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THE SYNTHESIS OF PERFLUOROALKYL AND PERFLUOROALKYLETHER
SUBSTITUTED BENZILS

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SUMMARY

Mono- and di-iodoperfluoroalkylethers were synthesized and their reactions, as well as those of iodofluoroalkanes, with 4-iodobenzil were investigated. The formation of $C_8F_{17}C_6H_4CHO$, $C_8F_{17}C_6H_4CO_2H$, $C_8F_{17}C_6H_4COCOC_6H_5$, and $C_8F_{17}OCF_2CF_2C_6H_4COCOC_6H_5$ proceeded readily. No $C_8F_{17}OCF_2C_6H_4COCOC_6H_5$ was produced from the reaction of $C_8F_{17}OCF_2I$ with 4-iodobenzil in the presence of copper bronze. Low yields of bridged bisbenzils were obtained from the coupling reactions of $ICF_2CF_2O(CF_2)_5OCF_2CF_2I$ and $I(CF_2CF_2O)_5CF_2CF_2I$ with 4-iodobenzil. Based on by-products formed, the operative mechanisms are postulated.

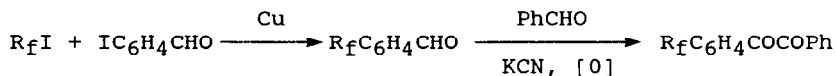
INTRODUCTION

The early studies of McLoughlin and Thrower [1] showed that copper assisted coupling of iodofluoroalkanes proceeds readily with both functional and nonfunctional iodoaromatics. Evers [2] extended this process to fluoroalkylether-bridged functional aromatics amenable to polymerization to polybenzoxazoles. Employing a related approach, our objective was to prepare polyquinoxalines by a reaction of tetramines with

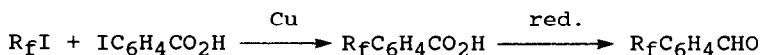
fluoroalkylether-bridged bisbenzils. Neither fluoroalkyl nor fluoroalkylether-substituted benzils were described to date. What needed to be determined was the feasibility of the above concept. Initial efforts were thus directed at the synthesis of 4-perfluoroalkyl- and 4-perfluoroalkyletherbenzils followed by the extension of this principle to difunctional systems. Included as part of this undertaking was the synthesis of the required fluoroalkylether iodides.

RESULTS AND DISCUSSION

For the synthesis of perfluoroalkyl/perfluoroalkylether-substituted benzils, the approach depicted below



offers the simplest route. However, in view of the exorbitant cost of 4-iodobenzaldehyde, the unknown stability of 4-iodobenzil, and for that matter 4-iodobenzaldehyde under the coupling conditions, the longer route was explored initially:



The results of the coupling reactions are presented in Table 1. For each of the systems listed, these are the optimum conditions. $\text{C}_7\text{F}_{15}\text{C}_6\text{H}_4\text{CO}_2\text{Me}$ was reported [1]. We were able to prepare $\text{C}_8\text{F}_{17}\text{C}_6\text{H}_4\text{CO}_2\text{H}$ by coupling directly $\text{C}_8\text{F}_{17}\text{I}$ and $\text{IC}_6\text{H}_4\text{CO}_2\text{H}$. Since the yield of the corresponding aldehyde, $\text{C}_8\text{F}_{17}\text{C}_6\text{H}_4\text{CHO}$, was higher (74 versus 67%) and since this process avoided the reduction step, an easy route to 4-iodobenzaldehyde needed to be developed. Olah and Arvanaghi [3] reported the formation of benzaldehyde via a reaction of lithiobenzene with *N*-formylpiperidine. Using a parallel approach, 4-iodolithio-benzene, obtained using a known procedure [4], was reacted with *N*-formylpiperidine giving essentially a quantitative yield of 4-iodobenzaldehyde. Unfortunately, the benzoin condensation of

TABLE 1

Coupling reactions of functional aromatics with iodofluoroalkanes and iodofluoroalkylethers

Aromatic type (mmol)	Alkane/Ether type (mmol)	Copper mmol	Solvent type (mL)	Time h	Temp °C	Yield %	Desired Product
p-IC ₆ H ₄ CHO ^a (4.3)	C ₈ F ₁₇ I (4.7)	14.2	DMF (25)	22	112	74	p-C ₈ F ₁₇ C ₆ H ₄ CHO
p-IC ₆ H ₄ CO ₂ H ^a (10.1)	C ₈ F ₁₇ I (11.1)	33.6	DMSO (25)	16	130	67	p-C ₈ F ₁₇ C ₆ H ₄ CO ₂ H
p-IC ₆ H ₄ COCOC ₆ H ₅ ^b (4.9)	C ₈ F ₁₇ I (3.30)	9.0	DMSO (15)	24	115	79	p-C ₈ F ₁₇ -benzil
p-IC ₆ H ₄ COCOC ₆ H ₅ ^b (2.8)	C ₈ F ₁₇ OCF ₂ CF ₂ I (1.4)	5.5	DMF (7)	93	115	71	p-C ₈ F ₁₇ OCF ₂ CF ₂ -benzil
p-IC ₆ H ₄ COCOC ₆ H ₅ ^b (1.5)	C ₈ F ₁₇ OCF ₂ I (0.8)	4.1	DMF (7)	96	115	0	p-C ₈ F ₁₇ OCF ₂ -benzil
p-IC ₆ H ₄ COCOC ₆ H ₅ ^a (5.4)	(ICF ₂ CF ₂ O) ₂ (CF ₂) ₅ (1.5)	9.5	DMF (35)	72	115	20	(CF ₂) ₅ (OCF ₂ CF ₂ -benzil) ₂
p-IC ₆ H ₄ COCOC ₆ H ₅ ^a (3.0)	I(CF ₂ CF ₂ O) ₅ CF ₂ CF ₂ I (1.0)	8.0	DMF (14)	120	105	15	(CF ₂ CF ₂ O) ₅ CF ₂ CF ₂ (benzil) ₂

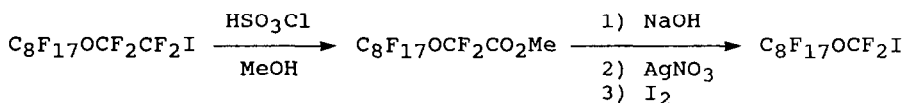
^a In this reaction the reagents were premixed, then heated at the denoted temperature for the denoted period of time.

