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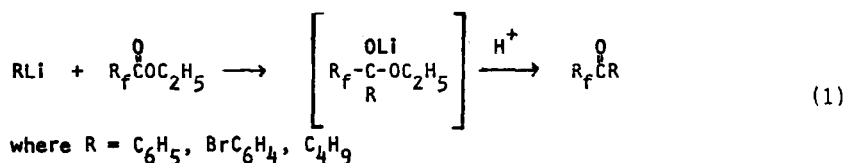
FLUORO-KETONES VI. SYNTHESIS OF PERFLUORO DI- AND TETRA-KETONES FROM
1,1-DICHLOROBENZYLLITHIUM AND PERFLUOROESTERS

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SUMMARY

The reaction of $C_6H_5CCl_2Li$ with perfluorinated mono and diesters yields
fluorochloroketones in high yield. Hydrolysis of such compounds produces
alpha-beta fluorinated di- and tetra-ketones, respectively. Various hydrates
of the fluorinated ketones have been identified.

INTRODUCTION

We have previously [1,2] reported a convenient and improved synthesis
procedure for the preparation of fluorinated ketones *via* organolithium inter-
mediates and fluorinated esters.

$$RLi + R_f\overset{O}{C}OC_2H_5 \longrightarrow \left[R_f-\underset{R}{\overset{OLi}{C}}-OC_2H_5 \right] \xrightarrow{H^+} R_f\overset{O}{C}R \qquad (1)$$

where $R = C_6H_5$, BrC_6H_4, C_4H_9

In our continuing studies in this area we have extended the reaction scheme to
the synthesis of fluorinated di- and tetra-ketones *via* a novel reaction

utilizing $C_6H_5CCl_2Li$ (I) as the organolithium reagent and fluorinated mono and diesters. As noted previously [1] the success of the procedure is based on the stabilizing effect of the R_f substituent on the lithium salt of the inter-mediate hemiketal.
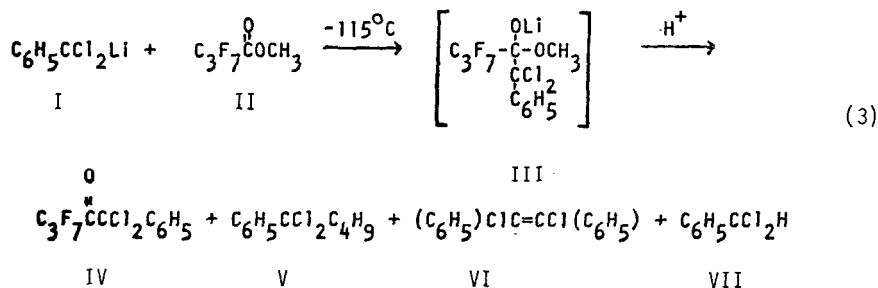
RESULTS AND DISCUSSION

Earlier studies [3,4] on the synthesis of fluorinated di- and tetra-ketones indicated the difficulties associated with the preparation of these compounds. Usually a multiple-step synthesis was involved which eventually gave products in low yield. We have found that $C_6H_5CCl_2Li$ [5] reacts with fluorinated esters to yield fluorochloroketones in excellent yield which subsequently can be converted to polyketones.

We have prepared $C_6H_5CCl_2Li$ in a diethyl ether -THF solution 1:1 volume ratio at $-110^\circ C$ to $-115^\circ C$.

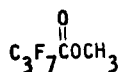$$C_6H_5CCl_3 + C_4H_9Li \longrightarrow C_4H_9Cl + \underset{(I)}{C_6H_5CCl_2Li} \tag{2}$$
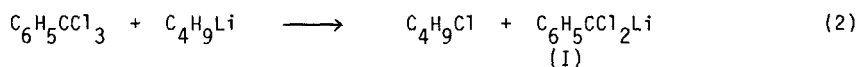
At $-115^\circ C$, the organolithium reagent I is stable for at least two hours. At $-100^\circ C$, it slowly begins to decompose and at $-78^\circ C$ the rate of decomposition is too fast for utility. At the decomposition temperature $C_6H_5CCl_2Li$ eliminates LiCl and forms a carbene $[C_6H_5\overset{-}{C}Cl]$. As was reported earlier [5] $C_6H_5CCl_2Li$ [in THF] at $-100^\circ C$ to $-115^\circ C$ has sufficient stability such that it behaves as a typical organolithium reagent. In our studies we have found, for example, that $C_6H_5CCl_2Li$ readily reacted with a perfluorinated ester at these low reaction temperatures to produce fluorochloroketones in high yields.

