

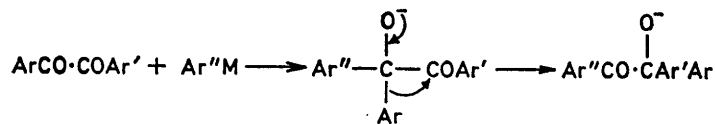
Polyfluoroaryl Organometallic Compounds. Part XVI.¹ Reactions of Organolithium Compounds with Halogenated Benzl

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Reactions of alkyl- or aryl-lithiums with decafluorobenzil gave adducts which undergo rapid pentafluorophenyl migration. A variety of products were obtained after hydrolysis, depending on the lithio-derivative used: keto-alcohols, a benzo[*b*]furan derivative (from C₆F₅Li), and bis(pentafluorophenyl)methyl pentachlorobenzoate (from C₆Cl₅Li). The mechanisms of these processes are discussed. Some analogous reactions of benzil are described for comparison and relative migratory aptitudes of groups in these processes are examined.

In the previous paper¹ we described the synthesis of decafluoro- and decachloro-benzil and the abnormally fast benzilic ester rearrangement shown by the fluorin-

benzils and we set out to investigate reactions of this type (Scheme 1), involving highly fluorinated and chlorinated benzils, with a view to establishing the



SCHEME 1

ated compound. Well known and related to this is the tertiary ketol rearrangement,² which sometimes occurs in the reactions of organometallic compounds with

relative migratory aptitudes of phenyl, pentafluorophenyl, and pentachlorophenyl groups. It will become clear from the results that conclusions concerning

¹ Part XV, R. D. Chambers, M. Clark, and D. J. Spring, preceding paper.

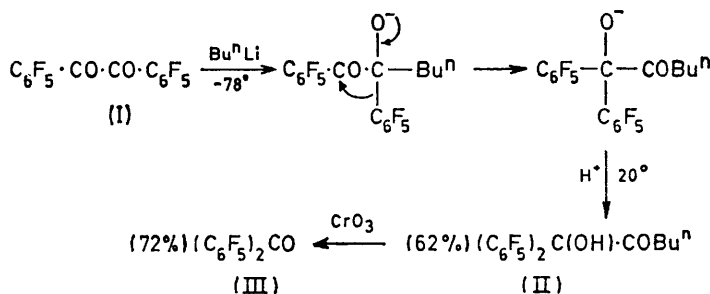
² S. Selman and J. F. Eastham, *Quart. Rev.*, 1960, **14**, 221.

migratory aptitudes are complicated by a series of interesting cyclisation reactions which occurred.

The reaction of butyl-lithium with decafluorobenzil (I) at -78° , followed by hydrolysis at room temperature, gave the keto-alcohol (II); the structure of this compound was confirmed by oxidation to decafluorobenzophenone (III) (Scheme 2). For comparison, the corresponding reaction between benzil and butyl-lithium was

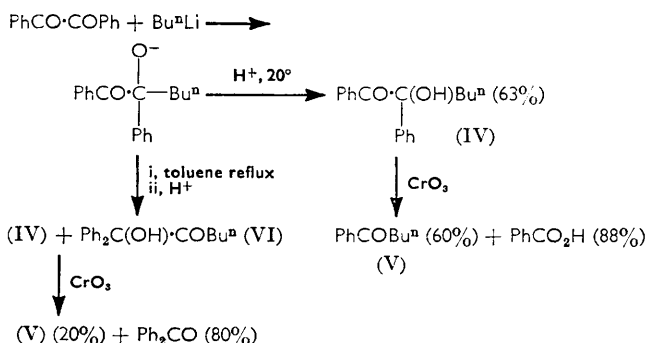
was obtained, together with (IV), and this was established by oxidation to give (V) plus benzophenone. That the rearrangement is still incomplete under these conditions underlines the difference between the mobility of phenyl and pentafluorophenyl groups.

Understandably, benzil and pentafluorophenyl-lithium gave α -pentafluorophenylbenzoin (VII); even after refluxing in toluene, no migration of phenyl occurred.



SCHEME 2

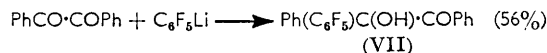
carried out and pure α -n-butylbenzoin (IV) was isolated, *i.e.* no phenyl migration had occurred. The structure



SCHEME 3

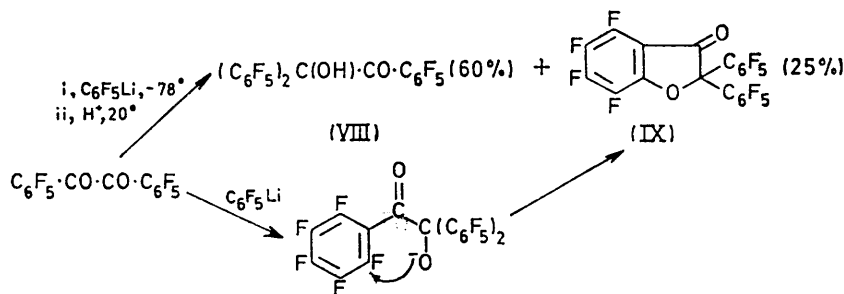
(IV) was confirmed by oxidation with chromic acid to the appropriate ketone (V) and benzoic acid.³ In a separate experiment the ether-hexane solvent was largely