^b In this reaction the iodofluoroalkane or iodofluoroether copper solution was heated at the denoted temperature for 1 h prior to addition of the iodoaromatic. The addition was performed over 1 h.

4-perfluorooctylbenzaldehyde with benzaldehyde followed by oxidation using ammonium nitrate/copper acetate reagents [5] gave a low yield of the desired product. The major problem was the formation of the acid. The alternate path utilizing copper assisted coupling of 4-iodobenzil and perfluorooctyl iodide in DMSO at 115°C resulted in a 79% yield of 4-perfluorooctylbenzil. At 125°C the yield of the latter was ~50% with 46% of the 4-iodobenzil being transformed to benzil.

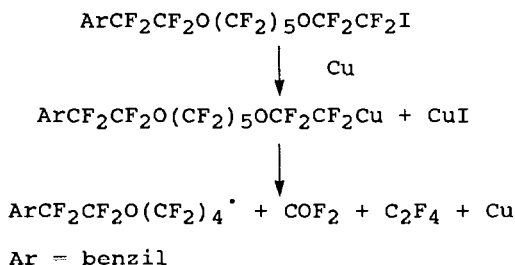
The iodide, $C_8F_{17}OCF_2CF_2I$, readily prepared from $C_8F_{17}COF$ and tetrafluoroethylene, when reacted with 4-iodobenzil under the conditions found optimum for perfluorooctyl iodide coupling, gave mainly benzil and 4-(methylthio)benzil. Only small quantities, ~10% yield, of the desired product was obtained. Employing DMF as solvent and extending reaction times (see Table 1) gave reasonable yields of $C_8F_{17}OCF_2CF_2C_6H_4COCOC_6H_5$. The yield increased almost linearly with time, e.g. 24 h, 28%; 48 h, 45%; 72 h, 66%; and finally 93 h, 71%. Longer exposures failed to increase the yield further.

It was of interest to determine whether perfluoroalkyl-ether iodides such as $C_8F_{17}OCF_2I$ will undergo the copper assisted coupling with aromatics. The iodide was synthesized using the sequence shown below:

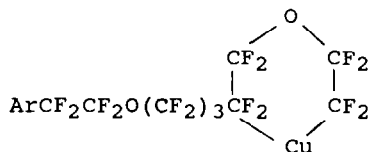


The ester $C_8F_{17}OCF_2CO_2\text{Me}$ was mentioned as a product of the photooxidation of sulfinates [6], but no physical property data were given. The selected process proceeded smoothly up to the production of $C_8F_{17}OCF_2CO_2\text{Ag}$. The subsequent Hunsdiecker reaction was accompanied by formation of COF_2 , $C_7F_{15}I$, $C_7F_{15}COF$, and $C_8F_{17}OCF_2COF$, (in addition of the desired $C_8F_{17}OCF_2I$); the two acid fluorides were analyzed as the methyl esters. It is believed that the mechanism responsible for the production of the acid fluorides is analogous to that postulated by Falk and Readio [7], *i.e.*:

and $C_6H_5COCOC_6H_4CF_2CF_2O(CF_2)_4C_6H_4COCOC_6H_5$ points clearly to the presence of a radical $\cdot(CF_2)_4OCF_2CF_2C_6H_4COCOC_6H_5$. It is our belief that this result is due to the following mechanism:

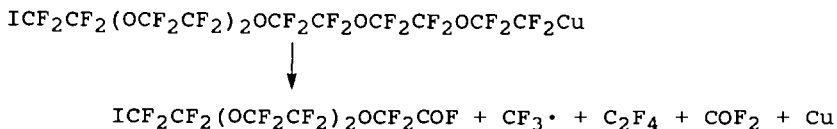


Whether this process takes place via a complex with 4-iodobenzil or solvent or whether a cyclic copper complex such as



is involved leading to $ArCF_2CF_2O(CF_2)_4Cu$ is unknown.

The synthesis of $I(CF_2CF_2O)_5CF_2CF_2I$ from the corresponding $MeCO_2(CF_2CF_2O)_5CF_2CF_2CO_2Me$ was straightforward and the yields were reasonable. However, the coupling reaction to form $C_6H_5COCOC_6H_4(CF_2CF_2O)_5CF_2CF_2C_6H_4COCOC_6H_5$ was again found to proceed with difficulty and the yields were low. The production of 4-trifluoromethylbenzil shows clearly that decomposition of the perfluoroalkylethercopper must occur. It is tempting to speculate, in view of some studies now in progress in related systems, that the mechanism involved is again evolution of C_2F_4 and COF_2 , *i.e.*



The workup makes it very difficult to isolate the resultant acids. The breakdown of perfluoroalkylcopper into metallic copper and perfluoroalkyl radicals was reported [1]. In the case of perfluoroalkanes, the abstraction of hydrogen from the solvent or incorporation of a portion of solvent molecule is the major process. However, the presence of the ether-oxygen in the molecule complicates the picture giving rise to the products observed. It is expected that perfluoroalkylether-copper compounds derived from arrangements such as $-\text{CF}_2\text{O}(\text{CF}_2)_x\text{I}$, $x > 2$, will more closely resemble the behavior and reactivity of perfluoroalkanes.