$$\underset{I}{C_6H_5CCl_2Li} + \underset{II}{C_3F_7\overset{O}{\overset{\|}{C}}OCH_3} \xrightarrow{-115^\circ C} \underset{III}{\left[C_3F_7-\overset{OLi}{\underset{\underset{C_6H_5}{CCl_2}}{\overset{|}{\underset{|}{C}}}}-OCH_3 \right]} \xrightarrow{\cdot H^+} \tag{3}$$

$$\underset{IV}{C_3F_7\overset{O}{\overset{\|}{C}}CCl_2C_6H_5} + \underset{V}{C_6H_5CCl_2C_4H_9} + \underset{VI}{(C_6H_5)ClC=CCl(C_6H_5)} + \underset{VII}{C_6H_5CCl_2H}$$
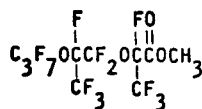
A GC/MS analysis of the reaction mixture indicated the following products (expressed in GC area %); IV 92%, V 3%, VI 0.5% (2 products), VII 3% and other unidentified products 1.5%. The same reaction, except in THF solvent and at $-100^{\circ}C$, produced a different ratio of products; IV 82%, V 4%, VI 7% (2 products), VII 4%, and other minor unidentified products 3%. At this higher reaction temperature ($-100^{\circ}C$) in THF it can be seen that the organolithium compound I reacts with C_4H_9Cl to form compound V and also decomposes to a higher extent yielding the carbene which dimerizes to yield the two products VI. These two products were found by GC/MS analysis to have identical molecular weights except a slightly different GC retention suggesting a cis-trans isomer mixture. A more complete characterization of these two components was not carried out.
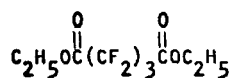
Since the reaction temperature was -110 to $-115^{\circ}C$ the solubility of the reactants, which affects rates of reaction, was an important factor to consider. Higher molecular weight esters and diesters, which may be less soluble at these temperatures or which may be sterically hindered, were therefore of interest to this study. The following esters were used to yield the fluorochloroketones, IV, XVII, XIV, XXIII shown in Table 1, thus indicating the versatility of this synthesis procedure:
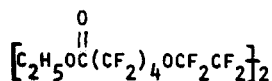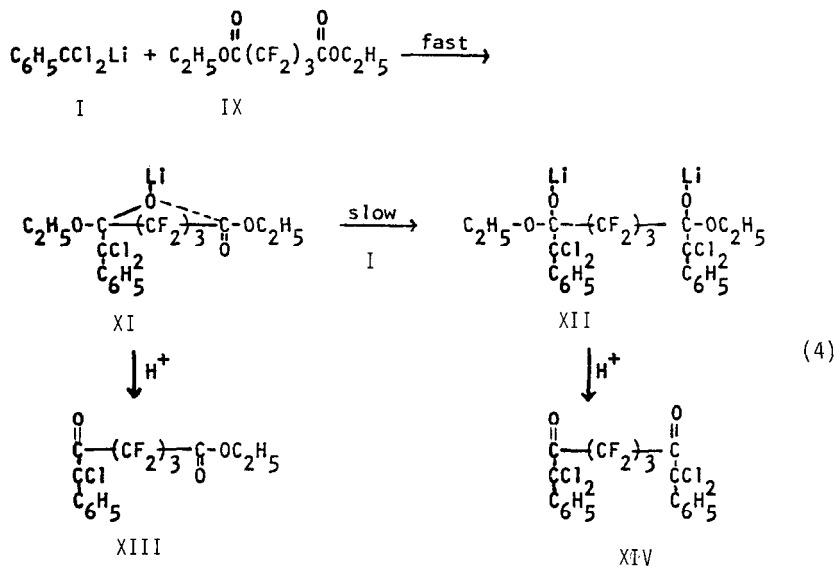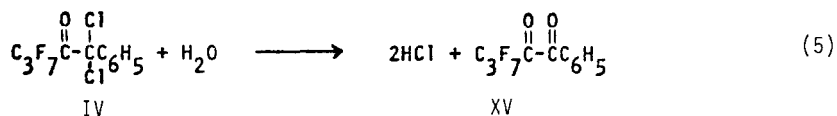
$$C_3F_7\overset{\overset{\displaystyle O}{\|}}{C}OCH_3$$