The corresponding perfluorinated compound (VIII) was obtained in better yield than (VII) when the appropriate reaction mixture was hydrolysed at low temperature,



but at room temperature an interesting intramolecular nucleophilic aromatic substitution occurred, giving the benzofuran derivative (IX). Cyclisation reactions of other polyfluoroaromatic compounds have been reported previously, in some cases to give benzofuran derivatives.⁴⁻⁶

An arnyne process could be written to account for the formation of (IX), but when butyl-lithium was added at -78° to compound (VIII) in the presence of durene, and the mixture was allowed to warm to room temperature a high yield of the cyclised product (IX) was obtained, and there was no evidence for the formation of an adduct of tetrafluorobenzene with durene.⁷



SCHEME 4

replaced by toluene and the mixture was heated under reflux for 10 h. Then the rearrangement product (VI)

³ S. Selman and J. F. Eastham, *J. Org. Chem.*, 1965, **30**, 3805.

⁴ G. M. Brooke, W. K. R. Musgrave, and T. R. Thomas, *J. Chem. Soc. (C)*, 1971, 3596.

⁵ N. N. Vorozhtsov, V. A. Barkhash, A. T. Prudchenko, and T. I. Khomenko, *Zhur. obshchei Khim.*, 1965, **35**, 1501.

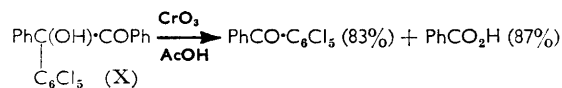
Reactions of pentachlorophenyl-lithium⁸ gave varied results; with benzil followed by hydrolysis at 20° , the

⁶ R. Filler, Y. S. Rao, A. Biezais, F. N. Miller, and V. D. Beauchaire, *J. Org. Chem.*, 1970, **35**, 930.

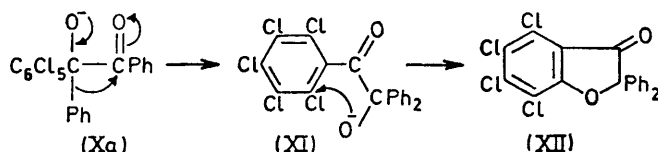
⁷ D. D. Callander, P. L. Coe, J. C. Tatlow, and A. J. Uff, *Tetrahedron*, 1969, **25**, 25.

⁸ M. D. Rausch, F. E. Tibbetts, and H. B. Gordon, *J. Organometallic Chem.*, 1966, **5**, 493.

benzoin derivative (X) was obtained, and its structure was confirmed by oxidation. It was anticipated that,

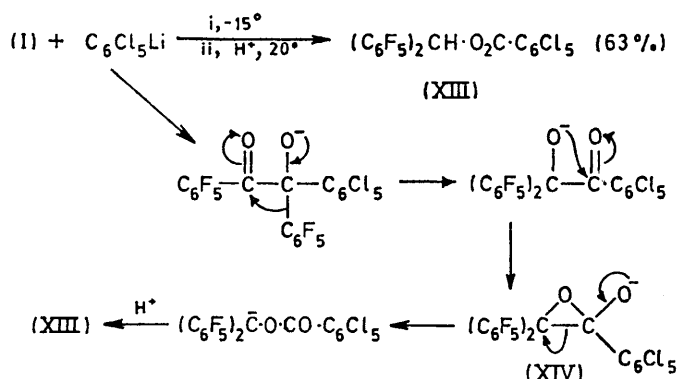


at high temperatures, phenyl would migrate to relieve steric strain,^{2,9} but when the solvent was replaced by toluene and the resulting mixture heated under reflux, intramolecular cyclisation of the intermediate ion (XI) also occurred, this time by replacement of chlorine to give a single product, tetrachloro-2,2-diphenylbenzofuran-3-one (XII). This result probably reflects the



greater migratory aptitude of phenyl over pentachlorophenyl but it must be emphasised that no firm conclusion can be drawn since the possibility cannot be ruled out that ion (Xa) is more stable than (XI) with the cyclisation to (XII) irreversibly affecting the equilibrium. An alternative structure for (XII), formed by cyclisation of (Xa) before rearrangement, giving a four-membered ring system is ruled out by the fragmentation pattern in the mass spectrum, *i.e.* $(\text{C}_6\text{H}_5)_2\text{C}^+$ and $\text{C}_6\text{Cl}_4(\text{CO})\text{O}^+$ are only consistent with (XII).

