Polyfluoroaryl Organometallic Compounds. Part IX.[1] Reactions of Polyfluoroaryl-lithiums with Dimethyl Carbonate. Octafluorofluoren-9-one

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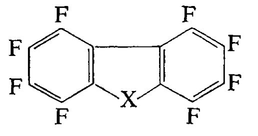
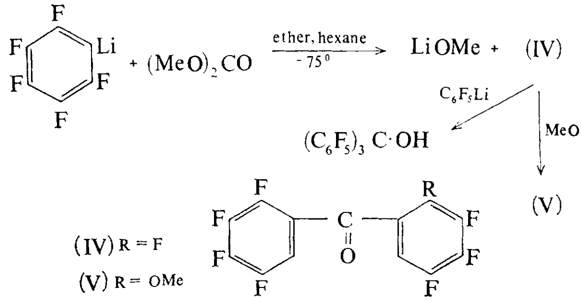
Pentafluorophenyl-lithium reacts with dimethyl carbonate, under special conditions, to give a high yield of decafluorobenzophenone, but the corresponding reaction of *o*-bromotetrafluorophenyl-lithium is complicated by a novel exchange reaction, which is discussed. Octafluorofluoren-9-one is synthesised by reaction of 2,2'-dilithio-octafluorobiphenyl with dimethyl carbonate.

SOME of the previous papers in this series [1-4] have been concerned with the synthesis of polyfluoro-derivatives of the dibenzo-series [*e.g.* (I) and (II)] by use of polyfluoroaryl-lithiums, and with nucleophilic substitution in these systems; the related work presented here has led to the synthesis of octafluorofluoren-9-one (III).

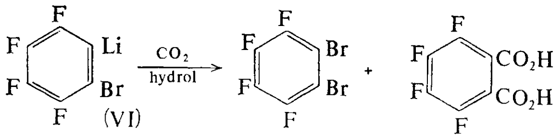


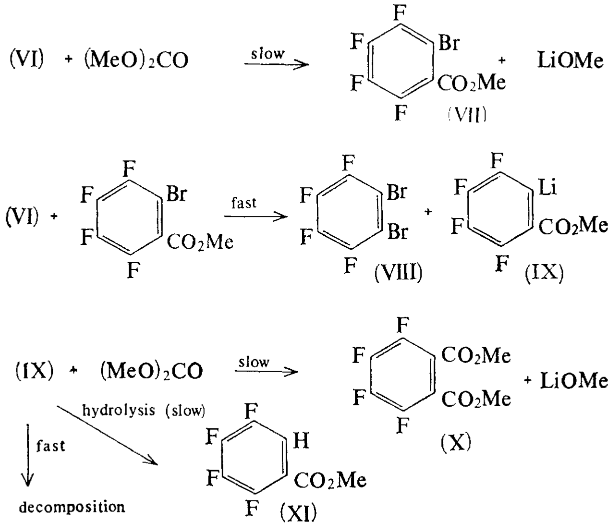
(I) X = S
(II) X = O
(III) X = CO

As a method of preparation of polyfluoroaryl ketones, the reaction of pentafluorophenyl-lithium with dimethyl carbonate was investigated, but the initial attempts were unsuccessful in that a methoxy-derivative (V) was the principal product, with some tris(pentafluorophenyl)methanol.[5] The orientation of the methoxy-substitution (V), *ortho* to the carbonyl group, is not that which is observed in the reaction of sodium methoxide with decafluorobenzophenone; this will be discussed in a later publication.[6] These difficulties were overcome by adding the stoicheiometric amount of dimethyl carbonate rapidly, to inhibit the formation of the carbinol, and the mixture was hydrolysed at —20°, thus reducing the extent of formation of the methoxy-derivatives.[7] Under these conditions a 70% yield of decafluorobenzophenone (IV) was obtained; this appears to be a more convenient synthesis of this compound than those previously reported.[8,9]



Attempts to extend this reaction to *o*-bromotetrafluorophenyl-lithium were, surprisingly, complicated by an exchange reaction which appears similar to that found recently by Tamborski and Soloski,[10] who obtained a mixture of 1,2-dibromotetrafluorobenzene and tetrafluorophthalic acid from carbonation of *o*-bromotetrafluorophenyl-lithium. The results of the reaction of *o*-bromotetrafluorophenyl-lithium with dimethylcarbonate are best accounted for according to Scheme 1.





