_2$[a] $(p\text{-}MeO_2C\cdot C_6H_4)_2$[a]	63 4	D	(i) 90 (ii) 60	100–120 115–120
 200	25	310	DMF 65		52	B	90	126
 62	11	90	DMF 40	 	18[d] <2[d]	B	120	110–120

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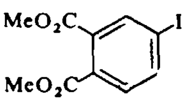
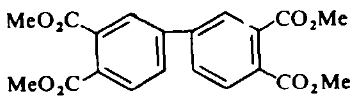
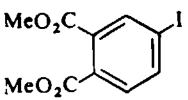
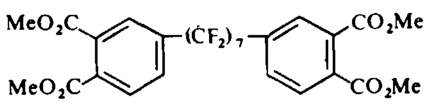
[a] Identified by MS

[b] By GLC

[c] Identified by IR

[d] Low yields possibly caused by reaction of 2-chloro-4,6-dimethoxy-1,3,5-triazine with DMF

TABLE 3. FLUOROALKYLATION REACTIONS INVOLVING OTHER α,ω-DIHALOGENOPERFLUOROALKANES

α,ω-Dihalogeno-perfluoroalkane mmole	Iodoaromatic mmole	Copper mmole	Solvent ml	Products	Yield %	Reaction conditions		
						Method	Time (min)	Temp (°C)
CBr_2F_2	C_6H_5I		HMPA	C_6H_5Br[a]	14[b]	D	(i) 150	120–150
48	100	240	150	$CF_2{=}CF_2$	[c]		(ii) 120	150
$I(CF_2)_2I$			DMSO		[c]	D	(i) 60	116–120
5·2	10	24	3	$CF_2{=}CF_2$[a, d]	[c]		(ii) 120	116–122
$I(CF_2)_4I$	C_6H_5I		DMF	$C_6H_5(CF_2)_4C_6H_5$	9[b]	D	(i) 35	115–125
44	260	310	75				(ii) 85	120–130
$I(CF_2)_7I$			DMSO		85	D	(i) 90	120–125
47	97	240	20				(ii) 720	120–125

[a] Identified by IR

[b] By GLC

[c] Not determined

[d] Identified by MS

for example, 0·15 to 1·0M solutions of iodofluoroalkanes in DMF or DMAC have been used, thus providing a useful heat sink for the reaction exotherm. However, smaller amounts of DMSO can be used very successfully, making it possible to conduct laboratory preparations involving up to 4 molar amounts of reagents. In large scale preparations where a small amount of solvent is being employed, the exothermic reaction is best controlled by adding either the iodofluoroalkane or the copper bronze to the other reagents at 110–130° (Methods D and E respectively), and the former technique has been used extensively. The reactions are remarkably clean and the insignificant side reactions make for easy isolation of pure products; only in the few instances where Ullmann aryl-coupling occurred was purification difficult. The most common by-products, formed in less than 1% yield, result from reductive dehalogenation of the iodoaromatic compound and the iodofluoroalkane. These side-reactions were virtually absent when DMSO was used as solvent.

Fluoroalkylcopper compounds

It was apparent that fluoroalkylcopper compounds were involved when it was found that these fluoroalkylations could be conducted in two separate stages. The first stage comprised metallation of the iodofluoroalkane with copper to give a solution of the fluoroalkylcopper compound. In the second stage, this reactive solution was treated with the haloaromatic compound to form the (fluoroalkyl)aromatic.

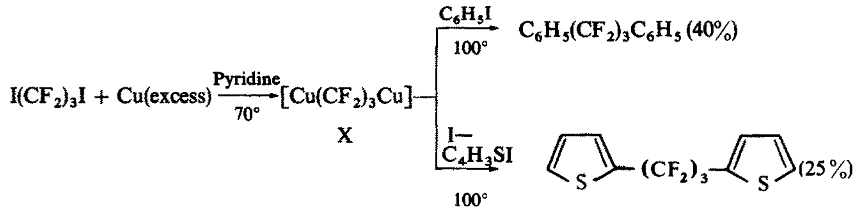
The fluoroalkylcopper compounds have been studied mainly as solutions, and evidence for copper(I) species is provided by the stoichiometry of the reactions of both monoiodofluoroalkanes and 1,3-di-iodohexafluoropropane with copper and iodobenzene:

$$\begin{array}{ccc} \mathrm{Y(CF_2)_nI + 2Cu \rightarrow} & \mathrm{Y(CF_2)_nCu \xrightarrow{C_6H_5I}} & \mathrm{Y(CF_2)_nC_6H_5} \\ \mathrm{I: Y = F} & \mathrm{III: Y = F} & \mathrm{V: Y = F} \\ \mathrm{II: Y = H} & \mathrm{IV: Y = H} & \mathrm{VI: Y = H} \end{array}$$

$$\begin{array}{cc} \mathrm{I(CF_2)_3I + 2Cu + C_6H_5I \rightarrow} & \mathrm{C_6H_5(CF_2)_3I} & \left[\begin{array}{c} \mathrm{+\ C_6H_5(CF_2)_3C_6H_5} \\ \mathrm{IX} \end{array}\right] \\ \mathrm{VII} & \mathrm{VIII} & \end{array}$$

Copper and the monoiodofluoroalkanes (e.g. I, $n = 3$; II, $n = 6$; or VIII) in DMSO at 100–120° react completely together in proportions which correspond precisely with those in the equation shown. Clear, homogenous solutions are formed which, on subsequent treatment with iodobenzene at 120°, give the corresponding (fluoroalkyl)benzene in 60–70% yields (Method A, Table 1). Also, the reaction between 1 mol of the di-iodide (VII) and 1 mol of iodobenzene in DMSO consumes 2 equivalents of copper and gives the monoiodide (VIII) as the major product (60% yield) together with a 10% yield of 1,3-diphenylhexafluoropropane, consistent with a monocopper(I) derivative being formed from the di-iodide (VII).

Metallation of VII in pyridine proceeds at a lower temperature (70–100°) than in the other solvents, apparently giving the difunctional copper compound (X), although the precise stoichiometry has not been established:



Subsequent reaction of a filtered solution of X with iodobenzene or with 2-iodothiophen[10] gave between 20 and 40% yields of the corresponding 1,3-diarylhexafluoropropane (Method A, Table 2). Attempts to prepare solutions of X in other solvents have not been conclusive and require further study.

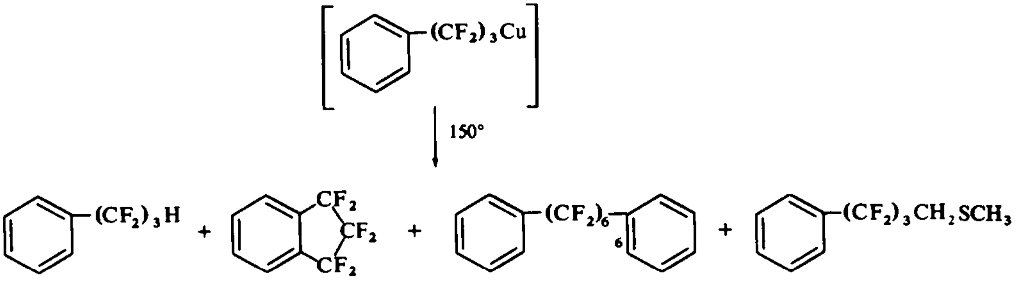
Solutions of fluoroalkylcoppers III and IV prepared under a nitrogen atmosphere are usually green-blue in colour, probably as a result of oxidation by traces of oxygen in the nitrogen used; similar preparations under a high-purity argon atmosphere are almost colourless. When dry air was passed through a DMSO solution of the copper compound derived from 1-iodo-3-phenylhexafluoropropane (VIII), in which no VIII remained, very deep colours developed which then faded to a pale green. Analysis by GLC then indicated that VIII had been regenerated, and a 65% recovery was obtained on distillation. A copper(II) species might be an intermediate in this reaction, which could account for the colour changes observed.

Addition of water to the solutions of the fluoroalkylcoppers in the absence of air results in a very slow formation of the corresponding hydrofluoroalkane. For example, perfluoroheptylcopper (III, $n = 7$) in DMSO in the presence of 5 mols of water formed 1*H*-perfluoroheptane to the extent of 10–15% during 3 days at room temperature. The compounds are also resistant to hydrolysis at higher temperatures: 1,3-diphenylhexafluoropropane (IX) could still be formed in good yield from a solution of 3-phenylhexafluoropropylcopper in DMSO which had been treated with 1·5 mols of water at 100° for 20 minutes; also 1,3-diphenylhexafluoropropane could be synthesised in high yield from 1,3-di-iodohexafluoropropane, at 130°, in DMSO or DMF containing up to 7½% of water. A very good yield was obtained even in a 1:2 mixture of water and DMSO (Table 2). Significantly, the reaction products from these experiments in wet DMSO did not contain any 1-phenyl-3*H*-hexafluoropropane, which compound might be expected if hydrolysis of the intermediate 3-phenylhexafluoropropylcopper had occurred. In wet DMF the amount of 1-phenyl-3*H*-hexafluoropropane formed was less than in dry DMF.