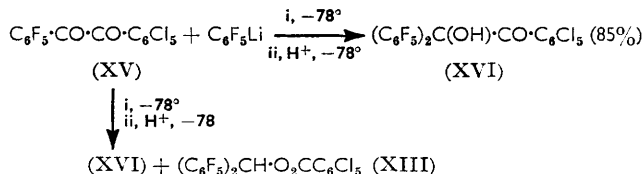
The reaction of pentachlorophenyl-lithium with decafluorobenzil (I) gives a further unusual product; after hydrolysis at 20° the main component of the mixture, obtained by recrystallisation, was bispentafluorophenyl-methyl pentachlorobenzoate (XIII) (Scheme 5). The



SCHEME 5

mechanism of the rearrangement producing the ester (XIII) is probably as shown, involving migration of pentafluorophenyl and the intermediate formation of an epoxide (XIV), followed by carbon-carbon bond cleavage. A similar process has been put forward to account for the product obtained from benzil and cyanide ion.^{10,11}

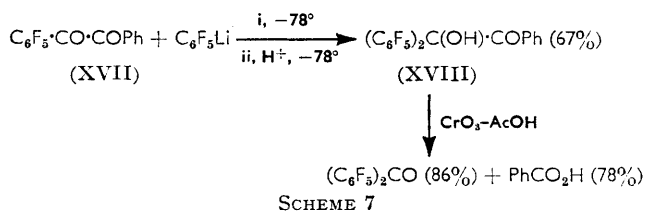
The structure (XIII) was deduced from the observations that the i.r. spectrum contained a carbonyl stretch-



SCHEME 6

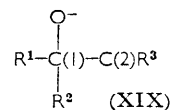
ing band consistent with an ester, but contained no hydroxy-absorption, and the mass spectrum showed a molecular ion and fragmentations consistent with (XIII). The hydroxy-isomer (XVI), was in fact obtained from the reaction between the mixed benzil (XV) and pentafluorophenyl-lithium when hydrogen chloride was added at -78°. At higher temperatures rearrangement again occurred to give a 1 : 4 mixture of (XVI) with the ester (XIII).

To complete the series a reaction between decafluorobenzil (I) and phenyl-lithium yielded a viscous liquid containing several products, none in a significant excess, and we have been unable to resolve this mixture by liquid chromatography. It was anticipated that the product from this reaction would be the derivative (XVIII); surprisingly, this was made readily from the mixed benzil (XVII) and pentafluorophenyl-lithium (Scheme 7). The oils obtained from (I) as just described could arise from nucleophilic displacement of fluorine, from the benzil, by the more reactive phenyl-lithium; the successful reaction of (I) with pentafluorophenyl-lithium has already been described.



SCHEME 7

It was stressed earlier that definitive experiments on the relative migratory aptitudes in these tertiary ketol rearrangements have been thwarted by a number of interesting side reactions. Nevertheless, the results can be understood if the following is taken as a model for the process. In relation to an anion (XIX) bulky (*i.e.*



pentachlorophenyl) or electron-donating (*i.e.* butyl) groups attached to the anionic centre C(1) destabilise the anion, whereas electron-withdrawing groups (*i.e.* pentafluorophenyl) attached to C(1) are stabilising. Likewise, the ease with which a group migrates to give

⁹ W. von E. Doering and R. S. Urban, *J. Amer. Chem. Soc.*, 1956, **78**, 5938.

¹⁰ H. Kwart and M. M. Baevesky, *J. Amer. Chem. Soc.*, 1958, **80**, 580.

¹¹ J. C. Trisler and J. L. Frye, *J. Org. Chem.*, 1965, **30**, 306.

the most stable ion (XIX) is closely related to the stability of that group as an anion. Hence the markedly easier migration of pentafluorophenyl over phenyl. The results obtained with highly halogenated systems in the tertiary ketol system therefore parallel those obtained for the benzil-benzilic ester rearrangement.¹

EXPERIMENTAL

All reactions involving organolithium 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 butyl-lithium was purchased from Alfa Inorganics Inc.

Pentafluorophenyl-lithium¹² was prepared from butyl-lithium and pentafluorobenzene in ether-hexane at -78° , and pentachlorophenyl-lithium⁸ was obtained by lithium-halogen exchange between butyl-lithium and hexachlorobenzene in ether at -15° .

Unless otherwise stated, the ^{19}F n.m.r. spectra were recorded with a Varian A56/60D spectrometer for samples dissolved in carbon tetrachloride. Fluorine chemical shifts refer to internal hexafluorobenzene, and negative signs refer to low field.

Reaction between Decafluorobenzil and Butyl-lithium.—2.3M-Butyl-lithium (3.4 ml, 7.7 mmol) in hexane (10 ml) was added dropwise to a stirred solution of decafluorobenzil (3.0 g, 7.7 mmol) in ether (200 ml) at -78° . The mixture was stirred at this temperature for 2 h, and then allowed to warm to room temperature overnight and hydrolysed with dilute hydrochloric acid. The organic layer was separated, dried (MgSO_4), and evaporated to leave a viscous liquid (3.1 g); analytical g.l.c. indicated the presence of one major component (ca. 80%) and several minor ones. Isolation of the major product by column chromatography [petroleum (b.p. $40-60^\circ$)-chloroform (4:1) eluant over silica] gave 1-hydroxy-1,1-bis(pentafluorophenyl)hexan-2-one (II), b.p. $93-95^\circ$ at 0.001 mmHg (Found: C, 48.3; H, 2.2; F, 42.8. $\text{C}_{18}\text{H}_{10}\text{F}_{10}\text{O}_2$ requires C, 48.2; H, 2.2; F, 42.4%), ^{19}F n.m.r. δ -9.5 (F-4), -1.5 (F-3), and -23.5 p.p.m. (F-2), $J_{3,4}$ 20.4, $J_{2,4}$ 3.4 Hz, ^1H n.m.r. τ (CCl_4 ; Me_4Si internal reference) 9.23 (t, Me), 8.4-8.9 (m, $\text{Me}[\text{CH}_2]_2$), 7.54 (t, $\text{CH}_2\cdot\text{CO}$), and 5.8br (s, OH), m/e 363 [$(\text{C}_6\text{F}_5)_2\text{COH}^+$, 17%], 253 [$\text{C}_6\text{F}_5(\text{C}_6\text{F}_5)^+$, 8%], 195 ($\text{C}_6\text{F}_5\text{CO}^+$, 100%), 167 (C_6F_5^+ , 24%), 117 (C_6F_3^+ , 14%), 85 ($\text{C}_4\text{H}_9\text{CO}^+$, 25%), and 59 (C_4H_9^+ , 25%), ν_{max} ca. 3420 (OH str) and ca. 1735 cm^{-1} ($\text{C}=\text{O}$ str).