(II)

$$C_3F_7OCCF_2OCCOCH_3$$

(VIII)

$$C_2H_5O\overset{\overset{\displaystyle O}{\|}}{C}(CF_2)_3\overset{\overset{\displaystyle O}{\|}}{C}OC_2H_5$$

(IX)

$$\left[C_2H_5O\overset{\overset{\displaystyle O}{\|}}{C}(CF_2)_4OCF_2CF_2\right]_2$$

(X)

The primary esters II and X reacted with $C_6H_5CCl_2Li$ faster than the sterically hindered ester as might be expected [1]. Surprisingly the other primary diester, IX, reacted very slowly. A possible explanation for the lower reaction rate might be attributed to the formation of a cyclic intermediate, XI, which then reacts very slowly with the second equivalent of I to yield the desired product.
A GC/MS analysis of aliquot samples removed during the early stages of the reaction indicated the presence of the monosubstituted product XIII, thus lending evidence to the suggested mechanism (Equation 4).

$$C_6H_5CCl_2Li + C_2H_5O\overset{\overset{O}{\|}}{C}(CF_2)_3\overset{\overset{O}{\|}}{C}OC_2H_5 \xrightarrow{\text{fast}}$$

$$\quad\quad I \quad\quad\quad\quad IX$$

$$C_2H_5O-\underset{\underset{C_6H_5}{\overset{|}{C}Cl_2}}{\overset{\overset{\overset{Li}{|}}{O}}{\overset{\diagdown}{C}}}\overset{\diagdown}{(CF_2)_3}\underset{\overset{\|}{O}}{C}-OC_2H_5 \xrightarrow[I]{\text{slow}} C_2H_5-O-\underset{\underset{C_6H_5}{\overset{|}{C}Cl_2}}{\overset{\overset{\overset{Li}{|}}{O}}{C}}(CF_2)_3\underset{\underset{C_6H_5}{\overset{|}{C}Cl_2}}{\overset{\overset{\overset{Li}{|}}{O}}{C}}-OC_2H_5$$

$$\quad\quad\quad XI \quad\quad\quad\quad\quad\quad\quad\quad XII \quad\quad\quad\quad\quad\quad\quad (4)$$

$$\Big\downarrow H^+ \quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad \Big\downarrow H^+$$

$$\underset{\underset{C_6H_5}{\overset{|}{C}Cl}}{\overset{\overset{O}{\|}}{C}}(CF_2)_3\underset{\overset{\|}{O}}{C}-OC_2H_5 \quad\quad\quad \underset{\underset{C_6H_5}{\overset{|}{C}Cl_2}}{\overset{\overset{O}{\|}}{C}}(CF_2)_3\underset{\underset{C_6H_5}{\overset{|}{C}Cl_2}}{\overset{\overset{O}{\|}}{C}}$$

$$\quad\quad XIII \quad\quad\quad\quad\quad\quad\quad\quad\quad\quad XIV$$

The fluorochloroketones could be hydrolyzed to alpha-beta diketones. The rates of hydrolysis varied depending on the nature of the fluoroketone. As an example, $C_3F_7C(O)CCl_2C_6H_5$ on refluxing with water for an extended time (7 days) yielded the diketone XV in 92% yield.

$$C_3F_7\overset{\overset{O}{\|}}{C}-\underset{\underset{Cl}{|}}{\overset{\overset{Cl}{|}}{C}}C_6H_5 + H_2O \longrightarrow 2HCl + C_3F_7\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}C_6H_5 \quad\quad (5)$$

$$\quad\quad IV \quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad XV$$

The rates of hydrolysis could be increased by using an ethanol-silver nitrate solution (see Experimental Section).

