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FLUORO-KETONES VII. SYNTHESIS OF PERFLUORO MONO- AND DI-KETONES FROM PERFLUORO-GRIGNARD OR LITHIUM REAGENTS AND DIETHYL CARBONATE AND DIETHYL OXALATE

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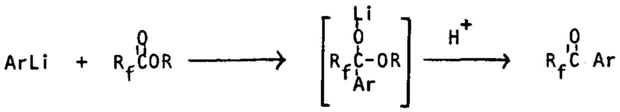
SUMMARY

The reaction between perfluoroalkyl-Grignard or lithium compounds and diethyl carbonate has been investigated. Under appropriate conditions, symmetric or asymmetric ketones can be prepared. The reactions of the perfluoro-Grignard or lithium compounds with diethyl oxalate can yield keto-esters and symmetric or asymmetric ketones.

INTRODUCTION

In our previous communications [1,2] we have reported on the synthesis of fluorine-containing aryl ketones through the reaction between aryllithium reagents and various perfluoroesters.



$$ArLi + R_f\overset{O}{\overset{\|}{C}}OR \longrightarrow \left[R_f\overset{\overset{Li}{|}}{\overset{O}{\underset{Ar}{\overset{|}{\underset{|}{C}}}}}\text{-}OR\right] \xrightarrow{H^+} R_f\overset{O}{\overset{\|}{C}}\ Ar$$

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A stabilizing effect by the R_f substituent on the lithium salt of the above intermediate hemiketal makes the synthesis of fluorine-containing ketones possible. In certain instances we have isolated and characterized the lithium salt at room temperature. A bis(perfluoropropyl)lithium hemiketal $(C_3F_7)_2C(OC_2H_5)OLi$ has been previously suggested [3] as a possible intermediate in the reaction between n-C_3F_7Li and n-$C_3F_7CO_2C_2H_5$. No attempt however was made to isolate or characterize the intermediate compound. The hydrocarbon hemiketal analogs are quite unstable and readily decompose by elimination of LiOR to yield the ketone which in turn may react further with the organometallic intermediate to yield alcohols [4]. Since the R_f group stabilizes the anion in hemiketals, it was of interest to us to determine whether other similar structures would likewise be affected and thus provide a synthesis means of preparing other perfluoroalkyl or perfluoroaryl acyl type compounds. Towards this objective we have extended our studies to the reaction between perfluoroaliphatic lithium or Grignard reagents and alkyl carbonates and alkyl oxalates.

DISCUSSION

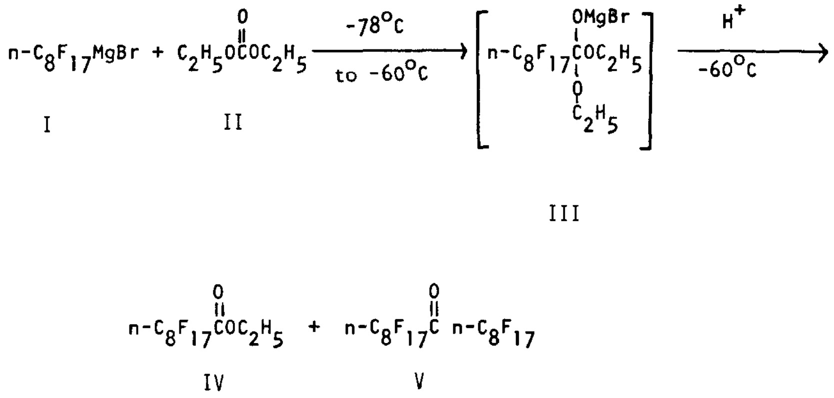
Reaction between polyhaloorganometallic compounds and dimethylcarbonate have previously been reported as a means of synthesizing ketones [5], acids [6] and esters [6]. Similarly reactions of haloarylorganometallics with oxalate esters have provided a means of synthesizing alpha-beta diketones [7], ketoesters [8] and alpha-omega diketones [8]. In order to better understand the limitations of this reaction, we have studied it in more detail with an objective of providing a general synthesis procedure for these compounds. The organometallic intermediates that we have examined were n-$C_8F_{17}MgBr$, n-$C_8F_{17}Li$, $FC(CF_3)_2OCF_2CF_2MgBr$, and $FC(CF_3)_2OCF_2CF_2Li$.