SCHEME 1

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[1] Part VIII, R. D. Chambers, J. A. Cunningham, and D. J. Spring, *J. Chem. Soc.* (*C*), 1968, 1560.

[2] R. D. Chambers, J. A. Cunningham, and D. J. Spring, *Tetrahedron*, 1968, **24**, 3997.

[3] R. D. Chambers and J. A. Cunningham, *Chem. Comm.*, 1966, 469.

[4] R. D. Chambers and J. A. Cunningham, *Chem. Comm.*, 1967, 583.

[5] R. Filler, Chen-Shen Wang, M. A. McKinney, and F. N. Miller, *J. Amer. Chem. Soc.*, 1967, **89**, 1026.

[6] R. D. Chambers and D. J. Spring, forthcoming publication.

[7] A similar result was communicated by R. Filler, at the 4th International Symposium on Fluorine Chemistry, Estes Park, Colorado, 1967.

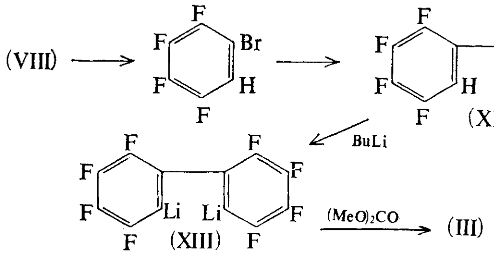
[8] A. K. Barbour, M. W. Buxton, P. L. Coe, R. Stephens, and J. C. Tatlow, *J. Chem. Soc.*, 1961, 808.

[9] P. Sartori and M. Weidenbruch, *Angew. Chem. Internat. Edn.*, 1965, **4**, 1072.

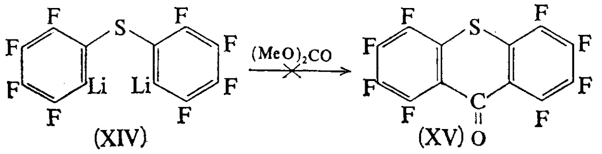
[10] C. Tamborski and E. J. Soloski, *J. Organometallic Chem.*, 1967, **10**, 385.

After hydrolysis, the principal component of the product was 1,2-dibromotetrafluorobenzene (VIII), but this does not reflect failure of the initial exchange reaction, in the preparation of *o*-bromotetrafluorophenyl-lithium (VI) from 1,2-dibromotetrafluorobenzene, since this exchange has been shown to proceed rapidly under these conditions.[10,11] Therefore the dibromo-compound (VIII) must be formed by a rapid exchange between *o*-bromotetrafluorophenyl-lithium and the intermediate ester (VII). A puzzling feature of the reaction is that the amount of 1,2-dibromotetrafluorobenzene formed was not matched by an equivalent quantity of the diester (X) or the hydro-compound (XI) formed on hydrolysis. This indicates that the lithio-ester (IX) does not react rapidly with dimethyl carbonate and that a decomposition process competes effectively with hydrolysis. The Table shows the variation in the product ratios under a variety of conditions. The instability of the lithio-ester (IX) is indicated by the higher yield of the ester (XI) when hydrogen chloride was bubbled through the mixture 15 min. after addition of the dimethyl carbonate, but even under these conditions *ca.* half of the lithio-ester (IX) had decomposed in this time. Also, as expected, the product ratios are quite sensitive to the relative proportions of the starting materials. By adding, rapidly, a ten-fold excess of dimethyl carbonate the proportion of the bromo-ester (VII) can be significantly increased, but not to the point where it predominates. This shows that the complicating bromine–lithium exchange is extremely rapid and must arise because of the well known carbanion-stabilising influence of the ester group.