As has previously been reported [6], highly fluorinated mono and diketones form hydrates and alcohol derivatives (hemiketals) quite readily. In our studies, the fluorochloroketones did not form any isolable hydrate, however the fluoroketones XV [3] and XXI formed the monohydrate while the ketone XVIII did not form any isolable hydrate due perhaps to steric hindrance of the alpha CF_3 group. Although a monohydrate could not be isolated,

evidence for a hemiketal XIX was indicated in the GC/MS analysis of the reaction mixture (see Experimental). Upon distillation however, this hemiketal must be thermally unstable since only the diketone XVIII was isolated. The tetraketone XXIV formed a dihydrate. It has been previously reported [3] that $C_6H_5C(O)C(O)(CF_2)_4C(O)C(O)C_6H_5$ also forms a dihydrate. The tetraketone XXI forms only a monohydrate XXII even though two alpha carbonyl groups activated by an adjacent perfluoro group are available for hydrate formation. The perfluoroglutaric acid derivatives have been reported [7] to have the capability of forming six-membered ring structures. It is quite possible that the monohydrate actually reacts with the second alpha carbonyl group forming a cyclic structure. The infrared analysis of monohydrate XXII indicated only one type of carbonyl group as well as only one type of OH group.

The hydrates of the various ketones could easily be dehydrated by azeotropic distillation with benzene or simply by distilling the hydrate which decomposes quite readily to form the free ketones characterized by their yellow color.

In the synthesis of compound XIV a H_2O-THF complex XX was isolated. Mass spectral, combustion, and thermogravimetric analysis indicated a 1:1:1 molar ratio complex. The monohydrate XXII and the H_2O-THF complex XX are suspected to be cyclic structures. Further studies elucidating their structure are in progress and will be reported at a later date.

EXPERIMENTAL

General comments

All reactions were carried out in oven dried glassware under an atmosphere of dry nitrogen. Diethyl ether was distilled from $LiAlH_4$ prior to use. Tetrahydrofuran was dried over sodium wire and was distilled from sodium-benzophenoneketyl. All melting and boiling points are uncorrected. Gas chromatographic analysis (GC) were performed on a Perkin-Elmer Sigma 1 using 6' stainless steel columns (1/4" d.) packed with 10% SE-30 on Chromosorb W. Mass spectra were obtained on a Du Pont Model 21-490 mass spectrometer using a chemical ionization mode. Infrared spectra were recorded on a Perkin-Elmer Model 600 computing infrared spectrophotometer. The physical measurements and analyses of the various reaction products are summarized in Table 1.
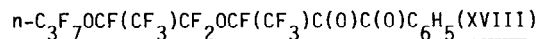
$n-C_3F_7C(O)CCl_2C_6H_5 (IV)$
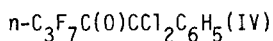
To a diethyl ether (350 ml) and THF (350 ml) solution of $C_6H_5CCl_3$ (39.1 g, 200 mmol) was slowly added $n-C_4H_9Li$ (83.3 ml of 2.4M hexane solution, 200 mmol) at $-115°C$ over 1.5 h. The colorless solution turned into a lavender slurry and the reaction temperature rose to $-110°C$. After an additional 20 min., $n-C_3F_7CO_2CH_3$ (47.9 g, 210 mmol) was added over 25 min. during which time the lavender slurry turned into a brown solution. After 1 h, the reaction mixture was hydrolyzed with a precooled solution of conc. HCl (20 ml) and ethanol (60 ml) at $-115°C$. After 10 min., the reaction mixture was poured into 2N HCl (300 ml), phase separated and the aqueous layer further extracted with diethyl ether (2 x 100 ml). The combined organic layers were dried with $MgSO_4$. Distillation yielded $n-C_3F_7C(O)CCl_2C_6H_5$, 60.5 g (85%). See Table 1.

$n-C_3F_7C(O)C(O)C_6H_5 (XV)$
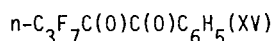
A mixture of $n-C_3F_7C(O)CCl_2C_6H_5$ (3.72 g, 104 mmol) and water (400 ml) was heated to reflux. After 7 days, the reaction mixture was allowed to cool to $25°C$, the mixture was filtered and the white solid was washed with hexane (3 x 5 ml). Pure white crystals of $n-C_3F_7C(O)C(O)C_6H_5 \cdot H_2O$ (XVI) were obtained, 30.5 g (92%). An anhydrous $n-C_3F_7C(O)C(O)C_6H_5$ yellow liquid was obtained on heating the hydrate in benzene and removing the water as an azeotrope.