Perfluoroheptylcopper (III, $n = 7$), prepared from 1-iodoperfluoroheptane and copper in DMSO, can be isolated by the addition of water, extracting the precipitate with ether, washing the ether solution free of cuprous iodide and DMSO, and evaporating the dried ether solution, oxygen being absent at all times. The isolated perfluoroheptylcopper reacts with iodobenzene to give (perfluoroheptyl)benzene (V, $n = 7$) both in ether and in DMSO, in the latter solvent a 65% yield being obtained. The stability of the fluoroalkylcoppers to water contrasts with the behaviour of alkylcopper[11] and arylcopper[12, 13] compounds, which are readily hydrolysed usually to the corresponding hydrocarbons, and so parallels the behaviour of fluoroalkylzinc compounds,[14] which are much less readily hydrolysed than alkylzinc compounds. In the presence of air and water, the fluoroalkylcopper compounds appear to undergo a rapid oxidative hydrolysis; for example, perfluoroheptylcopper in ether, and free from cuprous iodide, gives perfluoroheptanoic acid. This is formally similar to the slower wet photochemical oxidation of fluoroalkyl iodides.[15]

In the absence of air, at room temperature in DMSO or DMF, the fluoroalkylcoppers are quite stable: a solution of perfluoroheptylcopper (III, $n = 7$) in DMF was stored for 3 months at room temperature; it remained clear, no copper was deposited, and it retained most of its activity towards iodobenzene. A solution in ether was less stable as it gradually deposited copper metal at room temperature, although the rate of decomposition was low, about 1% per day. This decomposition was accelerated markedly when attempts were made to isolate the copper compound by precipitation with petrol or removal of ether. The solutions in DMSO or DMF also have considerable stability at temperatures up to 120°, since they are made and used at these temperatures (Table 1, Method A); subsequent yields of (fluoroalkyl)-benzenes show that the amount of decomposition is unimportant even after an hour at over 100°.

When solutions in DMSO or DMF are heated at about 150°, thermal decomposition of the fluoroalkylcopper occurs quite rapidly with the deposition of copper, the major volatile products being due to abstraction of hydrogen. For example, a solution of IV, $n = 10$, in DMSO gave a product tentatively identified as $H(CF_2)_{10}H$, in 65% yield. The decomposition of the copper derivative of VIII in DMSO has been examined more completely, the volatile products being isolated by preparative-scale GLC and identified by mass spectrometry

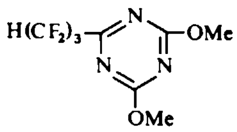


XI XII XIII XIV

Once again the major product, XI (ca. 35%),arose by hydrogen abstraction, and was accompanied by XII (ca. 25%), XIII (ca. 10%), and XIV (ca. 5%), the last being only tentatively identified. In one large-scale reaction between the di-iodide VII, *p*-iodophenylacetate, and copper in DMAC (Table 2), the reaction product contained equimolar amounts of 1,3-di-(*p*-acetoxyphenyl)hexafluoropropane and 1-(*p*-acetoxyphenyl)-3*H*-hexafluoropropane (XVI). It is usual to obtain less than 1% of products such as XVI, and the large amount of XVI could arise by thermal decomposition of the intermediate fluoroalkylcopper XV:

$$\begin{tikzcd}
p\text{-AcO}\cdot C_6H_4I + \underset{\text{VII}}{I(CF_2)_3I} + Cu \arrow[r] & \underset{\text{XV}}{p\text{-AcO}\cdot C_6H_4(CF_2)_3Cu} \arrow[dl] \arrow[d, "p\text{-AcO}\cdot C_6H_4I"] \\
\underset{\text{XVI}}{p\text{-AcO}\cdot C_6H_4(CF_2)_3H} & (p\text{-AcO}\cdot C_6H_4\cdot CF_2)_2CF_2
\end{tikzcd}$$