Oxidation of the hydroxy-ketone (II). Chromium trioxide (0.32 g, 3.2 mmol) in acetic acid (10 ml) and water (0.5 ml) was added to 1-hydroxy-1,1-bis(pentafluorophenyl)hexan-2-one (0.6 g, 1.34 mmol) in acetic acid (5 ml); the mixture was heated to 100° for 2 h, then poured into water (100 ml), and extracted with ether (3×50 ml). The extracts were washed once with water, extracted with 2N-potassium hydroxide, washed again with water, and dried (MgSO_4). Removal of solvent gave decafluorobenzophenone (0.35 g, 72%), showing the expected spectroscopic properties.

Reaction of Benzil with Butyl-lithium.—(a) α -n-Butylbenzoin (IV). 2.3M-Butyl-lithium (19.0 ml, 42.8 mmol) in hexane (20 ml) was added dropwise to benzil (9.0 g, 42.8 mmol) in ether (250 ml) at -78° . The mixture was stirred at this temperature for 2 h, then warmed to room tempera-

ture overnight and hydrolysed with dilute hydrochloric acid. The organic layer was separated, dried (MgSO_4) and evaporated to leave a viscous liquid. On addition of petroleum (b.p. $40-60^\circ$), a white precipitate was obtained which was recrystallised to yield α -n-butylbenzoin (IV) (7.1 g, 62%), m.p. $72-73^\circ$ (Found: C, 80.9; H, 7.2. Calc. for $\text{C}_{18}\text{H}_{20}\text{O}_2$: C, 80.6; H, 7.5%). The m.p. differs considerably from that (124°) quoted¹³ but neither chromatography nor oxidation revealed any impurity in our sample. The mass

spectrum showed m/e 183 [$(\text{C}_6\text{H}_5)_2\text{COH}^+$, 8%], 163 [$\text{C}_6\text{H}_5(\text{C}_6\text{H}_5)^+$, 100%], 105 ($\text{C}_6\text{H}_5\text{CO}^+$, 27%), 85 ($\text{C}_4\text{H}_9\text{CO}^+$, 8%), 77 (C_6H_5^+ , 26%), and 57 (C_4H_9^+ , 16%) and the i.r. spectrum ν_{max} ca. 3420s (OH str) and ca. 1680 cm^{-1} (CO str); ^1H n.m.r. τ (CCl_4 ; Me_4Si internal reference) 9.24 (t, Me), 8.6-8.9 (m, $\text{Me}[\text{CH}_2]_2$), 7.79 (t, $\text{CH}_2\cdot\text{CO}$), 5.41br (s, OH), and 2.15-3.0 (complex, $2 \times \text{Ph}$).

Oxidation of the benzoin (IV). Chromium trioxide (0.88 g, 8.8 mmol) in glacial acetic acid (10 ml) and water (0.5 ml) was added to α -n-butylbenzoin (1 g, 3.72 mmol) in acetic acid (15 ml); the mixture was heated to 100° for 2 h, then poured into water (100 ml), and extracted with ether (3×50 ml). The extracts were washed once with water, extracted with 2N-potassium hydroxide, washed again with water, and dried (MgSO_4). Removal of solvent gave n-butyl phenyl ketone (0.35 g, 60%), identified by a comparison (spectroscopic properties and g.l.c. retention time) with an authentic sample.

Acidification and work-up of the basic extracts gave benzoic acid (0.42 g, 88%), also showing the expected spectroscopic properties.