### $n-C_3F_7OCF(CF_3)CF_2OCF(CF_3)C(O)CCl_2C_6H_5 (XVII)$
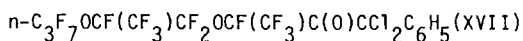
To a diethyl ether (500 ml) and THF (500 ml) solution of $C_6H_5CCl_3$ (40 g, 204.6 mmol) was slowly added $n-C_4H_9Li$ (95.8 ml of 2.2M hexane solution, 210.7 mmol) at $-115°C$ over 1.3 h during which the colorless solution turned into a lavender slurry. After 20 min., to the above reaction mixture at $-115°C$ was added dropwise, $n-C_3F_7OCF(CF_3)CF_2OCF(CF_3)CO_2CH_3$ (107.5 g, 210.7 mmol) in diethyl ether (50 ml) over 25 min. After 5.5 h, the reaction mixture was hydrolyzed with a precooled solution of conc. HCl (20 ml) and ethanol (60 ml). After 20 min., the reaction mixture was poured into 2N HCl (600 ml), and phase separated and dried $(MgSO_4)$. Distillation yielded 111 g (87%) (See Table 1) of $n-C_3F_7OCF(CF_3)CF_2OCF(CF_3)C(O)CCl_2C_6H_5$.

$n-C_3F_7OCF(CF_3)CF_2OCF(CF_3)C(O)C(O)C_6H_5 (XVIII)$

An ethanol (250 ml) and water (250 ml) mixture of $n-C_3F_7OCF(CF_3)CF_2OCF(CF_3)C(O)CCl_2C_6H_5$ (30.0 g, 46.9 mmol) and $AgNO_3$ (20.0 g, 117.3 mmol) was heated to reflux for 32.5 h. Aliquot samples were removed periodically and analyzed by GC. The reaction mixture was cooled, filtered to

remove the AgCl, resulting in a two-phase liquid. The bottom crude product layer was separated and the upper aqueous layer was extracted with diethyl ether. The diethyl ether extract and crude product were combined and dried ($MgSO_4$). A GC/MS analysis of the crude reaction mixture showed two products: n-$C_3F_7OCF(CF_3)CF_2OCF(CF_3)C(O)C(O)C_6H_5$ and n-$C_3F_7OCF(CF_3)CF_2OCF(CF_3)C(O)C(O)C_6H_5 \cdot C_2H_5OH$ (XIX). Distillation of the reaction mixture yielded only compound XVIII, b.p. 110°/5 mm, 25.8 g (94%). In order to verify the possible existence of XIX, an excess of C_2H_5OH was added to XVIII and heated gently for 1 h. Upon removing the excess C_2H_5OH, a liquid material remained which showed no carbonyl band, $R_fC=O$ at 1750 cm^{-1}. The $C_6H_5C=O$ carbonyl band at 1680 was still present indicating the preferential addition of C_2H_5OH to the more electrophilic site. The MS analysis indicated a peak at a mass of 630 (M^+) for a mono addition of C_2H_5OH to the diketone XVIII. On standing at room temperature for ~ 20 h, the weak addition product XIX decomposed to the free ketone XVIII.

$\underline{C_6H_5CCl_2C(O)(CF_2)_3C(O)CCl_2C_6H_5 (XIV)}$
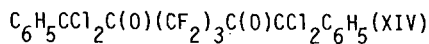
To a diethyl ether (500 ml) and THF (500 ml) solution of $C_6H_5CCl_3$ (58.7 g, 300 mmol) was slowly added n-C_4H_9Li (131.3 ml of 2.4M hexane solution, 315 mmol) at -115°C over 1.5 h. After 25 min., to the above lavender slurry mixture at -115°C was added dropwise $C_2H_5O(O)C(CF_2)_3C(O)OC_2H_5$ (46.6 g, 158 mmol) over 35 min. during which a reddish brown slurry was obtained. After 7 h, the reaction mixture was hydrolyzed with a precooled solution of conc. HCl (20 ml) and ethanol (50 ml). After 10 min., the reaction mixture was poured into 2N HCl (400 ml), phase separated and the aqueous layer further extracted with diethyl ether (2 x 300 ml). The combined organic layers were dried with $MgSO_4$ and the low boiling solvents were removed on a rotary evaporator at 60°C. The resulting mixture was filtered and the white filtered solid was washed with hexane (3 x 50 ml) resulting in a white crystalline product,
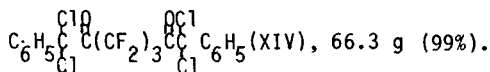
$$C_6H_5\underset{Cl}{\overset{Cl}{\underset{|}{\overset{|}{C}}}}\underset{}{\overset{O}{\underset{}{\overset{||}{C}}}}(CF_2)_3\overset{O}{\overset{||}{C}}\underset{Cl}{\overset{Cl}{\underset{|}{\overset{|}{C}}}}C_6H_5 \cdot THF(XX),$$ 76.3 g (85%). Product XX was heated
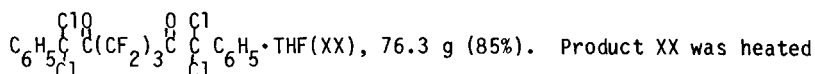
to 90°C under vacuum over 2 h to yield   .