Thermal stability of organometallic intermediates

Perfluoroalkylorganometallic (R_fM) compounds are temperature sensitive and therefore successful application of them as synthesis intermediates must be carried out with an understanding of their temperature limitations. R_fMgX compounds are generally more stable than R_fLi compounds. n-$C_8F_{17}MgBr$ [9] and $FC(CF_3)_2OCF_2CF_2MgBr$ [10] are sufficiently stable at -40°C in diethyl ether for reaction with reactive substrates. n-$C_7F_{15}Li$ [11] is very unstable at -75°C, however it can be used as an intermediate if it is prepared in-situ and allowed to react with a substrate [12] immediately. It was surprising therefore, to find that the $FC(CF_3)_2OCF_2CF_2Li$ [13] is stable at -78°C for at least 24 hours. Our only explanation of the greater thermal stability of this ether type organolithium is that the beta oxygen somehow stabilizes the organolithium compound. Studies directed at this observation of increase thermal stability are in progress. Even though R_fLi compounds are generally less thermally stable than their Grignard counterparts, they do offer faster reaction rates over the Grignards, because of their greater nucleophilic character. Within these temperature limitations, one can still use these organometallic intermediates effectively for the synthesis of numerous compounds.

Reaction with $C_2H_5O\overset{O}{\overset{\|}{C}}OC_2H_5$

At the low reaction temperatures used, $C_2H_5OC(O)OC_2H_5$ is more soluble than $CH_3OC(O)OCH_3$ and therefore was the ester of choice. n-$C_8F_{17}MgBr$ reacted slowly with the ester (1:1 mole ratio) to yield n-$C_8F_{17}C(O)OC_2H_5$ (IV) (96% G.C. yield) plus a trace of the ketone (n-$C_8F_{17})_2C(O)$ (V).



$$\underset{\text{I}}{n\text{-}C_8F_{17}MgBr} + \underset{\text{II}}{C_2H_5O\overset{O}{\overset{\|}{C}}OC_2H_5} \xrightarrow[\text{to } -60^\circ C]{-78^\circ C} \underset{\text{III}}{\left[n\text{-}C_8F_{17}\overset{OMgBr}{\underset{O\atop C_2H_5}{C}}OC_2H_5 \right]} \xrightarrow[-60^\circ C]{H^+}$$

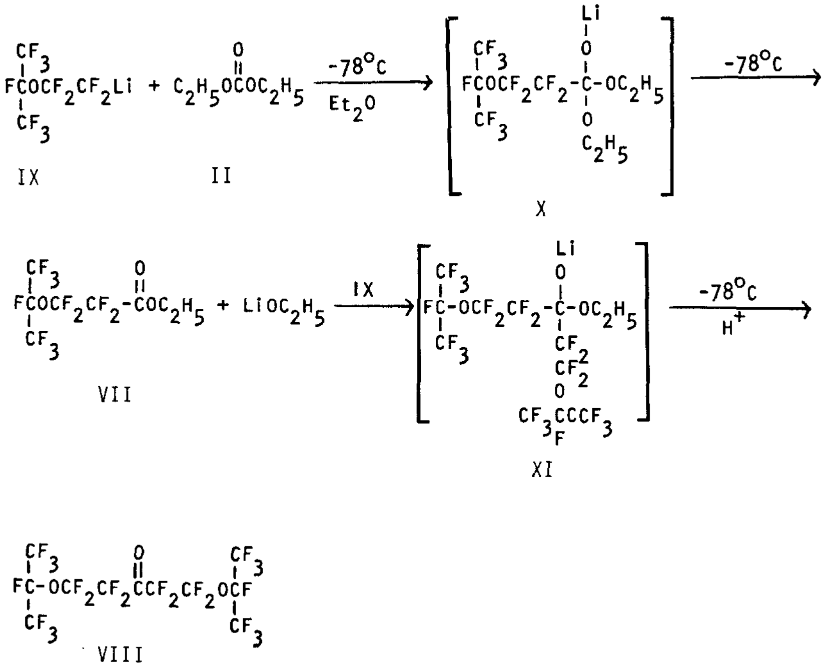
$$\underset{\text{IV}}{n\text{-}C_8F_{17}\overset{O}{\overset{\|}{C}}OC_2H_5} + \underset{\text{V}}{n\text{-}C_8F_{17}\overset{O}{\overset{\|}{C}}\ n\text{-}C_8F_{17}}$$

Attempts to isolate the intermediate III at room temperature were unsuccessful due to its thermal instability. At -60°C the intermediate

III must be sufficiently stable so as not to eliminate C_2H_5OMgBr to yield the ester IV. If any ester was formed it would react with the Grignard I to yield the ketone V as the major product.

The Grignard $FC(CF_3)_2OCF_2CF_2MgBr$ (VI) similarly reacted with II to yield the ester $FC(CF_3)_2OCF_2CF_2(O)OC_2H_5$ (VII). The rate of reaction of VI with the ester was considerably faster than with $C_8F_{17}MgBr$. Using an excess of VI (2:1 molar ratio) yielded no ketone $[FC(CF_3)_2OCF_2CF_2]_2C(O)$ (VIII) indicating that the magnesium salt intermediate (similar to III) must be quite stable at -78°C and does not decompose to yield the ester VII at this low reaction temperature. However by raising the reaction temperature slowly from -78°C to 0°C over a period of 3 hours, the magnesium salt intermediate must have slowly decomposed to the ester VII which then reacted with the second equivalent of VI to yield the ketone VIII in approximately 25% yield.