TABLE 4. SOME PHYSICAL CONSTANTS AND ANALYSIS OF FLUOROALKYL-ARENES PREPARED VIA FLUOROALKYL-COPPER COMPOUNDS

Compound	m.p.[a] (°C)	b.p. (°C/mmHg)	n_D^{20}	Analysis					
				Found %			Calculated %		
				C	H	F	C	H	F
$CF_3CH_2 \cdot C_6H_5$[b]		136–7[c]	1·4355						
$H(CF_2)_3C_6H_5$		95–100/100	1·4082	47·0	2·4	49·7	47·4	2·6	50·0
m-$H(CF_2)_3C_6H_4 \cdot OAc$		245–6[c]	1·4293	46·4	2·5	39·4	46·2	2·8	39·9
p-$H(CF_2)_3C_6H_4 \cdot OAc$		140–4/23 (246–7[c])	1·4300	46·4	2·8	39·4	46·2	2·8	39·9
	34–8			32·7	2·1	39·0	33·0	2·4	39·2
$(CF_3)_2CF \cdot C_6H_5$[b, d]		120	1·3860						
$C_3F_7 \cdot C_6H_5$[b, e]		132	1·3820						
o-$C_3F_7 \cdot C_6H_4 \cdot NO_2$[b]		238[c]	1·4221						
m-$C_3F_7 \cdot C_6H_4 \cdot OAc$		92–4/20	1·4075	43·5	2·1	44·1	43·4	2·3	43·8
$I(CF_2)_3C_6H_5$		98–9/20	1·4682	31·0	1·3	32·8	30·5	1·4	32·2
$HO_2C(CF_2)_3C_6H_5$	45–8	146–7/20		44·3	2·2	42·1	44·2	2·2	41·9
$EtO_2C(CF_2)_3C_6H_5$		130–2/20							

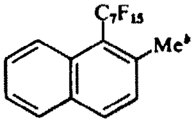
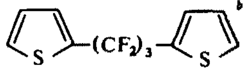
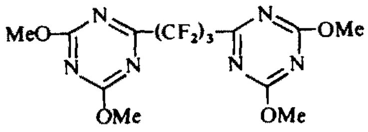
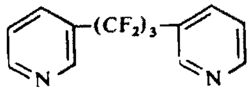
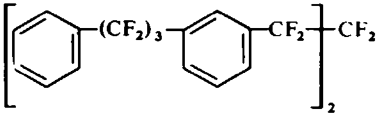
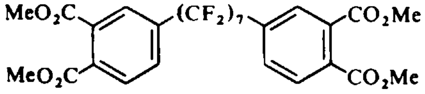
$p\text{-}C_5F_{11}\cdot C_6H_4\cdot CO_2H$[f]	189–91			37·2	1·5	53·3	36·9	1·3	53·6
$p\text{-}H(CF_2)_6C_6H_4Br$		119–20/13	1·4120						
$C_7F_{15}\cdot C_6H_5$[g]		88–90/16	1·3599						
$p\text{-}C_7F_{15}\cdot C_6H_4\cdot CH(Me)OH$	39–42	93–5/0·3		36·4	1·8		36·7	1·9	
$p\text{-}C_7F_{15}\cdot C_6H_4\cdot CO_2H$	193–4			34·5	1·1	58·3	34·3	1·0	58·1
$p\text{-}C_7F_{15}\cdot C_6H_4\cdot SO_2Cl$	79–83			28·7	1·0	52·0	28·6	0·7	52·3
		126/0·25	1·4370						
$C_7F_{15}\cdot C_6F_5$		213[c]	1·3451	29·2		70·4	29·1	0·0	70·9
$m\text{-}C_9F_{19}\cdot C_6H_4\cdot NH_2$	49–51			32·1	1·2	64·3	32·1	1·1	64·2
$H(CF_2)_{10}C_6H_5$[h]	46–7	166–8/56		33·5	1·1	66·2	33·2	1·0	65·8
$C_6H_5(CF_2)_3C_6H_5$[i]	49–50	86–8/0·05	1·4785[j]	59·0	3·0	37·4	59·2	3·3	37·5
$C_6F_5(CF_2)_3C_6F_5$[b]	38–9								
$p\text{-}ClC_6H_4(CF_2)_3C_6H_4\text{-}p\text{-}Cl$	107–8			48·3	2·2	30·5	48·2	2·1	30·6
$m\text{-}MeC_6H_4(CF_2)_3C_6H_4\text{-}m\text{-}Me$		160–2/18	1·4880	61·5	4·2	33·7	61·5	4·2	34·3
$m\text{-}O_2N\cdot C_6H_4(CF_2)_3C_6H_4\text{-}m\text{-}NO_2$	92–3			45·4	2·1	28·7	45·7	2·0	28·9
$m\text{-}MeO\cdot C_6H_4(CF_2)_3C_6H_4\text{-}m\text{-}OMe$		146–50/0·2	1·4969	55·9	3·6	31·4	56·1	3·9	31·3