$$C_6H_5\underset{Cl}{\overset{Cl}{\underset{|}{\overset{|}{C}}}}\overset{O}{\overset{||}{C}}(CF_2)_3\overset{O}{\overset{||}{C}}\underset{Cl}{\overset{Cl}{\underset{|}{\overset{|}{C}}}}C_6H_5(XIV),$$ 66.3 g (99%).

TABLE 1^a

Characterization of new compounds

PRODUCT	%YIELD^b	b.p. °C/mm (m.p. °C)	IR cm^{-1} C=O	OH	M.S.
n-C$_3$F$_7$CCC$_6$H$_5$(n.c.) (IV)	95 (85)	102°/14	1758	--	355, 357, 359 (M)$^+$
n-C$_3$F$_7$CCC$_6$H$_5$ (n.c.) (XV)	-- (92)		1754, 1687	--	302 (M)$^+$
n-C$_3$F$_7$CCC$_6$H$_5$·H$_2$O (n.c.) (XVI)	-- (92)	(60-63° dec.)	1688	3580 3395	320 (M)$^+$
C$_3$F$_7$OC CF$_2$OC CCC$_6$H$_5$ (n.c.) CF$_3$ CF$_3$Cl (XVII)	97 (87)	94°/1.2	1760	--	603, 605 (M-Cl)$^+$
C$_3$F$_7$OC CF$_2$OC CCC$_6$H$_5$ (n.c.) CF$_3$ CF$_3$ (XVIII)	-- (94)	110°/5	1750, 1685	--	584 (M)$^+$
C$_3$F$_7$OC CF$_2$OCCCC$_6$H$_5$·C$_2$H$_5$OH (n.c.) CF$_3$ CF$_3$ (XIX)	-- (0)	c	1680	3400	630 (M)$^+$

Structure	No.	G.C. area %	(isolated)	m.p./b.p.	IR (cm⁻¹)	(cm⁻¹)	Mass spectrum, m/e
$C_6H_5\overset{ClO}{\underset{Cl}{C}}C(CF_2)_3\overset{OCl}{\underset{Cl}{C}}C\,C_6H_5$ (n.c.)	(XIV)	--	(99)	(98)	1760	--	488, 490, 492 (M-HCl)⁺
$C_6H_5\overset{ClO}{\underset{Cl}{C}}C(CF_2)_3\overset{OCl\ \ (H_2O^+)}{\underset{Cl}{C}}C\,C_6H_5\cdot C_4H_8O$ (n.c.)	(XX)	--	(85)	(123-127°dec)	--	--	614, 616, 618 (M⁺) 488, 490, 492 (M-HCl-H₂O-THF)⁺
$C_6H_5\overset{OO}{CC}(CF_2)_3\overset{OO}{CC}C_6H_5$ (n.c.)	(XXI)	--	(100)	142°/0.015	1750, 1680	--	416 (M⁺)
$C_6H_5\overset{OO}{CC}(CF_2)_3\overset{OO}{CC}C_6H_5\cdot H_2O$ (n.c.)	(XXII)	--	(85)	(128-135°dec.)	--, 1660	3360	434 (M⁺), 416 (M-H₂O)⁺
$\left[C_6H_5\overset{ClO}{\underset{Cl}{C}}C(CF_2)_4OCF_2CF_2\right]_2$ (n.c.)	(XXIII)	94	(90)	c	1760	--	971, 973, 975 (M-Cl)⁺
$\left[C_6H_5\overset{OO}{CC}(CF_2)_4OCF_2CF_2\right]_2$ (n.c.)	(XXIV)	--	(81)	166/0.025	1740, 1680	--	898 (M)⁺
$\left[H_2O\cdot C_6H_5\overset{OO}{CC}(CF_2)_4OCF_2CF_2\right]_2$ (n.c.)	(XXV)	94	(--)	78-83° (dec.)	--, 1680	3420 3330	898 (M-2H₂O)⁺

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[a] All products isolated had correct C, H and Cl analyses.