(b) **With rearrangement in toluene under reflux.** 2.4M-Butyl-lithium (11.9 ml, 28.6 mmol) in hexane (10 ml) was added to benzil (6.0 g, 28.6 mmol) in ether (100 ml) at -78° . The mixture was stirred at this temperature for 2 h, and warmed to room temperature during 4 h. Most of the solvent was removed by distillation under nitrogen, and dry toluene (200 ml) was then added. The mixture was refluxed for 10 h, cooled, and hydrolysed with dilute hydrochloric acid (100 ml). The organic layer was separated, dried (MgSO_4), and evaporated to leave a residue which was distilled under reduced pressure. A volatile component was obtained first (1.0 g; b.p. $58-60^\circ$ at 0.002 mmHg), which was not investigated further. At higher temperatures ($110-150^\circ$ and 0.002 mmHg) a second fraction (5.8 g) was obtained. The i.r. spectrum indicated the presence of some α -n-butylbenzoin (IV); a second $\text{C}=\text{O}$ stretch absorption at 1715 cm^{-1} , typical of a carbonyl adjacent to an aliphatic group, and different intensities in the breakdown pattern of the mass spectrum [m/e 183 [$(\text{C}_6\text{H}_5)_2\text{COH}^+$, 60%],

163 [$\text{C}_6\text{H}_5(\text{C}_6\text{H}_5)^+$, 33%], 105 ($\text{C}_6\text{H}_5\text{CO}^+$, 100%), 85 ($\text{C}_4\text{H}_9\text{CO}^+$, 7%), 77 (C_6H_5^+ , 100%), and 57 (C_4H_9^+ , 20%)] suggested the presence of the rearranged material (VI) also. Further evidence for phenyl migration was obtained by oxidation.

Chromium trioxide (1.76 g, 17.6 mmol) in acetic acid (15 ml) and water (1 ml) was added to the reaction product (2.0 g) in acetic acid (10 ml); the mixture was heated at 100° for 2 h, then poured into water (100 ml), and extracted with ether. The extracts were washed once with water, extracted with 2N-potassium hydroxide, washed again with water, and dried (MgSO_4). Removal of solvent left a

¹² R. J. Harper, E. J. Soloski, and C. Tamborski, *J. Org. Chem.*, 1964, **29**, 2385.

¹³ H. M. Crawford, M. E. Saeger, and F. E. Warneke, *J. Amer. Chem. Soc.*, 1942, **64**, 2862.

viscous liquid (0.95 g) which analytical g.l.c. indicated to contain *n*-butyl phenyl ketone (20%) and benzophenone (80%).

α -Pentafluorophenylbenzoin (VII).—Benzil (3.0 g, 14.3 mol) in ether (40 ml) was added to pentafluorophenyl-lithium [from pentafluorobenzene (2.4 g, 14.3 mmol)] in ether-hexane at -78° . The mixture was stirred for 2 h, allowed to warm to room temperature during 1 h, and hydrolysed with dilute hydrochloric acid. The organic layer was separated, dried (MgSO_4), and evaporated to leave a pale yellow solid. Sublimation gave a product (5.0 g) which analytical g.l.c. indicated to contain one major component. After separation by column chromatography [petroleum (b.p. $40\text{--}60^\circ$)—chloroform (4 : 1) as eluant over silica], recrystallisation from petroleum (b.p. $40\text{--}60^\circ$) gave α -pentafluorophenylbenzoin (VII) (3 g, 56%), m.p. $112\text{--}114^\circ$ (Found: C, 63.6; H, 3.0; F, 25.5. $\text{C}_{20}\text{H}_{11}\text{F}_5\text{O}_2$ requires C, 63.5; H, 2.9; F, 25.2%), ^{19}F n.m.r. δ -8.4 (F-4), -0.6 (F-3), and -26.7 p.p.m. (F-2), $J_{3,4}$ 20.7, $J_{2,4}$ 3.3 Hz, ^1H n.m.r. τ (Et_2O ; Me_4Si internal reference) 4.42br (s, OH) and 2.0—2.8 (10H, complex aromatic), m/e 273 [$\text{C}_6\text{H}_5(\text{C}_6\text{F}_5)^+\text{COH}$, 9%], 195 ($\text{C}_6\text{F}_5\text{CO}^+$, 27%), 167 (C_6F_5^+ , 7%), 105 ($\text{C}_6\text{H}_5\text{CO}^+$, 100%), 77 (C_6H_5^+ , 43%), and 51 (C_4H_3^+ , 12%), ν_{max} ca. 3330s (O—H str) and ca. 1687 cm^{-1} (CO str).

No evidence for the migration of pentafluorophenyl was found when the reaction mixture was refluxed in toluene prior to hydrolysis.

Reaction between Decafluorobenzil and Pentafluorophenyl-lithium.—(a) **Preparation of perfluoro- α -phenylbenzoin (VIII).** Decafluorobenzil (3.0 g, 7.7 mmol) was added to pentafluorophenyl-lithium [from pentafluorobenzene (1.29 g, 7.7 mmol)] in ether-hexane at -78° . After being stirred for 6 h, the mixture was treated at -78° 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 pale yellow solid (3.7 g) which analytical g.l.c. indicated to contain decafluorobenzil (13%) and a second component (87%). Washing with cold petroleum (b.p. $40\text{--}60^\circ$) removed the decafluorobenzil, leaving perfluoro- α -phenylbenzoin (VIII) (2.8 g, 74% based on 88% conversion of decafluorobenzil), m.p. (from carbon tetrachloride) $116\text{--}117^\circ$ (Found: C, 42.8; H, 0.3; F, 51.5. $\text{C}_{20}\text{HF}_{15}\text{O}_2$ requires C, 43.0; H, 0.2; F, 51.1%), ^{19}F n.m.r. δ -11.0 (F-4), -1.5 (F-3), and -23.7 p.p.m. (F-2), $J_{3,4}$ 20, $J_{2,4}$ 4 Hz, for the two equivalent pentafluorophenyl groups, and δ -15.5 (F-4'), -2.05 (F-3'), and -25.2 p.p.m. (F-2'), $J_{3,4'}$ 20, $J_{2,4'}$ 6 Hz, for the pentafluorobenzoyl group, m/e 558 (<1%), 363 [$(\text{C}_6\text{F}_5)_2^+\text{COH}$, 53%], 195 ($\text{C}_6\text{F}_5\text{CO}^+$, 100%), 167 (C_6F_5^+ , 36%), and 117 (C_5F_5^+ , 18%), ν_{max} ca. 3470 (OH str) and ca. 1720 cm^{-1} (CO str).