The complications outlined above precluded the use of *o*-bromotetrafluorophenyl-lithium in the synthesis of octafluorofluoren-9-one (III), in a scheme analogous to that used for octafluorodibenzothiophen (I).[2,3] Instead, a synthesis was developed (Scheme 2) [12,13] from the commercially available 1,2-dibromotetrafluorobenzene (VIII). Choice of solvent was important in the reaction of the dilithio-derivative (XIII) with dimethyl carbonate. Use of ether–hexane gave a complex product from which the fluorenone (III) was obtained, in low yield, by recrystallisation of the product from hexane, but when tetrahydrofuran–hexane was used the product was mainly the fluorenone (III) (60% yield). Surprisingly, we could not achieve the corresponding synthesis of octafluorothioxanthone (XV) from the dilithio-derivative (XIV), even though the latter is known to react with sulphur dichloride to give octafluorothianthren.[11] Only polymeric products were obtained and the reason for the different behaviour of the two systems (XIII) and (XIV) is not yet clear.



Scheme



The mass spectrum of octafluorofluorenone showed an intense peak at m/e 296 (M — CO); a similar fragmentation is exhibited by fluorenone itself.[14] It was previously noted that octafluorodibenzothiophen 5,5-dioxide gave an intense peak corresponding to M — SO, and it was subsequently established that loss of SO could be achieved by pyrolysis, to give octafluorodibenzofuran.[1,4] Similar pyrolyses of octafluorofluorenone did not yield octafluorobiphenylene; instead, the fluorenone was recovered up to a temperature of *ca.* 800°, where extensive decomposition occurred. Nucleophilic substitutions in octafluorofluorenone will be described later.[6]

EXPERIMENTAL

1,2-Dibromotetrafluorobenzene was obtained from the Imperial Smelting Corporation Ltd. The ^{19}F and ^{1}H n.m.r. spectra were recorded with a Perkin-Elmer R 10 spectrometer and, unless otherwise stated, fluorine chemical shifts refer to internal hexafluorobenzene and negative signs refer to low field. Analyses were carried out under the supervision of T. F. Holmes.

Reaction between Pentafluorophenyl-lithium and Dimethyl Carbonate.— *Decafluorobenzophenone.* (*a*) 2·7M-Butyl-lithium (11·0 ml., 29·8 mmoles) was added dropwise to a solution of pentafluorobenzene (5·0 g., 29·8 mmoles) in a mixture of dry ether (60 ml.) and hexane (40 ml.) in a flask (250 ml.) previously purged with dry nitrogen and cooled to −78°. The mixture was stirred for 2 hr. at this temperature before neat freshly distilled dimethyl carbonate (1·34 g., 14·9 mmoles) was added, quickly, with vigorous stirring which was continued for a further 0·5 hr. The temperature of the mixture was then allowed to rise to −20° before addition of dil. sulphuric acid (30 ml.). Water was added and the organic layer was separated and dried (CaCl$_2$). Removal of the solvent left a yellow solid from which a white solid (4·0 g.) was sublimed at 70°/0·001 mm.; this was shown by analytical g.l.c. to be mainly decafluorobenzophenone (70%) with traces of nonafluoro-2-methoxybenzophenone (see later) (*ca.* 1%) and tris(pentafluorophenyl)-methanol (*ca.* 5%). Recrystallisation of the mixture from

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[11] R. D. Chambers, J. A. Cunningham, and D. A. Pyke, *Tetrahedron*, 1968, **24**, 2783.

[12] J. F. Tilney-Bassett, *Chem. and Ind.*, 1965, 693.

[13] L. J. Belf, M. W. Buxton, and J. F. Tilney-Bassett, *Tetrahedron*, 1967, **23**, 4719.