EXPERIMENTAL

All solvents used were reagent grade and were dried and distilled prior to use. All the operations involving moisture and/or air sensitive compounds were carried out either in an inert atmosphere enclosure (Vacuum Atmospheres Model HE-93B), under nitrogen bypass, or in vacuo. The commercially available starting materials were usually purified by distillation, crystallization, or other appropriate means.

All the melting points are uncorrected and were determined in evacuated sealed capillaries. Infrared spectra were recorded either neat (on liquids) or as double mulls (Kel-F oil No. 10 and Nujol) using a Perkin-Elmer Corporation infrared spectrophotometer Model 1330. The mass spectra were obtained by direct insertion probe and using combined gas chromatography/mass spectrometry (GC/MS) employing a Du Pont 21-491B double focusing mass spectrometer attached to a Varian Aerograph Model 2700 gas chromatograph (GC) equipped with a flame ionization detector and a Du Pont 21-094 data acquisition and processing system.

Preparation of 4-iodobenzaldehyde

To vigorously stirred p-diiodobenzene (165.0 g, 0.50 mol) in diethyl ether (500 mL) at -78°C was added a solution of butyllithium in hexane (2.5M, 200 mL) over a 2 h period. Stirring at -78°C was continued for an additional 3 h. This was followed by the addition (15 min) of N-formylpiperidine solution (62.24 g, 0.55 mol) in ether (100 mL). The reaction mixture was then allowed to warm to room temperature and was stirred for 17 h. Following the addition of hydrochloric acid (2.4N, 500 mL), the 4-iodobenzaldehyde 110.8 g (95.5% yield, purity >99%), mp $76-78^{\circ}\text{C}$ (after recrystallization, Lit. $77-78^{\circ}\text{C}$ [8]), was isolated from the ether solution.

Preparation of 4-iodobenzil from 4-iodobenzaldehyde

A mixture of 4-iodobenzaldehyde (10.00 g, 43.1 mmol), benzaldehyde (9.70 g, 91.4 mmol), ethanol (20 mL), potassium cyanide (0.70 g, 11 mmol), and water (20 mL) was heated at 110°C for 3 h. The intermediate 4-iodobenzoin was isolated by extraction with methylene chloride. Without purification it was treated with acetic acid (200 mL, 80%), ammonium nitrate (40.0 g, 0.50 mol), and copper acetate (0.80 g, 4.0 mmol), and heated at 122°C for 3.5 h. The product crystallized on cooling to room temperature. Additional material was obtained on water addition, resulting in 11.2 g (77.6% yield) of 4-iodobenzil, mp $93-95^{\circ}\text{C}$.

Preparation of $\text{C}_8\text{F}_{17}\text{OCF}_2\text{CF}_2\text{I}$ (nC)

In an inert atmosphere enclosure, into a Fischer Porter bottle (200 mL) were introduced $\text{C}_7\text{F}_{15}\text{COF}$ (39.0 g, 94.2 mmol), potassium fluoride (10.9 g, 188 mmol), iodine (47.9 g, 188 mmol), and diglyme (75 mL). Subsequently, the bottle was cooled to -196°C , evacuated, and then pressurized with

tetrafluoroethylene to 80 psi. The mixture was stirred at room temperature for 7 days with the pressure maintained at 80 psi. Following venting of C_2F_4 , the material was taken up in Freon-113 and washed with water and 10% $NaHCO_3$. After removal of Freon-113, the product was purified by distillation; bp $98-99^\circ C/40$ mm Hg (28.9 g, 46% yield, purity 97%). IR (capillary film, cm^{-1}): 1345 (s), 1300 (s), 1205 (vs, br), 1150 (vs), 1097 (s), 1000 (m), 906 (s), 878 (w), 716 (m), 705 (m), 660 (m). MS (70eV) m/e (relative intensity, ion): 662 (77.9%, M), 419 (17.7%, C_8F_{17}), 369 (65.4%, C_7F_{15}), 331 (14.7%, C_7F_{13}), 281 (20.6%, C_6F_{11}), 254 (43.7%, I_2), 227 (96.1%, CF_2CF_2I), 219 (47.9%, C_4F_9), 208 (14.9%, C_2F_3I), 177 (63.6%, CF_2I), 169 (65.6%, C_3F_7), 119 (100%, C_2F_5).

Preparation of $C_8F_{17}OCF_2CO_2CH_3$ (nc)

A mixture of $C_8F_{17}OCF_2CF_2I$ (16.5 g, 24.9 mmol) and chloro-sulfonic acid (45 g, 386 mmol) was heated under nitrogen bypass at $140^\circ C$ for 40 h. After cooling to room temperature, CH_3OH (100 mL) was slowly added. This was followed by 12 h reflux. Subsequently, water was added at room temperature, and the bottom layer was washed several times with water, giving 11.5 g (85% yield) of the $C_8F_{17}OCF_2CO_2CH_3$; purity 96%; bp $71-72^\circ C/40$ mm Hg. IR (capillary film, cm^{-1}): 2970 (w), 1794 (s), 1446 (w), 1340 (s), 1220 (vs, br), 1145 (vs), 1110 (s), 1087 (s), 1000 (s), 960 (w), 883 (m), 815 (w), 780 (m), 735 (m), 720 (m), 705 (s), 660 (s). MS (70eV) m/e (relative intensity, ion): 559 (11.8%, M + Me), 525 (17.3%, M - F), 419 (15.5%, C_8F_{17}), 231 (27.1%, C_5F_9), 219 (27.6%, C_4F_9), 169 (46.7%, C_3F_7), 131 (36.4%, C_3F_5), 119 (35.0%, C_2F_5), 109 (99.7%, CF_2CO_2Me), 59 (100%, CO_2Me).

