Polyfluoroaryl Organometallic Compounds. Part XV.[1] Synthesis and Rearrangement of Polyhalogenoaryl α-Diketones †

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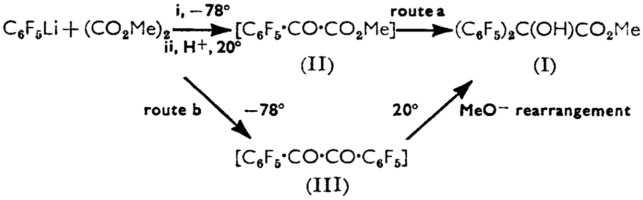
Decafluoro- and decachloro-benzil have been obtained by reactions of the corresponding aryl-lithiums with dimethyl oxalate in a process shown to involve the intermediacy of adducts. The unsymmetrical benzils $C_6F_5\cdot CO\cdot CO\cdot C_6H_5$ and $C_6H_5\cdot CO\cdot CO\cdot C_6Cl_5$ have been obtained by sequential additions of different aryl-lithiums to dimethyl or diethyl oxalate. Decafluorobenzil undergoes fast base-catalysed rearrangement to the benzilic acid or ester and it is proposed that the transition-state in the process has considerable benzenide character. Attempts to synthesise perfluorophenanthrene-9,10-quinone, by an analogous route, led only to products of rearrangement.

REACTIONS of polyfluoroaryl-lithiums with dimethyl carbonate provide good routes to decafluorobenzophenone and octafluorofluorenone.[2] In this paper we describe attempts to extend this approach to include similar reactions with dimethyl oxalate as routes to highly fluorinated α-diketones.

$$2Ar_FLi + (CO_2Me)_2 \longrightarrow (Ar_FCO)_2$$

Pentafluorophenyl-lithium [3] was prepared by lithium–hydrogen exchange between pentafluorobenzene and butyl-lithium, in a mixture of diethyl ether and hexane at —78°; its reaction with dimethyl oxalate at —78° followed by hydrolysis at room temperature gave no decafluorobenzil. Instead methyl decafluorobenzilate (I) was formed. The benzilic ester (I) could arise by either of two routes: (i) attack by two molecules of pentafluorophenyl-lithium at the same carbon atom in the dimethyl oxalate (route a) and (ii) initial formation of decafluorobenzil, followed by a benzilic ester rearrangement during the period of warm-up (route b). Therefore, in a comparable experiment, treatment with hydrogen chloride was carried out at —40° in an attempt to prevent rearrangement of the benzil (III), which was then obtained together with compounds (I) and (II), and tris(pentafluorophenyl)methanol (IV); the variation in percentage yield of products with the temperature at which hydrogen chloride was added is shown in the Table.



SCHEME 1

Isolation of the benzil (III) from these reactions indicates that the benzilic ester (I) is formed by rearrangement of compound (III), as indicated by route b, but

$$C_6F_5Li + (CO_2Me)_2 \downarrow$$

Temp. (°C)	(II)	+	(III)	+	(I)	+	$(C_6F_5)_3COH$ (IV)
−78	47		43				
−40	33		55		7		4
+20					79		11

the formation of tris(pentafluorophenyl)methanol (IV) is surprising. This alcohol (IV), is obtained readily, after hydrolysis, by reaction of pentafluorophenyl-lithium with decafluorobenzophenone [2,4] and it appears, therefore, that decafluorobenzophenone is formed, as an

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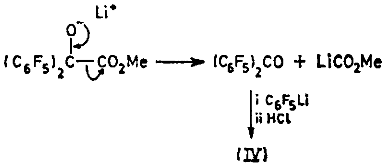
[1] Part XIV, R. D. Chambers and D. J. Spring, *J. Fluorine Chem.*, 1972, **1**, 309.

[2] R. D. Chambers and D. J. Spring, *J. Chem. Soc.* (*C*), 1968, 2394.

[3] R. J. Harper, E. J. Soloski, and C. Tamborski, *J. Org. Chem.*, 1964, **29**, 2385.

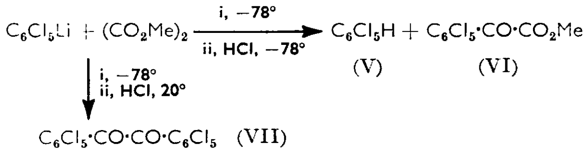
[4] R. Filler, Chen-Shen Wang, M. A. McKinney, and F. N. Miller, *J. Amer. Chem. Soc.*, 1967, **89**, 1026.

intermediate, by an unusual elimination process (Scheme 2).



SCHEME 2

Reactions of dimethyl oxalate with pentachlorophenyl-lithium,[5] generated by reaction of butyl-lithium with hexachlorobenzene, were carried out for comparison (Scheme 3). When hydrogen chloride was added at



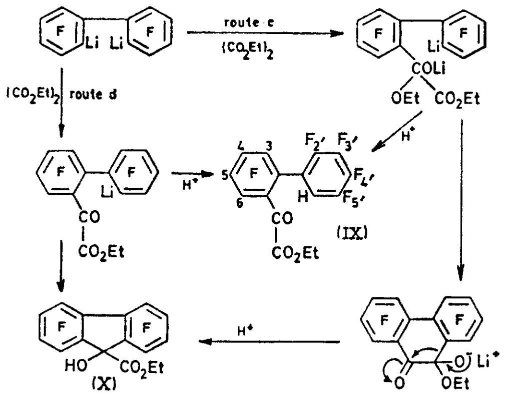
SCHEME 3

−78° then only compounds (V) and (VI) were obtained but a further reaction mixture which was hydrolysed at 20° gave a product from which a 20% yield of pure (VII) was obtained, after sublimation and recrystallisation, leaving further amounts of crude material. Also obtained from the reaction mixture was a small amount of a second component which appears to be the hydroxy-ester (VIII), but we were unable to confirm this structure by oxidation to decachlorobenzophenone.