(b) **Hydrolysis at 20° .** In a second experiment, the mixture was allowed to warm to room temperature and hydrolysed with dilute hydrochloric acid. The organic layer was separated, dried (MgSO_4), and evaporated to leave a white solid (4.1 g) which t.l.c. indicated to contain two components. These were separated by column chromatography (carbon tetrachloride as eluant over silica), into perfluoro- α -phenylbenzoin, as obtained in the previous experiment, and perfluoro-2,2-diphenylbenzofuran-3-one (IX), m.p. $158\text{--}159^\circ$ (Found: C, 44.3; F, 49.65. $\text{C}_{20}\text{F}_{14}\text{O}_2$ requires C, 44.6; F, 49.4%), ^{19}F n.m.r. δ -1.7 (F-7), -23.9 (F-6), -0.5 (F-5), and -25.5 p.p.m. (F-4), $J_{6,7}$ 18.5,

$J_{5,7}$ 2, $J_{5,6}$ 18.5, $J_{4,7}$ 16.3, $J_{4,6}$ 9.5, and $J_{4,5}$ 20.5 Hz, for the fused ring, and δ -12.2 (F-4'), -2.4 (F-3'), and -25.2 p.p.m. (F-2'), $J_{3,4'}$ 20, $J_{2,4'}$ 4.2 Hz, for the two equivalent pentafluorophenyl groups, m/e 538 (50%), 491 (loss of COF, 16%), 346 ($\text{C}_{13}\text{F}_{10}^+$, 24%), 343 ($\text{C}_{13}\text{F}_9\text{O}^+$, 14%), 327 ($\text{C}_{13}\text{F}_9^+$, 35%), 195 ($\text{C}_6\text{F}_5\text{CO}^+$, 83%), 176 ($\text{C}_6\text{F}_4\text{CO}^+$, 100%), and 148 (C_6F_4^+ , 45%). The C=O stretch absorption at ca. 1750 cm^{-1} is at higher wavenumber than normally observed for fluorinated ketones, but is consistent with a five-membered ring structure. The yield of perfluoro-2,2-diphenylbenzofuran-3-one, as estimated from a ^{19}F n.m.r. spectrum of the reaction product, was ca. 25%, and that of the benzoin ca. 60%.

Reaction of Perfluoro- α -phenylbenzoin with Butyl-lithium.—2.0*M*-Butyl-lithium (1.15 ml, 2.3 mmol) was added dropwise to perfluoro- α -phenylbenzoin (1.28 g, 2.3 mmol) in ether-hexane at -78° . After 1 h, durene (1.8 g) in ether was added, and the mixture was allowed to warm to room temperature overnight before hydrolysis with dilute hydrochloric acid. The organic layer was separated, dried (MgSO_4), and evaporated to leave a solid (3.0 g). T.l.c. and g.l.c. analysis of fractionally sublimed material showed no evidence for a tetrafluorobenzene adduct with durene; ⁷ recrystallisation of later fractions from acetone yielded perfluoro-2,2-diphenylbenzofuran-3-one (0.9 g, 72%).

Reaction of Benzil with Pentachlorophenyl-lithium.—(a) **Preparation of α -pentachlorophenylbenzoin (X).** Benzil (3.7 g, 17.6 mmol) in ether (30 ml) was added to pentachlorophenyl-lithium [from hexachlorobenzene (5.0 g, 17.6 mmol)] in ether (500 ml) at -15° . After being stirred at this temperature for 2 h, the mixture was allowed to warm to room temperature overnight, and hydrolysed with dilute hydrochloric acid. The organic layer was separated, dried (MgSO_4), and evaporated to leave an orange residue (7.9 g) which t.l.c. indicated to contain one major component. Sublimation yielded α -pentachlorophenylbenzoin (X) (6.1 g, 75%), m.p. $168\text{--}170^\circ$ (Found: C, 51.9; H, 2.5; Cl, 38.4. $\text{C}_{20}\text{H}_{11}\text{Cl}_5\text{O}_2$ requires C, 52.1; H, 2.4; Cl, 38.5%), m/e 353 [$\text{C}_6\text{H}_5(\text{C}_6\text{Cl}_5)^+\text{COH}$, 33%], 275 ($\text{C}_6\text{Cl}_5\text{CO}^+$, 23%), 183 [$(\text{C}_6\text{H}_5)_2^+\text{COH}$, 30%], 105 ($\text{C}_6\text{H}_5\text{CO}^+$, 100%), 77 (C_6H_5^+ , 46%), and 51 (C_4H_3^+ , 13%), ν_{max} ca. 3380 (OH str) and ca. 1657 cm^{-1} (CO str, consistent with $\text{C}_6\text{H}_5\text{CO}$ rather than $\text{C}_6\text{Cl}_5\text{CO}$).