[14] J. H. Beynon, "Mass Spectrometry," Elsevier, Amsterdam, 1960, p. 272.

light petroleum (b.p. 40—60°)–chloroform (4 : 1 v/v) gave pure decafluorobenzophenone, m.p. 90—91° (lit.,[8] 91—92°) (Found: C, 43·1; F, 52·2. Calc. for $C_{13}F_{10}O$: C, 43·1; F, 52·5%), ^{19}F n.m.r. peaks at −2·6, −16·4, and −21·3 p.p.m. and the following F–F coupling constants: $J_{2,3}$ 24·7 ∓ 0·3, $J_{2,4}$ 5·0 ∓ 0·1, $J_{2,5}$ 10·8 ∓ 0·2, and $J_{3,4}$ 19·7 ∓ 0·1 c./sec.

(*b*) In an experiment with quantities of reagents equivalent to those used in (*a*), the dimethyl carbonate in ether (20 ml.) was added dropwise and the mixture was allowed to attain room temperature before hydrolysis with dilute acid. Under these conditions a white solid (3·9 g.) was obtained by sublimation of the resultant oil at 70°/0·001 mm. Analysis by g.l.c. showed this to be a mixture of four components (35 : 40 : 5 : 20), which were separated by preparative-scale g.l.c. (silicone elastomer, 230°) into decafluorobenzophenone, *nonafluoro-2-methoxybenzophenone* (Found: C, 45·0; H, 0·8; F, 45·6. $C_{14}H_3F_9O_2$ requires C, 44·9; H, 0·8; F, 45·7%), m.p. 77—78°, an octafluorodimethoxybenzophenone (*m/e* 386), of unknown orientation, and tris(pentafluorophenyl)methanol (Found: C, 43·0; H, 0·4; F, 53·6. Calc. for $C_{19}HF_{15}O$: C, 43·0; H, 0·2; F, 53·8%), m.p. 115—116° (lit.,[5] 116—117°), in order of increasing retention time. The orientation of the nonafluoro-2-methoxybenzophenone was assigned on the basis of the ^{19}F n.m.r. spectrum, which showed the following absorptions (assignments in brackets): −7·7 (3), −12·9 (4), −0·0 (5), −19·3 (6); −20·9 (2′,6′), −2·0 (3′,5′), −14·5 (4′) p.p.m. These shifts correspond with those calculated for 2-substitution, by use of decafluorobenzophenone as reference, on the basis of the known effect on fluorine shifts of introducing a methoxy-group[15] into a polyfluorobenzene system, but differ from the calculated shifts for other orientations.

(*c*) Pentafluorophenyl-lithium was obtained by bromine–lithium exchange between bromopentafluorobenzene and butyl-lithium, and the lithio-derivative was used in an experiment similar to (*a*). A lower yield (*ca.* 55%) of decafluorobenzophenone was obtained in this case; this is partly attributable to the greater difficulty in final purification from butyl bromide, which is produced in the exchange reaction.

Reactions of o-*Bromotetrafluorophenyl-lithium with Dimethyl Carbonate.*—In a typical experiment, a 2·5M-solution (6·5 ml.) of butyl-lithium in hexane was added to dry hexane (20 ml.) and the resulting solution was added dropwise, during ½ hr., to 1,2-dibromotetrafluorobenzene (5·0 g., 16·2 mmoles) in ether–hexane (3 : 2; 100 ml.) in a flask which had been purged with dry nitrogen and cooled to −78°. The mixture was stirred for 2 hr. and dimethyl carbonate (14·6 g., 162·0 mmoles) was added, rapidly, with vigorous stirring, which was continued for 1 hr. Then the temperature was allowed to rise to −20° during 1 hr., and the red solution was hydrolysed with dilute sulphuric acid (30 ml.). The organic layer was separated and dried ($CaCl_2$) and the solvent was distilled off through a short packed column; the residue was then distilled at 80—100°/1 mm. to yield a colourless liquid (3 g.) and a tarry residue. Analytical scale g.l.c. indicated the presence of four components (3 : 44 : 45 : 8) which were separated by preparative-scale g.l.c. into *methyl* 2,3,4,5-*tetrafluorobenzoate* (XI) (Found: C, 45·7; H, 1·6. $C_8H_4F_4O_2$ requires C, 46·1; H, 1·9%), 1,2-dibromotetrafluorobenzene, identified spectroscopically, *methyl 2-bromotetrafluorobenzoate* (VII) (Found: C, 33·3. $C_8H_3BrF_4O_2$ requires C, 33·5%), and *dimethyl tetrafluorophthalate* (Found: C, 45·7; H, 2·2. $C_{10}H_6F_4O_4$ requires C, 45·1; H, 2·3%), in order of increasing retention time.