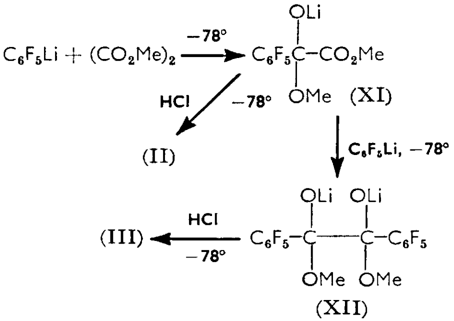
$$\underset{\text{(VIII)}}{(C_6Cl_5)_2C(OH){\cdot}CO_2Me} \xrightarrow{CrO_3}\!\!\!\!\!\!\!\times\;\; (C_6Cl_5)_2CO$$

In contrast to these results, attempts to extend these reactions with dimethyl oxalate to the synthesis of octafluorophenanthrene-9,10-quinone from 2,2'-dilithio-octafluorobiphenyl,[2,6] gave only the keto-ester [*i.e.* the methyl analogue of (IX)] on addition of hydrogen chloride at −78°. When diethyl oxalate was used the hydroxy-ester (X) was also obtained, together with (IX). In this case it is not possible to distinguish between the formation of (X) by a rearrangement reaction, route c (Scheme 4), or by stepwise nucleophilic attack at the same carbon atom routed; the complexities of this situation will become more apparent in the discussion of mechanism.

Mechanism.—Decafluorobenzil (III) is rearranged to the benzilic ester relatively rapidly even at −78°, in the presence of methoxide, and therefore appears to be of unprecedented activity in this process, *e.g.* in a comparable reaction with methoxide benzil required heating under reflux in methanol.[7] This raises an apparent anomaly because the benzil (III) is synthesised in a reaction which generates methoxide ion. The most likely explanation is that, during this synthesis, the intermediate keto-ester (II) exists in solution as the adduct (XI) and therefore directs further attack to the ester group. Likewise, the benzil (III) must exist in solution as an adduct, *e.g.* (XII), to prevent rearrangement to the benzilic ester (I). It is well known that compounds containing electronegative groups attached to carbonyl form stable adducts and the n.m.r. spectrum of (II), even in methanol, indicated that it exists in equilibrium with the adduct in solution.



SCHEME 4



SCHEME 5

Further support for the intermediacy of an adduct (XI) in the synthesis of decafluorobenzil comes from the reaction of pentafluorophenyl-lithium with methyl pentafluorobenzoylformate (II). The mixture was stirred for 3 h at −78° and hydrogen chloride was added at this temperature, but in this case the corresponding benzilic ester (I) was obtained in 79% yield with only 5% of the benzil (III). This contrasts with the reaction with dimethyl oxalate where, under similar conditions, addition of the second molecular proportion of pentafluorophenyl-lithium occurs much more slowly to yield the benzil (III).

Synthesis of Unsymmetrical Benzils.—Treatment of phenyl-lithium with ethyl pentafluorobenzoylformate (XIII), prepared in an analogous manner to (II), gave an intractable product, but when phenyl-lithium was added to the adduct (XIV), obtained by adding pentafluorophenyl-lithium to diethyl oxalate and maintaining the mixture at −78°, the unsymmetrical benzil (XV)

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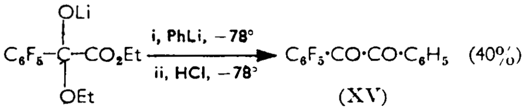
[5] M. D. Rausch, F. E. Tibbetts, and H. B. Gordon, *J. Organometallic Chem.*, 1966, **5**, 493.

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

[7] W. von E. Doering and R. S. Urban, *J. Amer. Chem. Soc.*, 1956, **78**, 5938.

was obtained. Nevertheless, with pentachlorophenyl-lithium and (XIV) no reaction occurred, but when pentafluorophenyl-lithium was added to methyl pentachlorobenzoylformate (VI), the mixed benzil (XVI) was obtained. These reactions reflect the greater reactivity of pentafluorophenyl-lithium over pentachlorophenyl-lithium and the fact that the benzil (XVI) is obtained in this reaction, rather than the corresponding benzilic ester, is most probably due to steric hindrance by the *ortho* chlorine atoms to attack at the carbonyl adjacent to the pentachlorophenyl group. It is surprising, therefore, that pentachlorophenyl-lithium reacts with (II) in the same way as pentafluorophenyl-lithium giving, in this case, the benzilic ester (XVII) by attack at the carbonyl attached to the aryl group in (II).