Preparation of $C_8F_{17}OCF_2I$ (nc)

$C_8F_{17}OCF_2CO_2Me$ (11.5 g, 21.1 mmol) was hydrolyzed by stirring with 10% $NaOH$ solution (40 mL) at $50^\circ C$ for 48 h.

Following acidification with conc. HCl, the free acid (10.0 g, 89% yield) was isolated with ether. The acid was subsequently converted into the sodium salt using potentiometric titration with 2N NaOH. Removal of water gave the sodium salt (10.1 g, 87% yield). $C_8F_{17}OCF_2CO_2Na$ (7.12 g, 12.9 mmol) in water (100 mL) was treated with $AgNO_3$ solution (4.30 g in 15 mL water, 25.3 mmol). The precipitate was filtered, washed with cold water and dried in vacuo at 50°C/0.001 mm Hg for 72 h to yield $C_8F_{17}OCF_2CO_2Ag$ (7.5 g, 92% yield). IR (Kel-F/Nujol, cm^{-1}): 1609 (s), 1345 (w), 1208 (br), 1150 (s), 1009 (w), 835 (w).

The silver salt (7.14 g, 11.6 mmol) and iodine (31.0 g, 122.0 mmol) were ground together in a mortar, placed into a 125 mL ampoule, which was then evacuated, sealed, and heated in an oven at 160°C for 24 h. After cooling and opening to the vacuum system, the volatile products were separated by vacuum line fractional condensations through traps held at -23, -78, and -196°C. In the -196°C cooled trap, CO_2 (73% yield) and COF_2 (0.98 mmol) were collected. The material (4.25 g) collected in the -23°C cooled trap was dissolved in Freon-113 (25 mL) and was washed with 10% sodium bicarbonate solution (2 x 25 mL) and water. After drying over anhydrous Na_2SO_4 , the organic layer was again separated by vacuum line fractional condensations through traps held at -45 and -196°C. $C_8F_{17}OCF_2I$ (2.1 g, 28% yield; purity 95%) was retained in the -45°C trap. IR (capillary film, cm^{-1}): 1345 (s), 1220 (vs, br), 1150 (s), 1100 (s), 1055 (s), 1027 (s), 1000 (m), 885 (m), 820 (m), 780 (m), 740 (m), 720 (s), 710 (s), 660 (s). MS (70eV) m/e (relative intensity, ion): 485 (10.7%, $C_8F_{17}OCF_2$), 419 (91.0%, C_8F_{17}), 331 (19.7%, C_7F_{13}), 231 (20.5%, C_5F_9), 219 (43.4%, C_4F_9), 177 (100%, CF_2I), 131 (58.3%, C_3F_5), 127 (56.0%, I).

Preparation of $I(CF_2CF_2O)_5CF_2CF_2I$ (nc)

$MeO_2C(CF_2CF_2O)_5CF_2CF_2CO_2Me$ (provided by the U. S. Air Force Wright Research and Development Center) was characterized by GC/MS. MS (70eV) m/e (relative intensity, ion): 813 (42.1%, M + Me), 779 (21.7%, M - F), 754 (100%, M - CO_2), 739 (21.7%, M

- CO₂Me), 623 (30.3%, CF₂CF₂(OCF₂CF₂)₄CO₂Me), 507 (32.5%, CF₂CF₂(OCF₂CF₂)₃CO₂Me), 391 (41.0%, CF₂CF₂(OCF₂CF₂)₂CO₂Me), 275 (71.5%, CF₂CF₂OCF₂CF₂CO₂Me), 159 (80.4%, CF₂CF₂CO₂Me), 131 (98.2%, C₃F₅), 119 (93.3%, C₂F₅), 109 (54.2%, CF₂CO₂Me), 100 (93.8%, C₂F₄), 97 (45.3%, CF₂COF), 81 (74.0%, C₂F₃), 69 (42.2%, CF₃), 59 (85.2%, CO₂Me).

The methyl ester (50.0 g, 62.7 mmol) was hydrolyzed by stirring with 10% NaOH solution (250 mL) at room temperature over 30 h. Following acidification with conc. HCl, the free acid (47.1 g, 98% yield) was isolated with ether and purified by distillation; bp 69-71°C/0.001 mm Hg. IR (capillary film, cm⁻¹): 3060 (m, br), 2910 (w, br), 1753 (s), 1445 (w), 1330 (m), 1180 (s, br), 1130 (s), 1095 (s), 1030 (s), 905 (w, br), 785 (w), 680 (s). MS (70eV) m/e (relative intensity, ion): 589 (13.1%, (CF₂CF₂O)₄CF₂CFCO₂), 473 (4.5%, (CF₂CF₂O)₃CF₂CFCO₂), 377 (10.7%, (CF₂CF₂O)₂CF₂CF₂CO₂H), 357 (3.3%, (CF₂CF₂O)₂CF₂CFCO₂), 261 (16.1%, CF₂CF₂OCF₂CF₂CO₂H), 241 (4.6%, CF₂CF₂OCF₂CFCO₂), 145 (19.5%, CF₂CF₂CO₂H), 125 (17.2%, CF₂CFCO₂), 95 (11.3%, CF₂CO₂H), 75 (20.9%, CFCO₂), 45 (22.7%, CO₂H).

The acid HO₂C(CF₂CF₂O)₅CF₂CF₂CO₂H (19.7 g, 25.6 mmol) was subsequently converted into the sodium salt using potentiometric titration with 3N NaOH (16 mL). The resultant solution was treated at 10°C with AgNO₃ solution (13.2 g, 77.4 mmol). The precipitated salt was filtered, washed with cold water, and dried in vacuo at room temperature/0.001 mm Hg for 8 h to yield AgO₂C(CF₂CF₂O)₅CF₂CF₂CO₂Ag (21.9 g, 87% yield). Titration with ammonium thiocyanate gave an equivalent weight of 511 (theory 491). IR (Nujol, cm⁻¹): 1609 (s), 1377 (m), 1320 (w), 1190 (s, br), 1100 (w), 1085 (w), 1032 (w), 823 (w), 639 (w).