This experiment was varied in a number of ways and the conditions and results are summarised in the Table.

Reactions of *o*-bromotetrafluorophenyl-lithium with dimethyl carbonate (in hexane–ether unless otherwise indicated)

Reagent ratio *	Hydrolysis temp.	Hydrolysis agent	Products (%) (XI)	(VIII)	(VII)	(X)
2 : 1	+20°	Dil. H_2SO_4	*ca.* 3	78	19	*ca.* 0
1 : 1	−20	Dil. H_2SO_4	<1	70	30	*ca.* 0
1 : 1 [a]	−20	Dil. H_2SO_4	<1	73	27	*ca.* 0
1 : 10	−20	Dil. H_2SO_4	3	44	45	8
1 : 35 [b]	−20	Dil. H_2SO_4	28	51	17	4
1 : 1	−20	MeOH [c]	3	55	36	6
1 : 1	−75	HCl [d]	28	52	15	5

* Aryl-lithium to dimethyl carbonate.

[a] Solvent hexane. [b] The lithio-derivative was poured on a dimethyl carbonate slush at −75°; the carbonate may not have been completely dry in this experiment. [c] Methanol (5 ml.) added, followed by dil. hydrochloric acid after a few min. [d] Anhydrous hydrogen chloride bubbled through the mixture at −75°.

^{19}F N.m.r. spectra: (VII) −24·2 (6), −8·3 (5), −12·1 (4), and −34·4 (3) p.p.m., $J_{5,6}$ 20·8, $J_{4,6}$ 4·4, $J_{3,6}$ 10·2, $J_{4,5}$ 19·5, $J_{3,5}$ 4·5, $J_{3,4}$ 21·0 c./sec., corresponding with the values previously observed for *ortho*-, *meta*-, and *para*-F–F coupling constants;[16] (XI) −24·1 (2), −14·2 (3), −8·3 (4), and −28·0 (5) p.p.m.

The mass-spectra of these three compound each showed M^+ and intense M − MeO and M − MeO − CO peaks, in each case supported by appropriate metastable peaks. In each case the M − MeO peak was the most abundant.

Octafluorofluoren-9-*one*.—(*a*) To tetrahydrofuran (60 ml.) freshly distilled from potassium, in a flask previously purged with dry nitrogen and cooled to *ca.* −75°, was added 2·4M-butyl-lithium (5·0 ml., 12·1 mmoles) in dry hexane (30 ml.), dropwise, followed by a solution of 2*H*,2′*H*-octafluorobiphenyl (1·8 g., 6·05 mmoles) in tetrahydrofuran (30 ml.). The mixture was stirred at −75° for 4 hr. and then dimethyl carbonate (0·55 g., 6·1 mmoles) was added rapidly with vigorous stirring. The temperature was maintained for a further 1·5 hr. and the mixture was then allowed to warm slowly to 0° before addition of dilute hydrochloric acid. The organic layer was separated and dried ($CaCl_2$), and the solvent was removed; the residue was sublimed at 120°/10^{-2} mm. to give an orange solid (1·2 g.) and a tarry residue. Analytical-scale g.l.c. indicated that the solid was a single component (60% yield); recrystallisation from hexane–methylene dichloride gave *octafluorofluoren*-9-*one*, m.p. 195° (sublimed) (Found: C, 48·0; F, 46·6. $C_{13}F_8O$ requires C, 48·2; F, 46·9%), ^{19}F n.m.r. peaks at −30·3, −24·9, −19·6, and −11·9 p.p.m. (from internal C_6F_6). The u.v. spectrum showed strong absorption at 256 (ε 55,700), 240sh (44,400), and 207 (19,200) mμ; compared with the spectrum of fluorenone this appeared to have more bands but the strongest bands from the perfluoro-compound

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[15] Data collected in ref. 2.