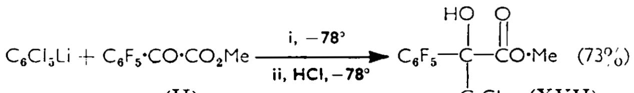


$$C_6F_5\text{—}\overset{\displaystyle OLi}{\underset{\displaystyle OEt}{C}}\text{—}CO_2Et \xrightarrow[\text{ii, HCl, }-78^\circ]{\text{i, PhLi, }-78^\circ} C_6F_5\cdot CO\cdot CO\cdot C_6H_5 \quad (40\%)$$

(XIV) (XV)

$$C_6F_5Li + C_6Cl_5\cdot CO\cdot CO_2Me \xrightarrow[\text{ii, HCl, }-78^\circ]{\text{i, }-78^\circ} C_6Cl_5\cdot CO\cdot CO\cdot C_6F_5 \quad (85\%)$$

(VI) (XVI)

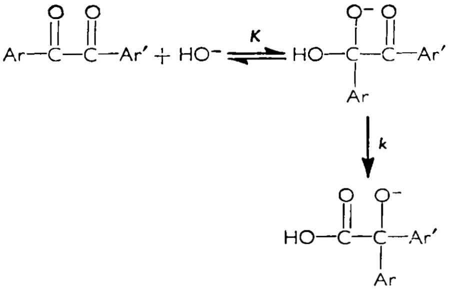


$$C_6Cl_5Li + C_6F_5\cdot CO\cdot CO_2Me \xrightarrow[\text{ii, HCl, }-78^\circ]{\text{i, }-78^\circ} C_6F_5\text{—}\overset{\displaystyle HO}{\underset{\displaystyle C_6Cl_5}{C}}\text{—}\overset{\displaystyle O}{C}\cdot Me \quad (73\%)$$

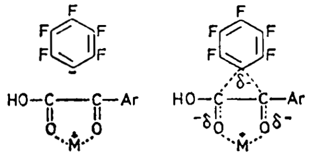
(II) (XVII)

These at first sight contradictory results probably arise because the steric effects from the *ortho* chlorine atoms in (VI) would be at a maximum in the transition state for attack at the adjacent carbonyl group, since the pentachlorophenyl group is fully bonded to the reaction centre. In the formation of (XVII), however, the steric effects from chlorine do not reach a maximum until well along the reaction co-ordinate. We cannot rule out possible effects arising from the degrees of association of pentafluorophenyl-lithium and pentachlorophenyl-lithium.

Mechanism of the Benzilic Acid and Ester Rearrangements.—The mechanism of the benzil–benzilic acid rearrangement is discussed even in relatively elementary textbooks, but the nature of the transition-state is by no means clearly defined. The rearrangement is generally recognised[8,9] as a two-stage process with the migration step rate-determining and the rate being given by Kk[base][benzil] (Scheme 6). The aryl group migrates with its electron pair and so this stage is, formally, an electrophilic aromatic substitution, but chloro-substituted phenyl groups migrate more quickly than phenyl[10] and the rate enhancement of five fluoro-substituents reported here is in keeping with the trend. This activating influence of electron-withdrawing groups has been rationalised by assuming a model for the transition state which is close to the initial state,[11] *i.e.* the adduct of base to the benzil. Nevertheless, a massive rate enhancement which we have now observed for decafluorobenzil relative to benzil (estimated as $\geqslant 10^5$) suggests a different situation. While pentafluorophenyl would stabilise the adduct of a benzil with base and result in activation, the aryl group is still relatively remote from the negative centre, whereas if the transition state involves formation of a tight ion pair, or even partial charge location on the aryl group (Scheme 7) the stabilising effect of fluorine would be massive and more in accord with the results reported here for pentafluorophenyl. The extent of this stabilising influence of fluorine on benzenide ions can be appreciated from the work of Streitweiser and his co-workers,[12] who have measured relative rates of base-catalysed H/D exchange and found, *e.g.* for fluorobenzene a rate of 6·3 × 10^5 for the *ortho*-position relative to benzene at 25°. They have also established that at 40° base-catalysed tritium exchange in pentafluorobenzene occurs much faster than in 1,3-difluorobenzene (1360 : 0·0061).[13]



SCHEME 6



SCHEME 7

The migration steps in the reactions described here are almost certainly intramolecular: rearrangement of decafluorobenzil by methoxide ion in excess of dimethyl carbonate gave solely methyl decafluorobenzilate and no cross-over products.

Doering and Urban[7] found that the reaction of benzil with ethoxide ion gave no ethyl benzilate but the product mixture arose from reduction of benzil to benzoin by hydride transfer from the alkoxide, followed by cleavage of the benzoin. In contrast, the reaction of decafluorobenzil (III) with ethoxide in ethanol, even at reflux temperature, gave ethyl decafluorobenzilate in quantitative yield, within seconds.

Since this work began, polyhalogenoarylcopper compounds have been developed and used to make deca-

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[8] K. C. Ingold, *Ann. Reports*, 1925, **25**, 124.

[9] S. Selman and J. F. Eastham, *Quart. Rev.*, 1960, **14**, 221.

[10] E. Pfeil, G. Geissler, W. Jacquemin, and F. Lomker, *Chem. Ber.*, 1956, **89**, 1210.