TABLE 4—*continued*

Compound	m.p.[a] (°C)	b.p. (°C/mmHg)	n_D^{20}	Analysis Found % C	H	F	Calculated % C	H	F
m-AcO · $C_6H_4(CF_2)_3C_6H_4$-*m*-OAc	58–9			54·1	3·3	27·1	54·3	3·3	27·2
m-HO · $C_6H_4(CF_2)_3C_6H_4$-*m*-OH	99–100			53·5	3·0	34·1	53·6	3·0	33·9
p-AcO · $C_6H_4(CF_2)_3C_6H_4$-*p*-OAc	125			54·7	3·3	27·3	54·3	3·3	27·2
m-EtO_2C · $C_6H_4(CF_2)_3C_6H_4$-*m*-CO_2Et		170/0·1		56·1	4·0	23·5	56·2	4·0	25·5
m-HO_2C · $C_6H_4(CF_2)_3C_6H_4$-*m*-CO_2H[k]	253			52·0	2·8	28·7	52·1	2·5	29·1
p-MeO_2C · $C_6H_4(CF_2)_3C_6H_4$-*p*-CO_2Me	128–30			55·7	3·5	26·1	54·3	3·3	27·2
p-HO_2C · $C_6H_4(CF_2)_3C_6H_4$-*p*-CO_2H[k]	355			52·0	2·5	28·9	52·1	2·6	29·1
 [b]		140/15	1·4910						
 [l]	115–8								
	62–4			51·1	2·9	37·1	51·0	2·6	37·2

		160(bath)/0·01	1·4740	52·1	2·7	44·8	52·4	2·4	45·2
$C_6H_5(CF_2)_4C_6H_5$[m]	55–6			54·0	3·0	43·4	54·3	2·8	42·9
	102–3			44·1	2·5	35·9	44·0	2·5	36·1

[a] uncorrected

[b] purified by preparative-scale GLC and analysed by MS

[c] by Siwoloboff's method

[d] lit[27] b.p. 127–127·6°, n_D^{20} 1·4112

[e] lit[28] b.p. 127–8°, n_D^{20} 1·3875

[f] equiv. 392; requires equiv. 390

[g] lit[2] b.p. 200°, n_D^{25} 1·3576

[h] lit[4] m.p. 43°, b.p. 193°

[i] lit[6] b.p. 74–6°/0·24 mmHg

[j] supercooled liquid

[k] Acid obtained by hydrolysis of corresponding ester

[l] analysed by MS

[m] lit[26] m.p. 52–3°.

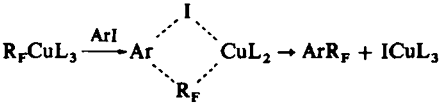
The rapid thermal decomposition of the fluoroalkylcopper XV to give XVI would be expected to occur at temperatures higher than the reaction temperature ($<127°$) in DMSO or DMF, but it is possible that XV and other fluoroalkylcoppers are less stable in DMAC. The products XI, XII, XIII, XIV, and XVI are consistent with decomposition by a radical mechanism, which is in contrast to the decomposition of arylcopper[13] and vinylcopper[16] compounds where free-radical intermediates are not formed, and is more akin to that of alkylcopper compounds where thermal decomposition can occur by both radical and non-radical pathways according to structure.[17] It is noteworthy than no olefinic products resulting from loss of fluorine by an ionic mechanism were formed, since it has been suggested[13] that perfluoro-t-butylcopper may be in equilibrium with cuprous fluoride and perfluoroisobutene.