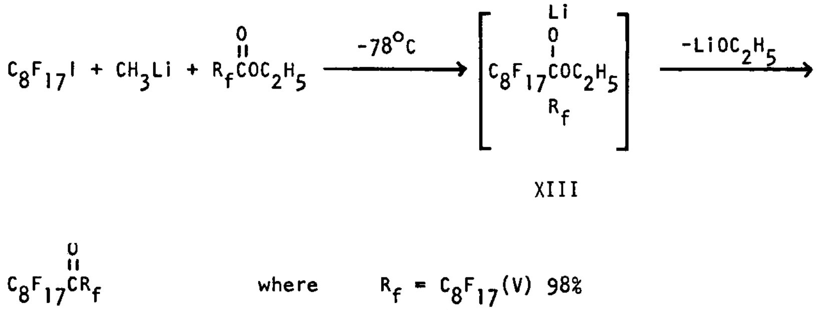
The reaction between $FC(CF_3)_2OCF_2CF_2Li$ (IX) and the diethyl carbonate (1:1 mole ratio) at -78°C produced a mixture of products VII and VIII.



The lithium salt X at -78°C, unlike its -MgBr salt, must be less thermally stable eliminating $LiOC_2H_5$ and forming the ester VII which in turn competes with the unreacted ester II for the organolithium reagent IX to form the ketone VIII. By using a 2:1 mole ratio of IX to II, the ketone VIII can be produced in near quantitative yield at -78°C. This result indicates the greater thermal stability of the magnesium salt over the lithium salt hemiketal. At a 1:1 mole ratio at -110°C, the intermediate X is thermally stable and does not decompose to the ester VII. Under these conditions the organolithium compound IX reacted only with the diethyl carbonate to give the ester VII in quantiative yield.

Because of its relative instability at -78°C, $n\text{-}C_8F_{17}Li$ (XII) must be prepared and reacted with substrates in an in-situ manner. Attempts to prepared the symmetric ketone $C_8F_{17}C(O)C_8F_{17}$, directly from $C_8F_{17}I$, CH_3Li and diethyl carbonate (2.3:1 mole ratio) by the in-situ method at -78°C, produced the ketone in only 55% yield. This lower yield can be rationalized by the fact that the intermediate lithium hemiketal X, [except $R_f=C_8F_{17}$] decomposes to the intermediate ester $C_8F_{17}C(O)OC_2H_5$ at a slower rate than the rate of decomposition of the transient $C_8F_{17}Li$ formed in-situ.

The transient $C_8F_{17}Li$ can however react very rapidly with perfluorinated esters at -78°C to form perfluorinated ketones. Apparently in this type of reaction, the rate of reaction of $n\text{-}C_8F_{17}Li$ with the perfluorinated ester is considerably faster than the rate of decomposition of the $n\text{-}C_8F_{17}Li$. This is shown by the following reaction whereby high yields of the symmetric or asymmetric perfluorinated ketones may be prepared.



$$C_8F_{17}I + CH_3Li + R_f\overset{\overset{O}{\|}}{C}OC_2H_5 \xrightarrow{-78^{\circ}C} \left[C_8F_{17}\underset{R_f}{\overset{\overset{Li}{O}}{C}}OC_2H_5 \right] \xrightarrow{-LiOC_2H_5} C_8F_{17}\overset{\overset{O}{\|}}{C}R_f$$