[11] G. S. Hammond, *J. Amer. Chem. Soc.*, 1955, **77**, 334.

[12] A. Streitwieser and F. Mares, *J. Amer. Chem. Soc.*, 1968, **99**, 644.

[13] A. Streitweiser, J. A. Hudson, and F. Mares, *J. Amer. Chem. Soc.*, 1968, **90**, 648.

fluoro- and decachloro-benzils[14] and decafluorobenzil has also been obtained from the reaction between bis-pentafluorophenylacetylene and bistrifluoromethyl nitroxide.[15]

EXPERIMENTAL

Unless otherwise stated the ^{19}F n.m.r. spectra were recorded with a Varian A56/60D or a Perkin-Elmer R10 spectrometer for samples dissolved in carbon tetrachloride. Fluorine chemical shifts refer to internal hexafluorobenzene, and negative signs refer to low field. Analyses were performed under the supervision of Mr. T. F. Holmes.

All reactions involving organo-lithium compounds were carried out in apparatus which had been baked in an oven and then purged with dry nitrogen. Ether and hexane were sodium-dried, and tetrahydrofuran was freshly distilled from lithium aluminium hydride.

Pentafluorophenyl-lithium[3] was prepared from pentafluorobenzene and butyl-lithium (commercial solution in hexane) in ether–hexane at $-78°$, and pentachlorophenyl-lithium[5] was obtained by lithium–halogen exchange between butyl-lithium and hexachlorobenzene at $-15°$.

Reaction between Pentafluorophenyl-lithium and Dimethyl Oxalate.—(a) *Formation of methyl decafluorobenzilate* (I). Dimethyl oxalate (1·4 g, 11·9 mmol) in ether was added to pentafluorophenyl-lithium [from pentafluorobenzene (4·0 g, 23·8 mmol)] in ether (90 ml) and hexane (60 ml) at $-78°$. The mixture was allowed to attain room temperature overnight, and dilute hydrochloric acid (100 ml) was added. The organic layer was separated, dried ($MgSO_4$), and evaporated to leave a viscous liquid (4·5 g). Analytical g.l.c. indicated the presence of two components (10 : 90), which were separated by column chromatography [petroleum (b.p. 40—60°)–chloroform (4 : 1) eluant over silica] into tris(pentafluorophenyl)methanol (IV),[4] identified spectroscopically, and *methyl decafluorobenzilate* (I), m.p. 79—80° (Found: C, 42·4; H, 0·95; F, 45·5. $C_{15}H_4F_{10}O_3$ requires: C, 42·7; H, 0·95; F, 45·0%), ^{19}F n.m.r. δ $-9·1$ (F-4), $-0·6$ (F-3), and $-22·6$ p.p.m. (F-2), $J_{3,4}$ 20·2, $J_{2,4}$ 3·5 Hz, *m*/*e* 422 (<1%), 363 [$(C_6F_5)_2\overset{+}{C}OH$, 100%], 195 ($C_6F_5\overset{+}{C}O$, 93%), 167 ($C_6F_5^+$, 26%), and 59 ($C_2H_3O_2^+$, 39%).

(b) *Formation of methyl pentafluorobenzoylformate* (II) *and decafluorobenzil* (III). Dimethyl oxalate (4·2 g, 35·6 mmol) in ether (40 ml) was added to pentafluorophenyl-lithium [from pentafluorobenzene (12·0 g, 71·5 mmol)] in ether (150 ml) and hexane (100 ml) at $-78°$. After being stirred at $-78°$ for 14 h, the mixture was treated with gaseous hydrogen chloride for *ca.* 30 min. It was then allowed to attain room temperature and water (100 ml) was added to dissolve precipitated salts. The organic layer was separated, dried ($MgSO_4$), and evaporated to leave a product which analytical g.l.c. indicated to contain two major components. Reduced pressure distillation yielded the more volatile compound, *methyl pentafluorobenzoylformate* (II) (4·3 g, 47%), b.p. 47—48° at 0·001 mmHg (Found: C, 42·8; H, 0·8; F, 37·8. $C_9H_3F_5O_3$ requires: C, 42·5; H, 1·2; F, 37·4%), ^{19}F n.m.r. δ $-16·1$ (F-4), $-2·0$ (F-3), and $-22·5$ p.p.m. (F-2), $J_{3,4}$ 19·5, $J_{2,4}$ 5·6 Hz [in methanol solution, peaks were observed at δ $-16·3$ (F-4), $-2·1$ (F-3), and $-23·0$ p.p.m. (F-2), arising from the keto-ester, and at $-7·8$ (F-4), $+0·4$ (F-3), and $-22·8$ (F-2) p.p.m. for the methanol adduct]; *m*/*e* 254 (3%), 195 ($C_6F_5CO^+$, 100%), 167 ($C_6F_5^+$, 23%), 117 ($C_5F_3^+$, 14%), and 59 ($C_2H_3O_2^+$, 14%); $\nu_{max.}$ 1700—1740 cm^{-1} (overlap of ketone C=O stretch with ester C=O stretch).