Clearly, the fluoroalkylcopper compounds are much more thermally stable than alkylcopper compounds: solutions of methylcopper-tributylphosphine complexes in ether are stable only at sub-ambient temperatures.[18] Recently, pentafluorophenylcopper and perfluoro-t-butylcopper have been prepared by metathetical reactions, and they also were found to be appreciably more thermally stable than their hydrocarbon analogues.[13] These as well as our own observations are in general agreement with the ability of fluorine to stabilise carbon to transition metal σ-bonds.[19]

Mechanism of the fluoroalkylation reaction

The mechanism of fluoroalkylation must be similar to that operating in reactions of halogenoaromatic compounds with cuprous salts[20] or cuprous acetylides.[21] In the metallation stage the fluoroalkylcopper compound would be formed as a solvated complex which may be associated with cuprous iodide remaining in solution. In the second stage, coordination of aromatic halide[21] is followed by an exchange of ligands at copper:

$$R_FI \xrightarrow[\text{Solvent L}]{\text{Cu}} R_FCuL_3 + ICuL_3$$



$$R_FCuL_3 \xrightarrow{\text{ArI}} \text{Ar}\overset{\text{I}}{\underset{R_F}{\cdots}}\text{CuL}_2 \rightarrow ArR_F + ICuL_3$$

A coordinating solvent must be present for the overall fluoroalkylation process to succeed, although a very small amount is effective: dilute solutions of either DMSO or pyridine in an inert diluent (e.g. hexafluorobenzene) promoted reactions in very high yield. These reactions were successful even when the molar ratio of coordinating solvent to iodofluoroalkane was less than one, although reaction times were a factor of 10 or more greater than usual. The metallation stage requires a solvent which is a reasonably good ligand for copper in order to stabilise the fluoroalkylcopper compound and to assist reaction by dissolving cuprous halides, thus keeping the copper clean. The second stage should have similar solvent requirements to reactions involving cuprous salts,[20] and similar changes of reaction rate on changing from one solvent to another might be expected to occur, reactions being slower in solvents which are better ligands for copper. However, even at the lower temperatures of 70–100° fluoroalkylations were not noticeably slower in pyridine, which is a better ligand for copper than the other solvents studied. To some extent the two stages of reaction have conflicting solvent requirements, and with some solvents the metallation stage could be the rate-controlling step in the overall process. The solvent requirements of the whole fluoroalkylation reaction appear to be best met by DMSO.

The mechanism is well supported by the observed order of ease of displacement of aromatic halogen, I > Br ≫ Cl. It would also be expected from observations on the reactions of cuprous salts[20] that this reaction would be uniquely effected by copper, that is by the fluoroalkylcoppers. This is supported by our finding that many other metals were ineffective under the same conditions, including some which are known to form stable fluoroalkylorganometallic compounds, for example, zinc and mercury.

The fluoroalkylcopper compounds represent a very useful addition to the range of copper derivatives available for this general class of aromatic substitution reactions; their interaction with halogenoethylenes has also been described.[22] Their lack of reactivity towards water and other protic reagents allows the fluoroalkylation in good yield of aromatic halides bearing free carboxyl, amino or hydroxyl groups. This is in direct contrast to the Ullmann biaryl synthesis which is strongly inhibited[23,24] by the presence of such groups. The stability of the fluoroalkylcopper compounds in solution indicates that they are not ionically dissociated, and even on thermal decomposition, products resulting from radicals rather than from free carbanions are formed. Nor are ionic decomposition products formed during reaction with the halogenoaromatics, indicating that free carbanions are not involved in the fluoroalkylation.

In comparison with other methods,[2–6] this route to (fluoroalkyl)aromatic compounds offers certain advantages: fluoroalkyl groups can be introduced at predetermined positions on the aromatic nucleus; the products are isomerically pure; both the iodoaromatic and iodofluoroalkane may bear a variety of substituents; and a very convenient method is provided for the direct introduction of certain fluoroalkylene groups into aromatic structures.

EXPERIMENTAL

Starting materials. Monoidofluoroalkanes were used as purchased (CF_3I, C_3F_7I, and $C_7F_{15}I$), prepared by telomerization of C_2F_4 with C_3F_7I, or prepared from fluoroalkanoyl chlorides.[9] Di-iodoperfluoroalkanes were prepared from perfluoroalkanedioyl dichlorides.[9] The halogenoaromatic compounds were used as purchased, or prepared from the corresponding amines. Polar aprotic solvents were dried by standard procedures: distillation at reduced pressure from P_2O_5 for DMF, DMAC and HMPA; distillation from KOH for pyridine and 2,6-lutidine; distillation at reduced pressure from CaH_2 for DMSO; distillation at reduced pressure for sulpholane. Copper bronze was activated by treatment with iodine and then washed with HCl in acetone, followed by acetone alone.