The silver salt (13.5 g, 13.7 mmol) was ground with iodine (17.3 g, 68.0 mmol) and placed in a tube (15 cm x 22 mm) on top of iodine (17.3 g, 68.0 mmol). The mixture was heated under nitrogen bypass at 120°C for 2 h, then at 140°C for 3 h. After cooling, extraction with Freon-113 gave 8.0 g (63% yield) of I(CF₂CF₂O)₅CF₂CF₂I; purity 99%; bp 88-90°C/5 mm Hg. IR (capillary film, cm⁻¹): 1380 (w), 1308 (s), 1210 (vs, br), 1040 (vs, br), 916 (s), 790 (m), 755 (m), 643 (m). MS (70eV) m/e

(relative intensity, ion): 1061 (5.7%, M + I), 934 (100%, M), 343 (19.4%, $\text{CF}_2\text{CF}_2\text{OCF}_2\text{CF}_2\text{I}$), 227 (83.1%, $\text{CF}_2\text{CF}_2\text{I}$), 185 (17.5%, $\text{C}_3\text{F}_7\text{O}$), 177 (69.3%, CF_2I), 127 (27.2%, I), 100 (64.6%, CF_2CF_2), 97 (52.0%, CF_2COF), 69 (35.0%, CF_3).

Coupling reactions

Two general procedures were employed in the coupling reactions of the iodoaromatics and iodofluoroalkanes/iodofluoroalkylethers listed in Table 1. In all instances as received copper bronze (product of BDH Chemicals Ltd., Poole, England) was used. In the first procedure, all the reactants were mixed together and heated under nitrogen bypass for the denoted period of time. In the second procedure, under nitrogen bypass, to a mixture of the iodofluoro-compound and copper preheated at the reaction temperature for 1 h was added the iodoaromatic in the given solvent over a period of 1 h. The total heating period is given in Table 1. Following cooling to room temperature, the products were isolated by the addition of ether, methylene chloride, or Freon-113. The inorganic salts were filtered and washed with more solvent. When either ether or Freon-113 were employed, the final washing of the residue was performed with methylene chloride. The combined solution was then washed with water, dried over MgSO_4 , and the solvent removed by evaporation in vacuo. The involatile residue was analyzed by GC/MS and the product purified by crystallization, sublimation, and/or silica gel chromatography.

4-Perfluorooctylbenzaldehyde (nc). MP 55-56°C (purity 99.7%). IR (melt, capillary film, cm^{-1}): 3060 (w), 2850 (w), 1705 (m), 1610 (w) 1580 (w), 1507 (w), 1420 (w), 1393 (w), 1368 (w), 1328 (w), 1296 (m), 1200 (s), 1145 (s), 1115 (m), 1090 (m), 1048 (w), 943 (w), 835 (m), 800 (w), 732 (w), 703 (m), 650 (m). MS (70eV) m/e (relative intensity, ion): 524 (11.8%, M), 505 (10.8%, $\text{C}_8\text{F}_{16}\text{C}_6\text{H}_4\text{CHO}$), 155 (100%, $\text{CF}_2\text{C}_6\text{H}_4\text{CHO}$), 131 (11.3%, C_3F_5), 127 (34.7%, $\text{CF}_2\text{C}_6\text{H}_5$), 126 (22.8%, $\text{CF}_2\text{C}_6\text{H}_4$), 77 (15.5%, C_6H_5), 69 (30.2%, CF_3).

4-Perfluorooctylbenzoic acid (nc). MP 202-203°C (crystallized from ethanol). IR (Kel-F/Nujol mull, cm^{-1}): 3000 (w, br), 1690 (s), 1580 (w), 1512 (w), 1430 (m), 1410 (m), 1370 (w), 1200 (s), 1145 (s), 865 (m), 770 (m), 715 (m), 707 (m), 687 (m), 650 (s). MS determined as trimethylsilyl derivative (70eV) m/e (relative intensity, ion): 612 (17.6%, M), 597 (100%, $\text{C}_8\text{F}_{17}\text{C}_6\text{H}_4\text{CO}_2\text{SiMe}_2$), 523 (29.4%, $\text{C}_8\text{F}_{17}\text{C}_6\text{H}_4\text{CO}$), 243 (15.0%, $\text{CF}_2\text{C}_6\text{H}_4\text{CO}_2\text{SiMe}_3$), 228 (15.0%, $\text{CF}_2\text{C}_6\text{H}_4\text{CO}_2\text{SiMe}_2$), 176 (15.2%, $\text{CF}_2\text{CF}_2\text{C}_6\text{H}_4$), 126 (26.0%, $\text{CF}_2\text{C}_6\text{H}_4$), 77 (16.0%, C_6H_5), 73 (23.5%, SiMe_3), 69 (23.2%, CF_3).