Sublimation (70° and 0·001 mmHg) of the remaining material gave a yellow solid (6 g, 43%) which yielded decafluorobenzil (III), m.p. 79—80° [from petroleum (b.p. 40—60°)] (lit.,[14] 80—80·5°) (Found: C, 43·3; F, 49·1. Calc. for $C_{14}F_{10}O_2$: C, 43·2; F, 48·8%), ^{19}F n.m.r. δ $-18·3$ (F-4), $-2·6$ (F-3), and $-24·6$ p.p.m. (F-2), $J_{3,4}$ 20·0, $J_{2,4}$ 6·1 Hz, *m*/*e* 390 (<1%), 362 (loss of CO, 6%), 195 ($C_6F_5CO^+$, 100%), 167 ($C_6F_5^+$, 20%), 148 ($C_6F_4^+$, 15%), and 117 ($C_5F_3^+$, 12%).

Decafluorobenzil (0·33 g, 0·85 mmol) and freshly sublimed *o*-phenylenediamine (0·088 g, 0·85 mmol) were heated together at 100° for 10 min. The brown solid obtained on cooling was recrystallised from methanol to give 2,3-*bis*(*pentafluorophenyl*)*quinoxaline* (0·25 g, 64%), m.p. 161—163° (Found: C, 52·2; H, 0·85; N, 5·9. $C_{20}H_4F_{10}N_2$ requires C, 51·9; H, 0·85; N, 6·05%), ^{19}F n.m.r. δ $-10·9$ (F-4′), $-1·4$ (F-3′), and $-20·8$ p.p.m. (F-2′), ^{1}H n.m.r. τ (CCl_4; Me_4Si internal reference) 1·85 (m) and 2·0 (m), *m*/*e* 462 (69%), 269 (loss of C_6F_5CN, 51%), 76 ($C_6H_4^+$, 100%), and 50 ($C_4H_2^+$, 40%).

Reaction between Pentachlorophenyl-lithium and Dimethyl Oxalate.—(a) *Hydrogen chloride added at* $-78°$. Dimethyl oxalate (1·65 g, 14 mmol) was added to a solution of pentachlorophenyl-lithium [from hexachlorobenzene (8 g, 28 mmol)] in ether (400 ml) cooled to $-78°$. The mixture was stirred for 8 h before treatment with gaseous hydrogen chloride. It was allowed to attain room temperature, water (100 ml) was added, and the organic layer was separated and dried ($MgSO_4$). Removal of solvent left a residue (9·4 g) which analytical g.l.c. indicated to contain two components. Fractional sublimation (70° and 0·001 mmHg) gave pentachlorobenzene (V) (3·3 g, 47%), m.p. (from methanol) 85—86° (lit.,[5] 87·8—88·6°), showing the expected spectroscopic properties; and (120° and 0·001 mmHg) *methyl pentachlorobenzoylformate* (VI) (3·1 g, 34%), m.p. 131—132° (Found: C, 32·8; H, 1·15; Cl, 54·3. $C_9H_3Cl_5O_3$ requires C, 33·1; H, 0·9; Cl, 54·4%), *m*/*e* 334 (6%), 275 ($C_6Cl_5CO^+$, 100%), and peaks showing loss of Cl from *m*/*e* 247 ($C_6Cl_5^+$, 14%), to *m*/*e* 107 (C_6Cl^+, 3%), $\nu_{max.}$ (C=O str) *ca.* 1729 and *ca.* 1758 cm^{-1}. The residual material did not sublime under conditions up to 220° and 0·001 mmHg.

(b) *Decachlorobenzil* (VII). Dimethyl oxalate (1·65 g, 14 mmol) was added to pentachlorophenyl-lithium [from hexachlorobenzene (8 g, 28 mmol)] in ether (400 ml) at $-15°$. The mixture was allowed to attain room temperature overnight, and hydrolysed with dilute hydrochloric acid (100 ml). After filtration the organic layer was separated, dried ($MgSO_4$), and evaporated to leave an orange residue which was combined with the previous precipitate (total 8·9 g). Fractional sublimation (120° at 0·001 mmHg) gave first a mixture (1·2 g) of pentachlorobenzene and methyl pentachlorobenzoylformate as indicated by analytical g.l.c., and, at a higher temperature (200° and 0·001 mmHg) a solid (4·7 g) which gave decachlorobenzil (VII) (1·5 g, 20%), m.p. 328—329° (from nitrobenzene) (lit.,[14] 310·5—311°) (Found: C, 30·6; Cl, 64·0. Calc. for $C_{14}Cl_{10}O_2$: C, 30·3; Cl, 64·0%), *m*/*e* 275 ($C_6Cl_5CO^+$, 100%) and peaks corresponding to loss of Cl from *m*/*e* 247 ($C_6Cl_5^+$, 17%) to *m*/*e* 107 (C_6Cl^+, 2%) (no molecular ion). The nitrobenzene filtrate slowly yielded white crystals (1·0 g),

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[14] S. S. Dua, A. E. Jukes, and H. Gilman, *Organometallic Chem. Synth.*, 1970/71, **1**, 87.

[15] R. E. Banks, R. N. Haszeldine, and T. Myerscough, *J. Chem. Soc.* (*C*), 1971, 1951.

probably methyl decachlorobenzilate (VIII), m.p. 234—235° (Found: C, 31·0; H, 0·7; Cl, 60·4. $C_{15}H_4Cl_{10}O_3$ requires C, 30·7; H, 0·85; Cl, 60·6%), $\nu_{max.}$ *ca.* 3420 (OH str), *ca.* 2940 (CH str), and *ca.* 1725 cm⁻¹ (C=O str), *m/e* 275 ($C_6Cl_5CO^+$).