Gas-liquid chromatography. The progress of all the fluoroalkylation reactions was followed by GLC where possible, using a low loading of silicone elastomer gum on a diatomite support (e.g. column 0·25 in dia × 5 ft, 3 to 5% E301 on AW DMCS Chromosorb G, 60–70 mesh). Many products were purified by by preparative-scale GLC (column 0·375 in dia × 20 ft, 30% SE30 on Chromosorb W, 45–60 mesh; or column 0·5 in dia × 10 ft, 20% SE52 on AW DMCS Chromosorb W, 60–80 mesh).

Preparation of fluoroalkyl-substituted aromatic compounds

Five experimental procedures (A–E) were employed, which had many features in common. All preparations were done either *in vacuo*, or under an inert atmosphere of nitrogen or argon. Where possible, the internal temperature of the reaction mixture and the external temp of the heating bath were continuously monitored, enabling the course of the exothermic reaction to be observed and good temp control to be maintained. The results of some preparations are summarized in Tables 1, 2, and 3, and the physical properties of the various products in Table 4. Mass spectroscopy was used extensively to identify the products, and some of these results have been reported.[25]

Method A by preforming the fluoroalkylcopper. The iodofluoroalkane was heated with a stirred suspension of copper bronze in the selected solvent to a temp at which reaction occurred (usually indicated by an exotherm) until reaction was adjudged to be complete, the temp and time being indicated at (i) in Tables 1 and 2. The rate at which the iodofluoroalkane was consumed could often be followed by GLC. The resulting soln was filtered in an inert atmopshere if an excess of Cu bronze was present before treatment with the halogenaromatic compound; the temp and time required to complete the reaction is indicated at (ii) in Tables 1 and 2. The products were isolated by treating the mixture with water and either Et_2O or CH_2Cl_2, filtering to remove cuprous salts, washing the organic phase with water until free from the reaction solvent, and finally distilling the organic phase.

Method B by having all the reactants together initially—open flask. The iodofluoroalkane, halogenoaromatic compound, Cu bronze, and solvent were stirred and heated at the required temp for the time indicated in Tables 1 and 2. In the initial stages, careful temp control of the mixture was required to prevent over-heating caused by the exothermic reaction. The products were isolated as in A.

Method C by having all the reactants together initially—sealed tube. The reactants were sealed in a borosilicate glass tube *in vacuo* and heated in a Carius furnace at the temp and for the time indicated in Table 1. It was possible to judge whether reaction had occurred by the state of the Cu bronze, and in this way the temp could be increased until reaction took place. The products were isolated as in A.

Method D by addition of the iodofluoroalkane at the reaction temperature. The halogenoaromatic compound, Cu bronze, and solvent were stirred together, generally at about 120°, while the iodofluoroalkane, alone or in soln, was added (with materials b.p. $<100°$, the addition was made below the surface of the hot soln). The time and temp for the addition is shown at (i) in Tables 1, 2 and 3; the reaction mixture was stirred and heated for the further time shown at (ii). The products were isolated as in A.

Method E by addition of the copper at the reaction temperature. The iodofluoroalkane, halogenoaromatic compound, and DMSO were stirred together at the the reaction temp. Cu was added in several portions at the rate at which it was consumed in the exothermic reaction. The temp and time for the addition appear at (i) in Table 2, and the further period at (ii). The products were isolated as in A.

Perfluoroheptylcopper

1-Iodoperfluoroheptane (10 g, 0·020 mole), Cu bronze (3·0 g, 0·048 g atom) and DMSO (20 ml) were stirred and heated in an argon atm at 106° (bath) for 45 min. On standing and cooling, the excess of Cu and a ppt settled, leaving a clear green-amber soln. In an argon atm (glove box), the clear soln was decanted into deoxygenated water (50 ml); cuprous iodide and a pale blue oil were precipitated. The oil was taken into ether (30 ml), the ether soln was washed with water (5 × 30 ml), dried ($MgSO_4$) and filtered to give a clear, pale amber soln (26 ml). 1-Iodoperfluoroheptane was shown to be absent from this soln by GLC and the soln was also free from cuprous iodide and DMSO (Na fusion).