4-Perfluorooctylbenzil (nc). MP 89-90°C (purity >99%, crystallized from ethanol). IR (Kel-F/Nujol mull, cm^{-1}): 3060 (w), 2970 (w), 1678 (s), 1595 (w), 1450 (w), 1411 (m), 1323 (s), 1300 (s), 1210 (vs, br), 1150 (s), 1115 (s), 1093 (s), 1045 (w), 1018 (w), 965 (w), 946 (m), 890 (m), 852 (m), 797 (w), 763 (m), 734 (m), 716 (s), 659 (s). MS (70eV) m/e (relative intensity, ion): 609 (9.7%, $\text{C}_8\text{F}_{16}\text{C}_6\text{H}_4\text{COCOC}_6\text{H}_5$), 523 (55.8%, $\text{C}_8\text{F}_{17}\text{C}_6\text{H}_4\text{CO}$), 176 (26.2%, $\text{CF}_2\text{CF}_2\text{C}_6\text{H}_4$), 173 (12.3%, $\text{CF}_2\text{C}_6\text{H}_4\text{CO}$), 154 (28.1%, $\text{CF}_2\text{C}_6\text{H}_4\text{CO}$), 127 (28.1%, $\text{CF}_2\text{C}_6\text{H}_5$), 105 (100%, $\text{C}_6\text{H}_5\text{CO}$), 77 (88.4%, C_6H_5), 69 (27.9%, CF_3).

$\text{C}_8\text{F}_{17}\text{OCF}_2\text{CF}_2\text{C}_6\text{H}_4\text{COCOC}_6\text{H}_5$ (nc). MP 69.5-70.5°C (purity 98%, crystallized from DMSO). IR (Kel-F/Nujol mull, cm^{-1}): 3050 (w), 2910 (w), 1680 (m), 1602 (w), 1458 (w), 1418 (w), 1352 (w), 1329 (m), 1290 (m), 1240 (s), 1210 (s), 1155 (s), 1143 (m), 1099 (m), 1008 (w), 977 (w), 963 (w), 880 (w), 860 (w), 842 (w), 800 (w), 760 (w), 720 (w), 710 (w), 688 (w), 655 (w). MS (70eV) m/e (relative intensity, ion): 744 (1.8%, M), 725 (13.5%, M - F), 639 (59.8%, $\text{C}_8\text{F}_{17}\text{OCF}_2\text{CF}_2\text{C}_6\text{H}_4\text{CO}$), 473 (11.5%, ?), 309 (15.6%, $\text{CF}_2\text{CF}_2\text{C}_6\text{H}_4\text{COCOC}_6\text{H}_5$), 145 (26.6%, $\text{CF}_3\text{C}_6\text{H}_4$), 105 (100%, $\text{C}_6\text{H}_5\text{CO}$), 77 (63.4%, C_6H_5).

Reaction of 4-iodobenzil with $\text{C}_8\text{F}_{17}\text{OCF}_2\text{I}$

A mixture of products was obtained; no $\text{C}_8\text{F}_{17}\text{OCF}_2\text{C}_6\text{H}_4\text{COCOC}_6\text{H}_5$ was detected. The materials were quantified and identified using GC/MS. The components were $\text{CF}_3\text{C}_6\text{H}_4\text{COCOC}_6\text{H}_5$, $\text{C}_2\text{F}_5\text{C}_6\text{H}_4\text{COCOC}_6\text{H}_5$, $\text{C}_7\text{F}_{15}\text{C}_6\text{H}_4\text{COCOC}_6\text{H}_5$, $\text{C}_3\text{F}_7\text{C}_6\text{H}_4\text{COCOC}_6\text{H}_5$, and $\text{C}_7\text{F}_{15}\text{CONMe}_2$ in the ratio of 2.0:2.0:1.5:1.0:trace.

CF₃C₆H₄COCOC₆H₅. MS (70eV) m/e (relative intensity, ion): 278 (9.9%, M), 173 (51.6%, CF₃C₆H₄CO), 145 (55.5%, CF₃C₆H₄), 105 (100%, C₆H₅CO), 77 (93.6%, C₆H₃).

C₂F₅C₆H₄COCOC₆H₅. MS (70eV) m/e (relative intensity, ion): 223 (17.1%, C₂F₅C₆H₄CO), 195 (7.8%, C₂F₅C₆H₄), 126 (7.8%, CF₂C₆H₄), 105 (100%, C₆H₅CO), 77 (47.6%, C₆H₅), 51 (21.2%, C₄H₃).

C₃F₇C₆H₄COCOC₆H₅. MS (70eV) m/e (relative intensity, ion): 273 (8.3%, C₃F₇C₆H₄CO), 145 (9.0%, CF₃C₆H₄), 126 (6.3%, CF₂C₆H₄), 123 (22.6%, FC₆H₄CO), 105 (100%, C₆H₅CO), 77 (42.5%, C₆H₅).

C₇F₁₅C₆H₄COCOC₆H₅. MS (70eV) m/e (relative intensity, ion): 473 (29.0%, C₇F₁₅C₆H₄CO), 176 (14.5%, CF₂CF₂C₆H₄), 154 (12.3%, CF₂C₆H₄CO), 145 (9.4%, CF₃C₆H₄), 126 (22.8%, CF₂C₆H₄), 105 (100%, C₆H₅CO), 77 (51.0%, C₆H₅).

C₇F₁₅CON(CH₃)₂. MS (70eV) m/e (relative intensity, ion): 441 (5.5%, M), 422 (6.5%, M - F), 131 (5.5%, C₃F₅), 119 (4.8%, C₂F₅), 72 (100%, CONMe₂), 69 (6.6%, CF₃), 42 (13.7%, CHNCH₃).

Reaction of 4-iodobenzil with ICF₂CF₂O(CF₂)₅OCF₂CF₂I

A mixture of products was obtained. The materials were quantified and identified using GC/MS. The components were C₆H₅COCOC₆H₅, Me₂NCOC₆H₄COCOC₆H₅, C₆H₅COCOC₆H₄CF₂CF₂O(CF₂)₅OCF₂CF₂C₆H₄COCOC₆H₅, HCF₂CF₂O(CF₂)₅OCF₂CF₂C₆H₄COCOC₆H₅, H(CF₂)₄OCF₂CF₂C₆H₄COCOC₆H₅, C₆H₅COCOC₆H₄(CF₂)₄OCF₂CF₂C₆H₄COCOC₆H₅, and ICF₂CF₂O(CF₂)₅OCF₂CF₂C₆H₄COCOC₆H₅ in the ratio of 13:8:7:4:4:1.5:1.