After attempted oxidation of the compound with chromium trioxide in acetic acid at 120° for 2 h starting material (90%) was recovered.

*Reaction between Octafluoro-*2,2′-*dilithiobiphenyl and Diethyl Oxalate.*—1·15M-Butyl-lithium (14·6 ml, 16·8 mmol) in hexane (10 ml) was added dropwise to tetrahydrofuran (150 ml) at −78°, followed by a solution of octafluoro-2,2′-dihydrobiphenyl (2·5 g, 8·4 mmol) in tetrahydrofuran (30 ml). The mixture was stirred at −78° for 4 h, and diethyl oxalate (1·22 g, 8·4 mmol) was added. The temperature was maintained for a further 1·5 h and then gaseous hydrogen chloride was passed through the mixture. The product was allowed to attain room temperature, water (100 ml) was added, and the organic layer was separated, and dried ($MgSO_4$). Removal of solvent left a residue, distillation of which (90—120° at 0·005 mmHg) gave a viscous liquid (2·7 g). G.l.c. showed this to be a mixture of two components (71 : 29) which were separated by column chromatography [petroleum (b.p. 40—60°)–benzene (1 : 1) as eluant over silica]. The major product, eluted first, was *ethyl tetrafluoro-*2-(2,3,4,5-*tetrafluorophenyl*)*benzoylformate* (IX), b.p. 95—97° at 0·005 mmHg (Found: C, 48·5; H, 1·5; F, 38·7. $C_{16}H_6F_8O_3$ requires C, 48·2; H, 1·5; F, 38·2%), ^{19}F n.m.r. δ −24·5 (F-6), −10·2 (F-5), −14·8 (F-4), −25·5 (F-3), −25·5 (F-5′), −9·8 (F-4′), −8·0 (F-3′), and −26·1 p.p.m. (F-2′), $J_{5,6}$ 21·5, $J_{4,6}$ 7·5, $J_{4,5}$ 20, $J_{3,6}$ 12, $J_{3,5}$ 4·7, $J_{3,4}$ 20, $J_{4',5'}$ 19, $J_{4',H}$ 4·2, $J_{3',5'}$ 7·5, $J_{3',4'}$ 19, $J_{3',H}$ 2·4, $J_{2',3'}$ 19 Hz, *m/e* 398 (6%), 325 (loss of $C_3H_5O_2$, 100%), 298 ($C_{12}H_2F_8^+$, 12%), 278 ($C_{12}HF_7^+$, 15%), and 247 ($C_{11}HF_6^+$, 12%).

Continued elution yielded *ethyl octafluoro-*9-*hydroxyfluorene-*9-*carboxylate* (X), m.p. 77—78° (Found: C, 48·1; H, 1·6; F, 37·8. $C_{16}H_6F_8O_3$ requires C, 48·2; H, 1·5; F, 38·2%), ^{19}F n.m.r. δ −11·9, −16·3, −26·4, and −27·3 p.p.m., *m/e* 354 (loss of CO_2, OC_2H_4, 22%), 325 (loss of $C_3H_5O_2$, 100%), 324 ($C_{13}F_8O^+$, 42%), 296 ($C_{12}F_8^+$, 25%), and 277 ($C_{12}F_7^+$, 14%).

In a similar reaction with the dimethyl ester in place of diethyl oxalate, the only product isolated was *methyl tetrafluoro-*2-(2,3,4,5-*tetrafluorophenyl*)*benzoylformate* (49%), m.p. 47—48° (Found: C, 47·2; H, 1·2; F, 39·9. $C_{15}H_4F_8O_3$ requires C, 46·9; H, 1·05; F, 39·6%), ^{19}F n.m.r. δ −23·6 (F-6), −10·0 (F-5), −14·6 (F-4), −24·0 (F-3), −24·0 (F-5′), −9·6 (F-4′), −8·2 (F-3′), and −25·1 p.p.m. (F-2′), $J_{5,6}$ 21, $J_{4,6}$, 7, $J_{4,5}$ 19·3, $J_{3,6}$ 11·5, $J_{3,5}$ 5, $J_{3,4}$ 20·5, $J_{3',4'}$ 19, $J_{3',H}$ 3, $J_{2',5'}$ 11·5, $J_{2',4'}$ 5·7, $J_{2',3'}$ 20·5, $J_{2',H}$ 5·7 Hz, *m/e* 384 (3%), 325 (loss of $C_2H_3O_2$, 100%), 278 ($C_{12}HF_7^+$, 20%), 247 ($C_{11}HF_6^+$, 17%), and 59 ($C_2H_3O_2^+$, 11%).

Rearrangement of Decafluorobenzil.—(a) *With methoxide ion.* A precooled solution of sodium methoxide (0·069 g, 1·28 mmol) in methanol (10 ml) was added to decafluorobenzil (0·50 g, 1·28 mmol) in methanol (10 ml) at −78°. After 2 h the mixture was treated with gaseous hydrogen chloride, allowed to warm to room temperature, and poured into water (100 ml). The product was extracted with ether (3 × 50 ml) and the organic extracts were dried ($MgSO_4$). Removal of solvent left a residue which analytical g.l.c. indicated to contain decafluorobenzil (12%) and methyl decafluorobenzilate (88%).