Oxidation of the benzoin (X). Chromium trioxide (0.75 g, 7.5 mmol) in acetic acid (10 ml) and water (0.5 ml) was added to a solution of α -pentachlorophenylbenzoin in warm glacial acetic acid. The mixture was heated for 1 h at 100° , then poured into water, and extracted with ether (3×50 ml). The extracts were washed once with water, extracted with 2*N*-potassium hydroxide (3×50 ml), washed again with water, and dried (MgSO_4). Removal of solvent left a white solid (0.95 g, 83%); recrystallisation (ethanol) gave 2,3,4,5,6-pentachlorobenzophenone, m.p. $153\text{--}154^\circ$ (lit.¹⁴ 154°) (Found: C, 44.2; H, 1.5; Cl, 49.75. Calc. for $\text{C}_{13}\text{H}_5\text{Cl}_5\text{O}$: C, 44.0; H, 1.4; Cl, 50.0%), ν_{max} ca. 1690 cm^{-1} (CO str). Work-up of the basic extracts gave benzoic acid (0.35 g, 87%).

(b) **Preparation of tetrachloro-2,2-diphenylbenzofuran-3-one (XII).** Benzil (3.0 g, 14.3 mmol) was added to pentachlorophenyl-lithium [from hexachlorobenzene (4.0 g, 14.3 mmol)] in ether (200 ml) at -15° . After being stirred for 1 h, the mixture was allowed to warm to room temperature and most of the solvent was removed under nitrogen. Toluene (150 ml) was added, and the mixture was refluxed

¹⁴ G. Lock, *Ber.*, 1939, 72B, 300.

for 4 days. It was then cooled and hydrolysed with dilute hydrochloric acid, and the organic layer was separated and dried (MgSO_4). Removal of solvent left a residue (5.5 g) which sublimed with some decomposition to give a white solid (2.7 g, 43%); recrystallisation [petroleum (b.p. 40–60°)–chloroform] yielded *tetrachloro-2,2-diphenylbenzofuran-3-one* (XII), m.p. 196–197° (Found: C, 56.9; H, 2.4; Cl, 34.05. $\text{C}_{20}\text{H}_{10}\text{Cl}_4\text{O}_2$ requires C, 56.7; H, 2.35; Cl, 33.6%), m/e 422 (1%), 256 ($\text{C}_7\text{Cl}_4\text{O}_2^+$, 16%), 228 ($\text{C}_6\text{Cl}_4\text{O}^+$, 14%), 166 ($\text{C}_{13}\text{H}_{10}^+$, 24%), 165 ($\text{C}_{13}\text{H}_9^+$, 57%), 165 (C_6Cl_3^+ , 26%), 139 ($\text{C}_{11}\text{H}_7^+$, 24%), 130 (C_5Cl_2^+ , 24%), 105 ($\text{C}_6\text{H}_5\text{CO}^+$, 33%), 77 (C_6H_5^+ , 100%), and 51 (C_4H_3^+ , 65%), ν_{max} (no OH str) *ca.* 1730 cm^{-1} (CO str).

Reaction of Decafluorobenzil with Pentachlorophenyl-lithium. Preparation of Bis(pentafluorophenylmethyl) Pentachlorobenzoate (XIII).—Decafluorobenzil (3.0 g, 7.7 mmol) was added to pentachlorophenyl-lithium [from hexachlorobenzene (2.2 g, 7.7 mmol)] in ether (200 ml) at -15° . The mixture was allowed to warm to room temperature and after 10 h, hydrolysed with dilute hydrochloric acid. The organic layer was separated, dried (MgSO_4), and evaporated to leave a residue (4.4 g) which analytical g.l.c. indicated to contain one major component. Recrystallisation from petroleum (b.p. 40–60°) yielded *bis(pentafluorophenylmethyl) pentachlorobenzoate* (XIII) (3.1 g, 63%), m.p. 145–147° (Found: C, 37.4; H, 0.15; Cl, 27.9; F, 30.0. $\text{C}_{20}\text{HCl}_5\text{F}_{10}\text{O}_2$ requires C, 37.4; H, 0.15; Cl, 27.7; F, 29.65%), ^{19}F n.m.r. δ –10.9 (F-4), –1.5 (F-3), and –21.8 p.p.m. (F-2), $J_{3,4}$ 20 Hz, m/e 638 (19%), 347 [$(\text{C}_6\text{F}_5)_2\text{CH}^+$, 100%], 346 ($\text{C}_{13}\text{F}_{10}^+$, 31%), 278 ($\text{C}_{12}\text{HF}_7^+$, 15%), 275 ($\text{C}_6\text{Cl}_5\text{CO}^+$, 15%), 247 (C_6Cl_5^+ , 12%), and 195 ($\text{C}_6\text{F}_5\text{CO}^+$, 10%), ν_{max} (no OH str) *ca.* 2980 (aliph. CH str) and *ca.* 1767 cm^{-1} (C=O str), ^1H n.m.r. τ (CCl_4 ; Me_4Si internal reference) 2.4.