C₆H₅COCOC₆H₄CF₂CF₂O(CF₂)₅OCF₂CF₂C₆H₄COCOC₆H₅. MS (70eV) m/e (relative intensity, ion): 900 (5.2%, M), 795 (14.9%, C₆H₅COCOC₆H₄CF₂CF₂O(CF₂)₅OCF₂CF₂C₆H₄CO), 145 (3.8%, CF₃C₆H₄), 126 (6.5%, C₆H₄CF₂), 105 (100%, C₆H₅CO), 78 (8.1%, C₆H₆), 77 (31.4%, C₆H₅).

ICF₂CF₂O(CF₂)₅OCF₂CF₂C₆H₄COCOC₆H₅. MS (70eV) m/e (relative intensity, ion): 818 (1.5%, M), 713 (19.4%, ICF₂CF₂O(CF₂)₅OCF₂CF₂C₆H₄CO), 691 (5.8%, CF₂CF₂O(CF₂)₅OCF₂CF₂C₆H₄COCOC₆H₅), 586 (4.0%,

$\text{CF}_2\text{CF}_2\text{O}(\text{CF}_2)_5\text{OCF}_2\text{CF}_2\text{C}_6\text{H}_4\text{CO}$), 309 (5.5%, $\text{CF}_2\text{CF}_2\text{C}_6\text{H}_4\text{COCOC}_6\text{H}_5$), 259 (6.1%, $\text{CF}_2\text{C}_6\text{H}_4\text{COCOC}_6\text{H}_5$), 227 (11.5%, $\text{CF}_2\text{CF}_2\text{I}$), 204 (8.8%, $\text{CF}_2\text{CF}_2\text{C}_6\text{H}_4\text{CO}$), 177 (6.6%, CF_2I), 154 (9.1%, $\text{CF}_2\text{C}_6\text{H}_4\text{CO}$), 127 (17.2%, I), 126 (16.8%, $\text{CF}_2\text{C}_6\text{H}_4$), 119 (14.3%, C_2F_5), 105 (100%, $\text{C}_6\text{H}_5\text{CO}$), 77 (54.6%, C_6H_5), 69 (11.5%, CF_3), 51 (20.4%, CF_2H).

$\text{HCF}_2\text{CF}_2\text{O}(\text{CF}_2)_5\text{OCF}_2\text{CF}_2\text{C}_6\text{H}_4\text{COCOC}_6\text{H}_5$. MS (70eV) m/e (relative intensity, ion): 692 (6.3%, M), 673 (22.2%, M - F), 641 (15.5%, $\text{CF}_2\text{O}(\text{CF}_2)_5\text{OCF}_2\text{CF}_2\text{C}_6\text{H}_4\text{COCOC}_6\text{H}_5$), 587 (81.5%, $\text{HCF}_2\text{CF}_2\text{O}(\text{CF}_2)_5\text{OCF}_2\text{CF}_2\text{C}_6\text{H}_4\text{CO}$), 575 (27.4%, $(\text{CF}_2)_5\text{OCF}_2\text{CF}_2\text{C}_6\text{H}_4\text{COCOC}_6\text{H}_5$), 309 (18.7%, $\text{CF}_2\text{CF}_2\text{C}_6\text{H}_4\text{COCOC}_6\text{H}_5$), 259 (22.4%, $\text{CF}_2\text{C}_6\text{H}_4\text{COCOC}_6\text{H}_5$), 145 (38.8%, $\text{CF}_3\text{C}_6\text{H}_4$), 126 (34.1%, $\text{CF}_2\text{C}_6\text{H}_4$), 105 (100%, $\text{C}_6\text{H}_5\text{CO}$), 101 (42.5%, $\text{CF}_2\text{CF}_2\text{H}$), 77 (67.5%, C_6H_5), 69 (13.0%, CF_3), 51 (39.3%, CF_2H).

$\text{C}_6\text{H}_5\text{COCOC}_6\text{H}_4(\text{CF}_2)_4\text{OCF}_2\text{CF}_2\text{C}_6\text{H}_4\text{COCOC}_6\text{H}_5$. MS (70eV) m/e (relative intensity, ion): 734 (1.9%, M), 629 (17.3%, M - $\text{C}_6\text{H}_5\text{CO}$), 105 (100%, $\text{C}_6\text{H}_5\text{CO}$), 77 (32.6%, C_6H_5).

$\text{H}(\text{CF}_2)_4\text{OCF}_2\text{CF}_2\text{C}_6\text{H}_4\text{COCOC}_6\text{H}_5$. MS (70eV) m/e (relative intensity, ion): 526 (1.6%, M), 421 (37.7%, M - $\text{C}_6\text{H}_5\text{CO}$), 309 (8.6%, $\text{CF}_2\text{CF}_2\text{C}_6\text{H}_4\text{COCOC}_6\text{H}_5$), 259 (10.8%, $\text{CF}_2\text{C}_6\text{H}_4\text{COCOC}_6\text{H}_5$), 154 (10.3%, $\text{CF}_2\text{C}_6\text{H}_4\text{CO}$), 145 (24.5%, $\text{CF}_3\text{C}_6\text{H}_4$), 126 (19.4%, $\text{CF}_2\text{C}_6\text{H}_4$), 105 (100%, $\text{C}_6\text{H}_5\text{CO}$), 101 (6.3%, $\text{CF}_2\text{CF}_2\text{H}$), 77 (72.9%, C_6H_5), 69 (17.4%, CF_3), 51 (35.4%, CF_2H).