(b) *With ethoxide ion.* Sodium ethoxide (4·5 mg, 0·07 mmol) in ethanol (2 ml) was added to a refluxing solution of decafluorobenzil (0·5 g, 1·28 mmol) in ethanol (3 ml). The mixture was poured into water (100 ml) and extracted with ether (3 × 50 ml), and the extracts were dried ($MgSO_4$). Removal of solvent yielded *ethyl decafluorobenzilate* (0·50 g, 90%), b.p. 88—90° at 0·001 mmHg (Found: C, 44·2; H, 1·3; F, 44·0. $C_{16}H_6F_{10}O_3$ requires C, 44·1; H, 1·4; F, 43·6%), ^{19}F n.m.r. δ (Et_2O) −8·8 (F-4), −0·1 (F-3), and −24·0 p.p.m. (F-2), $J_{3,4}$ 20·2, $J_{2,4}$ 3·4 Hz, *m/e* 436 (<1%), 363 [$(C_6F_5)_2\overset{+}{C}OH$), 100%], 195 ($C_6F_5\overset{+}{C}O$, 70%), 167 ($C_6F_5^+$, 23%), 117 ($C_5F_3^+$, 12%), and 29 ($C_2H_5^+$, CHO^+, 85%).

(c) *With hydroxide ion.* Decafluorobenzil (0·8 g, 2·05 mmol) in ether (15 ml) was stirred at room temperature with 1·2M-sodium hydroxide (12 ml, 18 mmol) for 5 min, after which the characteristic yellow colour of the α-diketone had disappeared. The mixture was acidified with dilute hydrochloric acid and extracted with ether. The dried extracts were evaporated to leave a solid which gave *decafluorobenzilic acid* (0·7 g, 83%), m.p. 135—136° (from carbon tetrachloride) (Found: C, 41·0; H, 0·5; F, 46·8. $C_{14}H_2F_{10}O_3$ requires C, 41·2; H, 0·5; F, 46·6%), ^{19}F n.m.r. δ −8·4 (F-4), −0·1 (F-3), and −23·2 p.p.m. (F-2), $J_{3,4}$ 20·5, $J_{2,4}$ *ca.* 3 Hz, *m/e* 363 [$(C_6F_5)_2\overset{+}{C}OH$, 45%], 327 ($C_{13}F_9^+$, 19%), 195 ($C_6F_5CO^+$, 100%), 167 ($C_6F_5^+$, 54%), and 117 ($C_5F_3^+$, 33%), $\nu_{max.}$ *ca.* 3420s (OH str) and *ca.* 2850—3220 cm⁻¹ (CO·O–H str).

When aqueous dioxan was used as solvent, discharge of the yellow colour occurred on mixing.

Reaction of Pentafluorophenyl-lithium with Methyl Pentafluorobenzoylformate.—*Hydrogen chloride added at* −78°. Methyl pentafluorobenzoylformate (2·0 g, 7·8 mmol) was added to pentafluorophenyl-lithium [from pentafluorobenzene (1·3 g, 7·8 mmol)] in ether (90 ml) and hexane (60 ml) at −78°. The mixture was stirred for 3 h at this temperature and treated with gaseous hydrogen chloride. Water (100 ml) was added and the dried organic layer was evaporated to leave an oil (2·7 g); analytical g.l.c. indicated that the mixture contained methyl pentafluorobenzoylformate (5%), decafluorobenzil (5%), and methyl decafluorobenzilate (90%).

2,3,4,5,6-*Pentafluorobenzil* (XV).—Diethyl oxalate (4·35 g, 29·8 mmol) was added to pentafluorophenyl-lithium [from pentafluorobenzene (5·0 g, 29·8 mmol)] in ether–hexane at −78°. The mixture was stirred for 3 h and then to it was added a pre-cooled (−78°) solution of phenyl-lithium, prepared by exchange between iodobenzene (6·07 g, 29·8 mmol) and 2·4M-butyl-lithium (12·4 ml, 29·8 mmol) in ether–hexane solution.

The mixture was stirred at −78° for 36 h, treated with gaseous hydrogen chloride, and allowed to warm to room temperature. Water (100 ml) was added; the organic layer was separated, dried ($MgSO_4$), and evaporated to leave a residue which analytical g.l.c. indicated to contain three major components. Reduced pressure distillation yielded butyl iodide, identified spectroscopically, and *ethyl pentafluorobenzoylformate* (XIII) (3 g, 38%), b.p. 58° at 0·002 mmHg (Found: C, 44·7; H, 1·6; F, 35·9. $C_{10}H_5F_5O_3$ requires C, 44·8; H, 1·9; F, 35·4%), ^{19}F n.m.r. δ (neat liquid) −16·2 (F-4), −2·0 (F-3), and −23·3 p.p.m. (F-2), $J_{3,4}$ 19·4, $J_{2,4}$ 5·6 Hz, *m/e* 268 (<1%), 195 ($C_6F_5\overset{+}{C}O$, 100%), 167 ($C_6F_5^+$, 19%), 117 ($C_5F_3^+$, 12%), and 29 ($C_2H_5^+$, $CH\overset{+}{O}$, 48%), $\nu_{max.}$ (C=O str) *ca.* 1738 and *ca.* 1755 cm⁻¹.