Reaction between 2,3,4,5,6-Pentachloropentafluorobenzil and Pentafluorophenyl-lithium.—(a) **Preparation of pentachlorobenzoylbis(pentafluorophenyl)methanol (XVI).** 2,3,4,5,6-Pentachloropentafluorobenzil (1.0 g, 2.12 mmol) in ether was added to pentafluorophenyl-lithium [from pentafluorobenzene (0.35 g, 2.12 mmol)] in ether–hexane at -78° . After being stirred for 3 h the mixture was treated at -78° 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 white solid (1.3 g); recrystallisation (carbon tetrachloride) gave *pentachlorobenzoylbis(pentafluorophenyl)methanol* (XVI) (1.15 g, 85%), m.p. 235–237° (Found: C, 37.6; H, 0.15; Cl, 27.3; F, 29.6. $\text{C}_{20}\text{HCl}_5\text{F}_{10}\text{O}_2$ requires C, 37.4; H, 0.15; Cl, 27.7; F, 29.65%), ^{19}F n.m.r. δ (acetone) –10.1 (F-4), –1.1 (F-3), and –28.9 p.p.m. (F-2), m/e 443 [$\text{C}_6\text{Cl}_5(\text{C}_6\text{F}_5)\text{COH}^+$, <1%], 363 [$(\text{C}_6\text{F}_5)_2\text{COH}^+$, 6%], 275 ($\text{C}_6\text{Cl}_5\text{CO}^+$, 100%), 247 (C_6Cl_5^+ , 20%), 212 (C_6Cl_4^+ , 18%), 195 ($\text{C}_6\text{F}_5\text{CO}^+$, 26%), and 167 (C_6F_5^+ , 11%), ν_{max} *ca.* 3540 (OH str) and *ca.* 1730 cm^{-1} (CO str).

(b) **Hydrolysis at 20°.** In a second experiment, hydroly-

sis was effected at room temperature with dil. hydrochloric acid. The product (1.2 g) was shown by t.l.c. chromatography to contain two components. A comparison of the ^{19}F n.m.r. spectrum of the mixture and the R_F values of the components with those of authentic samples indicated the presence of *bis(pentafluorophenylmethyl) pentachlorobenzoate* (*ca.* 80%) and *pentachlorobenzoylbis(pentafluorophenyl)methanol* (*ca.* 20%).

Reaction of Decafluorobenzil with Phenyl-lithium.—2.1M-Butyl-lithium (1.83 ml, 3.85 mmol) in hexane (10 ml) was added to iodobenzene (0.8 g, 3.85 mmol) in ether (90 ml) and hexane (60 ml) at -15° . The mixture was stirred for 2 h and decafluorobenzil (1.6 g, 3.85 mmol) was added. After being stirred for a further 2 h, the mixture was allowed to warm to room temperature and hydrolysed with dilute hydrochloric acid. The organic layer was separated, dried (MgSO_4), and evaporated to leave a red viscous oil (2.0 g) which analytical g.l.c. indicated to contain at least ten components, with no one peak accounting for a major proportion of the mixture.

Benzoylbis(pentafluorophenyl)methanol (XVIII).—2,3,4,5,6-Pentafluorobenzil (2.0 g, 6.67 mmol) in ether (20 ml) was added to pentafluorophenyl-lithium [from pentafluorobenzene (1.12 g, 6.67 mmol)] in ether (60 ml) and hexane (40 ml) at -78° . After being stirred for 3 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 viscous liquid which analytical g.l.c. indicated to contain two components (95:5). Column chromatography [petroleum (b.p. 40–60°)–chloroform (4:1) as eluant over silica] yielded the major component, *benzoylbis(pentafluorophenyl)methanol* (XVIII) (2.1 g, 67%), b.p. 124–126° at 0.001 mmHg (Found: C, 51.3; H, 1.2; F, 40.2. $\text{C}_{20}\text{H}_6\text{F}_{10}\text{O}_2$ requires C, 51.3; H, 1.3; F, 40.6%), ^{19}F n.m.r. δ –9.9 (F-4), –0.9 (F-3), and –22.5 p.p.m. (F-2), $J_{3,4}$ 20.4, $J_{2,4}$ 3.8 Hz, ^1H n.m.r. τ 4.45br (s, OH) and 1.9–2.65 (complex, Ph), ν_{max} *ca.* 3390 (O–H str) and *ca.* 1695 cm^{-1} (CO str).

Oxidation of the alcohol (XVIII). Chromium trioxide (0.33 g, 3.3 mmol) in acetic acid (10 ml) and water (0.5 ml) was added to a solution of *benzoylbis(pentafluorophenyl)methanol* (0.7 g, 1.5 mmol) in acetic acid (10 ml). The mixture was heated for 2 h at 100°, then poured into water (100 ml) and extracted with ether (4 × 50 ml). The extracts were washed once with water, extracted with 2N-potassium hydroxide, washed again with water, and dried (MgSO_4). Removal of solvent gave decafluorobenzophenone (0.47 g, 86%), which had the expected spectroscopic properties. Work-up of the basic extracts yielded benzoic acid (0.14 g, 78%).

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