[b] %Yield: G.C. area % (isolated yield).

[c] Not isolated.

$C_6H_5C(O)C(O)(CF_2)_3C(O)C(O)C_6H_5(XXI)$
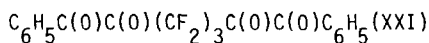
An ethanol (250 ml), water (250 ml) mixture of $AgNO_3$ (28.4 g, 167 mmol) and $C_6H_5CCl_2C(O)(CF_2)_3C(O)CCl_2C_6H_5$· THF (XX) (20.0 g, 33.4 mmol) was heated to reflux for 2.5 h during which time aliquot samples were removed and analyzed by GC. The reaction mixture was cooled and the solids (AgCl plus product) were filtered. The filtrate was extracted with diethyl ether which was combined with a diethyl ether extract of the above solids. The diethyl ether solution was dried ($MgSO_4$) and aspirated up to $60^{\circ}C$ to remove low boiling materials. The remaining solids were washed with hexane yielding a white crystalline product $C_6H_5C(O)C(O)(CF_2)_3C(O)C(O)C_6H_5$· $H_2O(XXXII)$, 12.3 g (85%). Distillation of XXII yielded the yellow liquid product XXI, b.p. $142^{\circ}C/0.015$ m

$[C_6H_5CCl_2C(O)(CF_2)_4O(CF_2)_2]_2(XXXIII)$
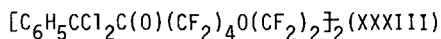
To a diethyl ether (250 ml) and THF (250 ml) solution of $C_6H_5CCl_3$ (8.09 g, 41.4 mmol) was slowly added $n-C_4H_9Li$ (17.3 ml of 2.4M hexane solution, 41.4 mmol) at $-115^{\circ}C$ over 1.5 h. The colorless solution turned into a lavender slurry and the reaction temperature rose to $-110^{\circ}C$. After 30 min., to the above reaction mixture, at $-115^{\circ}C$, was slowly added (14.0 g, 18.0 mmol) $[C_2H_5O(O)C(CF_2)_4O(CF_2)_2]_2$ over 36 min. After 1.5 h, the reaction mixture was hydrolyzed with a precooled solution of conc. HCl (5 ml) and ethanol (10 ml) at $-115^{\circ}C$. After 5 min., the reaction mixture was poured into a 2N HCl (400 ml), phase separated and the aqueous layer further extracted with diethyl ether (2 x 200 ml). The combined organic layers were dried ($MgSO_4$) and the low boiling liquids were removed with a rotary evaporator at $40^{\circ}C$. The crude product was passed through a silica-gel column and eluted with a 1:4 (volume ratio) of diethyl ether and hexane. Purification by this method yielded $[C_6H_5CCl_2C(O)(CF_2)_4O(CF_2)_2]_2(XXIII)$, 16.3 g (90%). See Table 1.

$[C_6H_5C(O)C(O)(CF_2)_4O(CF_2)_2]_2(XXIV)$
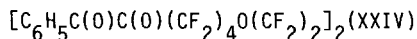
An ethanol (120 ml) and water (120 ml) mixture of $AgNO_3$ (7.0 g, 41.2 mmol) and $[C_6H_5CCl_2C(O)(CF_2)_4O(CF_2)_2]_2$ (7.31 g, 7.25 mmol) was heated to reflux temperature. After 20 h, the mixture was cooled and filtered. The filtrate was extracted with diethyl ether while the filtered solid (AgCl plus crude product) was also extracted with diethyl ether. The combined diethyl ether extracts were dried ($MgSO_4$) and aspirated under vacuum up to $50^{\circ}C$. The residue was distilled yielding the product XXIV, b.p. $166^{\circ}C/0.025$ mm, 5.3 g (81%). On standing in moist air XXIV changed to the dihydrate XXV.

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