Reaction of 4-iodobenzil with $\text{I}(\text{CF}_2\text{CF}_2\text{O})_5\text{CF}_2\text{CF}_2\text{I}$

A mixture of products was obtained. The materials were quantified and identified using GC/MS. The components were $\text{C}_6\text{H}_5\text{COCOC}_6\text{H}_5$, $\text{C}_6\text{H}_5\text{COCOC}_6\text{H}_4\text{CF}_3$, $\text{C}_6\text{H}_5\text{COCOC}_6\text{H}_4(\text{CF}_2\text{CF}_2\text{O})_5\text{CF}_2\text{CF}_2\text{C}_6\text{H}_4\text{COCOC}_6\text{H}_5$, $\text{Me}_2\text{NCOC}_6\text{H}_4\text{COCOC}_6\text{H}_5$, and $\text{C}_6\text{H}_5\text{COCOC}_6\text{H}_4(\text{CF}_2\text{CF}_2\text{O})_5\text{CF}_2\text{CF}_2\text{H}$ in the ratio of 16:14:10:1:1.

$\text{C}_6\text{H}_5\text{COCOC}_6\text{H}_4(\text{CF}_2\text{CF}_2\text{O})_5\text{CF}_2\text{CF}_2\text{C}_6\text{H}_4\text{COCOC}_6\text{H}_5$ (nc). MP 64-67°C (purity 98%). IR (Kel-F/Nujol, cm^{-1}): 3050 (w), 2920 (w), 1670 (s), 1595 (w), 1579 (w), 1450 (w), 1410 (m), 1325 (m), 1284 (m), 1200 (s, br), 1150 (s), 1097 (s), 975 (m), 960 (m), 872 (m), 840 (m), 795 (m), 758 (m), 717 (m), 682 (s), 657 (m). MS (70eV) m/e (relative intensity, ion): 1060 (9.3%, M - 2F), 993 (35.4%, M - $\text{C}_6\text{H}_5\text{CO}$), 937 (11.0%, ?), 154 (10.5%, $\text{CF}_2\text{C}_6\text{H}_4\text{CO}$),

145 (10.9%, $\text{CF}_3\text{C}_6\text{H}_4$), 126 (16.7%, $\text{CF}_2\text{C}_6\text{H}_4$), 105 (100%, $\text{C}_6\text{H}_5\text{CO}$), 77 (58.8%, C_6H_5), 69 (11.5%, CF_3), 66 (15.2%, COF_2), 51 (23.1%, CF_2H), 50 (22%, CF_2), 47 (18.0%, COF).

$\text{C}_6\text{H}_5\text{COCOC}_6\text{H}_4(\text{CF}_2\text{CF}_2\text{O})_5\text{CF}_2\text{CF}_2\text{H}$. MS (70eV) m/e (relative intensity, ion): 890 (5.1%, M), 871 (21.2%, M - F), 839 (18.7%, $\text{C}_6\text{H}_5\text{COCOC}_6\text{H}_4(\text{CF}_2\text{CF}_2\text{O})_5\text{CF}_2$), 785 (44.6%, M - $\text{C}_6\text{H}_5\text{CO}$), 773 (16.9%, $\text{C}_6\text{H}_5\text{COCOC}_6\text{H}_4(\text{CF}_2\text{CF}_2\text{O})_4\text{CF}_2\text{CF}_2$), 657 (12.4%, $\text{C}_6\text{H}_5\text{COCOC}_6\text{H}_4(\text{CF}_2\text{CF}_2\text{O})_3\text{CF}_2\text{CF}_2$), 607 (11.2%, $\text{C}_6\text{H}_5\text{COCOC}_6\text{H}_4(\text{CF}_2\text{CF}_2\text{O})_3\text{CF}_2$), 541 (13.0%, $\text{C}_6\text{H}_5\text{COCOC}_6\text{H}_4(\text{CF}_2\text{CF}_2\text{O})_2\text{CF}_2\text{CF}_2$), 491 (8.1%, $\text{C}_6\text{H}_5\text{COCOC}_6\text{H}_4(\text{CF}_2\text{CF}_2\text{O})_2\text{CF}_2$), 320 (11.3%, $\text{COC}_6\text{H}_4\text{CF}_2\text{CF}_2\text{OCF}_2\text{CF}_2$), 173 (14.3%, $\text{COC}_6\text{H}_4\text{CF}_3$), 154 (14.5%, $\text{COC}_6\text{H}_4\text{CF}_2$), 145 (18.8%, $\text{CF}_3\text{C}_6\text{H}_4$), 126 (27.5%, $\text{CF}_2\text{C}_6\text{H}_4$), 105 (100%, $\text{C}_6\text{H}_5\text{CO}$), 101 (37.0%, $\text{CF}_2\text{CF}_2\text{H}$).

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REFERENCES

- 1 V. C. R. McLoughlin and J. Thrower, *Tetrahedron*, 25 (1969) 5921.
- 2 R. C. Evers, *J. Polym. Sci.*, 16 (1978) 2833-2848.
- 3 G. A. Olah and M. Arvanaghi, *Angew. Chem. Int. Ed. Engl.*, 20(10) (1981) 878.
- 4 C. Tamborski, C. E. Snyder, Jr., and J. B. Christian, U. S. Pat. 4 454 349, June 12, 1984.
- 5 K. J. L. Paciorek, R. H. Kratzer, and D. W. Karle, U. S. Pat. 4 024 067, May 17, 1977.
- 6 C. M. Hu, Z. Q. Xu, and W. Y. Huang, *J. Fluorine Chem.*, 42 (1989) 145.
- 7 R. A. Falk and J. D. Readio, *J. Org. Chem.*, 34 (1969) 4088.
- 8 P. P. T. Sah, *J. Am. Chem. Soc.*, 64 (1942) 1487.