Further distillation (110—112° at 0·001 mmHg) yielded a solid (3·6 g, 40%) which analytical g.l.c. indicated to be a single component; recrystallisation from light petroleum (b.p. 40—60°) gave yellow crystals of 2,3,4,5,6-*pentafluorobenzil* (XV), m.p. 70—71° (Found: C, 56·2; H, 1·8; F, 31·8. $C_{14}H_5F_5O_2$ requires C, 56·0; H, 1·7; F, 31·7%), ^{19}F n.m.r. δ −16·2 (F-4), −1·9 (F-3), and −25·0 p.p.m. (F-2), $J_{3,4}$ 20·1, $J_{2,4}$ 5·5 Hz, *m/e* 195 ($C_6F_5CO^+$, 11%), 167 ($C_6F_5^+$, 21%), 117 ($C_5F_3^+$, 27%), 105 ($C_6H_5C\overset{+}{O}$, 63%), 77 ($C_6H_5^+$, 100%), and 51 ($C_4H_3^+$, 75%), $\nu_{max.}$ (C=O str) *ca.* 1685 and *ca.* 1715 cm^{-1}.

Distillation at higher temperatures (112—130° and 0·001 mmHg) gave a fraction (0·8 g) containing several unidentified components, leaving a black residue (1·3 g).

Reaction of phenyl-lithium with ethyl pentafluorobenzoylformate rather than its diethyl oxalate adduct, gave a mixture containing several products, none of which was 2,3,4,5,6-pentafluorobenzil.

2,3,4,5,6-*Pentachloropentafluorobenzil* (XVI).—(*a*) Pentachlorophenyl-lithium and the diethyl oxalate addition complex of pentafluorophenyl-lithium did not react under the conditions which led to the formation of 2,3,4,5,6-pentafluorobenzil from phenyl-lithium.

(*b*) Methyl pentachlorobenzoylformate (2·6 g, 7·8 mmol) in ether (30 ml) was added to pentafluorophenyl-lithium [from pentafluorobenzene (1·3 g, 7·8 mmol)] in ether–hexane at −78°. After being stirred for 4 h the mixture was treated with gaseous hydrogen chloride. It was then allowed to warm to room temperature, water (100 ml) was added, and the organic layer was separated and dried ($MgSO_4$). Removal of solvent left a solid which analytical g.l.c. indicated to be a single component (3·2 g, 87%); recrystallisation (CCl_4) gave yellow crystals of 2,3,4,5,6-*pentachloropentafluorobenzil* (XVI), m.p. 132—133° (Found: C, 35·2; Cl, 37·5; F, 20·7. $C_{14}Cl_5F_5O_2$ requires C, 35·5; Cl, 37·5; F, 20·1%), ^{19}F n.m.r. δ −16·2 (F-4′), −2·4 (F-3′), and −25·2 p.p.m. (F-2′), $J_{3',4'}$ 20·2, $J_{2',4'}$ 5·5 Hz, *m/e* 275 ($C_6Cl_5C\overset{+}{O}$, 100%), 247 ($C_6Cl_5^+$, 17%), 212 ($C_6Cl_4^+$, 9%), and 195 ($C_6F_5CO^+$, 12%), $\nu_{max.}$ (C=O str) *ca.* 1705 and *ca.* 1720 cm^{-1}.

Reaction of Pentachlorophenyl-lithium with Methyl Pentafluorobenzoylformate.—Methyl 2,3,4,5,6-*pentachloropentafluorobenzilate* (XVII). Methyl pentafluorobenzoylformate (2·67 g, 10·5 mmol) was added rapidly to pentachlorophenyl-lithium [from hexachlorobenzene (3·0 g, 10·5 mmol)] in ether (300 ml) cooled to −78°. After being stirred for 3 h, the mixture was treated with gaseous hydrogen chloride. It was warmed to room temperature, water (100 ml) was added, and the organic layer was separated and dried ($MgSO_4$). Removal of solvent left a residue (5·3 g) which was washed with cold petroleum (b.p. 40—60°) to give a white solid (4·1 g, 72%), which analytical g.l.c. indicated to be a single component; recrystallisation from chloroform yielded *methyl* 2,3,4,5,6-*pentachloropentafluorobenzilate* (XVII) m.p. 161—162° (Found: C, 35·8; H, 0·9; Cl, 34·8; F, 19·2. $C_{15}H_4Cl_5F_5O_3$ requires C, 35·7; H, 0·8; Cl, 35·2; F, 18·7%), ^{19}F n.m.r. δ −8·4 (F-4′), −0·5 (F-3′), −22·9 p.p.m. (F-2′), $J_{3',4'}$ 20·8, $J_{2',4'}$ 3·2 Hz, *m/e* 502 (2%), 443 (loss of $C_2H_3O_2$, 30%) 195 ($C_6F_5C\overset{+}{O}$, 37%), 167 ($C_6F_5^+$, 18%), 117 ($C_5F_3^+$, 18%), 59 ($C_2H_3O_2^+$, 100%), and 15 (CH_3^+, 80%), $\nu_{max.}$ *ca.* 1740s cm^{-1} (ester C=O str).

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