Portions of the ether soln were evaporated (at 20°/0·05 mmHg) for 90 min to give a clear green-amber syrup which was essentially *perfluoroheptylcopper* (Found: Cu, 12·3, 13·3. $C_7F_{15}Cu$ requires: Cu, 14·6. $C_7F_{15}Cu \cdot C_4H_{10}O$ requires: Cu, 12·6%). The compound solidified on standing at room temp, but decomposition also occurred with separation of free Cu.

Perfluoroheptylcopper (0·72 g, 0·0017 mole), obtained similarly from the ether soln (4 ml), was dissolved in DMSO (3 ml) and the soln heated with iodobenzene (0·70 g, 0·0034 mole) in an argon atm at 120° (bath) for 15 min. The usual isolation procedure gave (perfluoroheptyl)benzene (0·47 g, 65%), identified by GLC and its IR spectrum.

The ether soln rapidly discoloured in air, finally becoming green, and a green solid was obtained on evaporation. Treatment of this with dil H_2SO_4aq gave perfluoroheptanoic acid, identified by its IR spectrum and converted into its *S*-benzylisothiouronium salt, m.p. 180–182° (Found: C, 34·5; H, 2·0; F, 47·8. Calc. for $C_{15}H_{11}O_2F_{13}N_2S$: C, 34·9; H, 2·2; F, 47·9%).

Preparation and decomposition of 3-*phenylhexafluoropropylcopper*

1-Iodo-3-phenylhexafluoropropane (7·1 g, 0·020 mole), Cu bronze (2·5 g, 0·040 g atom) and dry DMSO (30 ml) were stirred and heated in an argon atm at 120° (bath) until all the Cu had been consumed (25 min). On allowing the mixture to cool to 20°, the ppt settled to leave a clear soln. GLC analysis showed that all the iodo compound had been consumed.

An aliquot of the soln (5 ml) gave, on reaction with iodobenzene at 120° for 10 min, 1,3-diphenylhexafluoropropane in 60% yield (Table 1).

Dry air was bubbled through another aliquot (4 ml) at 20° for 100 min. A deep, clear, blue-green colour developed which became very dark and then faded to pale green. GLC analysis indicated the presence of 1-iodo-3-phenylhexafluoropropane. Water was added, the mixture extracted with CH_2Cl_2, and the dried soln distilled to give a residue of 1-iodo-3-phenylhexafluoropropane (0·6 g, 64%), identified by its IR spectrum.

The remaining soln (21 ml) was heated in an argon atm at 150–155° (bath) for 5 hr. A sample (1 ml) of the heated soln was removed and treated with iodobenzene (0·07 g) at 120°. GLC analysis showed that no 1,3-diphenylhexafluoropropane was formed. The remaining mixture was treated with CH_2Cl_2 (100 ml), filtered, washed thoroughly 4 times with water, dried, and the CH_2Cl_2 removed to give a brown oil (2·35 g). GLC analysis indicated the presence of 3 components. A portion of the oil was separated by preparative-scale GLC to give (i) a mixture of 1-phenyl-3*H*-hexafluoropropane (yield, by GLC and MS, 35%) and 1,1,2,2,3,3-hexafluoroindane (yield, by GLC and MS, 25%) identified by MS, molecular ions at 228 ($C_6H_6F_6$) and 226 ($C_6H_4F_6$) and a consistent fragmentation pattern; (ii) 4-phenyl-2,2,3,3,4,4-hexafluorobutyl methyl sulphide (yield, by GLC, 4%) identified by MS, molecular ion at 288 ($C_{11}H_{10}F_6S$) and a consistent fragmentation pattern; and (iii) 1,6-diphenyldodecafluorohexane (yield, by GLC, 13%) identified by MS, molecular ion at 454 ($C_{18}H_{10}F_{12}$) and a consistent fragmentation pattern.

NMR spectroscopy. Fluorine- and proton-magnetic resonance spectra were recorded[8] for the compounds: 1-phenyl-3*H*-hexafluoropropane; 2-phenylheptafluoropropane; 1-(*m*-acetoxyphenyl)-3*H*-hexafluoropropane; 1-(*m*-acetoxyphenyl)heptafluoropropane; 1-phenylpentadecafluoroheptane; 1,3-diphenylhexafluoropropane; and 1,3-di(*m*-tolyl)hexafluoropropane. The spectrum in each case confirmed the structure given.

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