[16] J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," vol. 2, Pergamon, Oxford, 1965, p. 903.

were of lower intensity than those from fluorenone. The mass spectrum showed an intense parent peak (m/e 324) and an intense peak at m/e 296 (M — CO) (metastable peak at *ca.* 270). The i.r. spectrum showed a strong C=O stretch at 1737 $cm.^{-1}$; this corresponds to the value of 1720 $cm.^{-1}$ for fluorenone [17] and indicates that the fluorine atoms have little effect.

(*b*) 2·4M-Butyl-lithium in hexane (5·6 ml., 13·5 mmoles) was mixed with dry hexane (20 ml.) and added, dropwise, during ½ hr. to a solution of 2*H*,2′*H*-octafluorobiphenyl (2·0 g., 6·7 mmoles) in ether–hexane (3 : 2, 100 ml.) in a flask previously purged with dry nitrogen and cooled to *ca.* −75°. The mixture was stirred for *ca.* 5 hr. at this temperature and dimethyl carbonate (0·6 g., 6·7 mmoles) was added, rapidly, with vigorous stirring, which was continued for 1 hr. more. The temperature was then allowed to rise to −20°, during 1 hr., and the red solution was hydrolysed with dilute sulphuric acid. Then the organic layer was separated and dried ($CaCl_2$), and the solvent was distilled off. Sublimation of the residue gave a yellow solid, shown by g.l.c. to contain about six components, including starting material. Recrystallisation of the mixture from hexane gave pure octafluorofluoren-9-one. The other components of the mixture were not identified.

Pyrolysis.—Octafluorofluoren-9-one was pyrolysed in a flow system, as previously described for octafluorodibenzothiophen 5,5-dioxide.[1] At 800°, only starting material emerged from the tube (42% recovery) and g.l.c. analysis gave no indication of the presence of any other product. At lower temperatures, more starting material was recovered.

1-*Bromo*-2,3,4,5-*tetrafluorobenzene.*—The procedure was essentially that of Tilney-Bassett,[12] except that certain modification was necessary on the smaller scale. 1,2-Dibromotetrafluorobenzene (15·0 g., 48·7 mmoles) was added to zinc dust (3·5 g., 53·4 mmoles) in glacial acetic acid (80 ml.). The mixture was heated under reflux for 2 hr., during which time the zinc dissolved, and then steam was passed through for 1 hr. while the distillate was collected. The distillate was extracted with methylene dichloride and the organic layer was washed with sodium hydrogen carbonate solution until carbon dioxide evolution ceased. It was then separated and dried ($CaCl_2$) and the solvent was distilled off to leave 1-bromo-2,3,4,5-tetrafluorobenzene (8·3 g., 75%), which had the expected spectroscopic properties.

2H,2′H-*Octafluorobiphenyl.*—A mixture of dimethylformamide (40 ml.), copper bronze (5 g.), and 1-bromo-2,3,4,5-tetrafluorobenzene (8·0 g., 34·9 mmoles) was heated under reflux for 7 hr. in a flask previously purged with dry nitrogen. The excess of copper and the copper bromide produced were filtered off and the filtrate was poured into water and then extracted with ether. The combined extracts were separated and dried ($CaCl_2$), and the solvent was distilled off to yield a brown semi-crystalline solid which, when sublimed (70°/10^{-2} mm.), gave 2*H*,2′*H*-octafluorobiphenyl (3·6 g., 71%), which had the expected spectroscopic properties.[2]

We thank the S.R.C. for a grant (to D. J. S.), the Imperial Smelting Corporation for gifts of chemicals, and Professor W. K. R. Musgrave for his interest.

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[17] J. Deschamps, *Compt. rend.*, 1958, **246**, 2622.