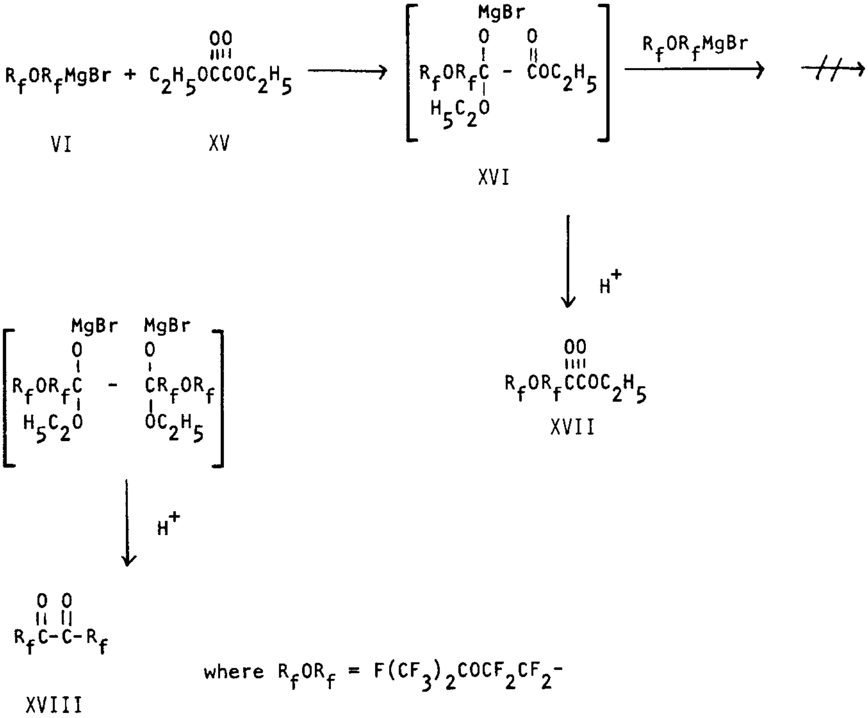
XIII

where $R_f = C_8F_{17}$(V) 98%

$R_f = (CF_3)_2CFOCF_2CF_2$(XIV) 96%

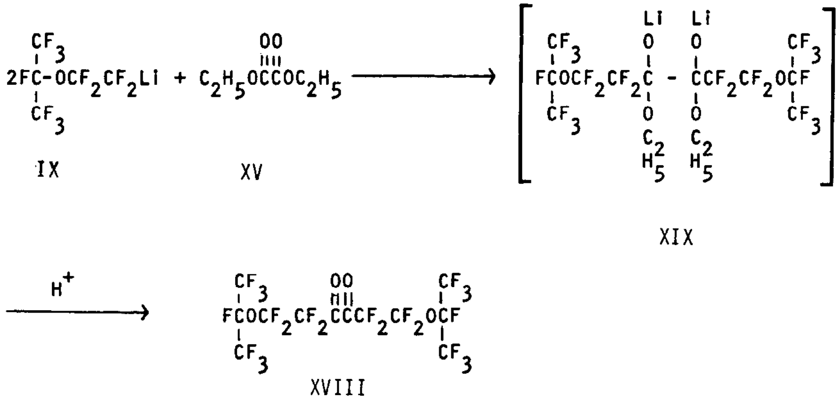
Reaction with $C_2H_5O\overset{O}{\overset{\|}{C}}\overset{O}{\overset{\|}{C}}OC_2H_5$ (XV)

In an attempt to prepare the bis-substituted diketone XVIII, the reaction between the Grignard $FC(CF_3)_2OCF_2CF_2MgBr$ and diethyl oxalate in a 2:1 mole ratio was attempted. The only acyl product isolated however was the monosubstituted keto ester XVII and $F(CF_3)_2COCF_2CF_2H$ from the hydrolysis of the unreacted Grignard.



where $R_fOR_f = F(CF_3)_2COCF_2CF_2$-

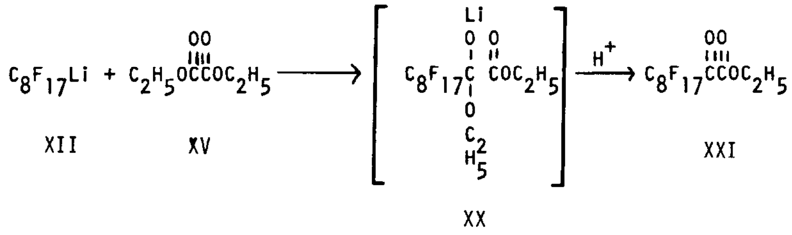
It is not known at this time, whether there is a free carbonyl group in the intermediate XVI available for the second equivalent of the Grignard VI to react with. It may be possible that the -MgBr is involved in a cyclic complex between both carbonyl groups. Grignard VI may not be nucleophilic enough to react with such a complex or the intermediate XVI. The more nucleophilic organolithium compound IX however reacted with the diethyl oxalate (2:1 mole ratio) to give a high yield of the symmetric diketone XVIII. This observation suggests that lithium analog of XVI does not complex with the unsubstituted acyl group or that the organolithium IX being more nucleophilic than the Grignard VI reacts with the second acyl group more readily.



$$2\,\mathrm{F\overset{CF_3}{\underset{CF_3}{C}}\text{-}OCF_2CF_2Li} + \mathrm{C_2H_5O\overset{O}{C}\overset{O}{C}OC_2H_5} \longrightarrow \left[\mathrm{F\overset{CF_3}{\underset{CF_3}{C}}OCF_2CF_2\overset{OLi}{\underset{OC_2H_5}{C}} - \overset{OLi}{\underset{OC_2H_5}{C}}CF_2CF_2O\overset{CF_3}{\underset{CF_3}{C}}F}\right] \xrightarrow{H^+} \mathrm{F\overset{CF_3}{\underset{CF_3}{C}}OCF_2CF_2\overset{O}{C}\overset{O}{C}CF_2CF_2O\overset{CF_3}{\underset{CF_3}{C}}F}$$

IX XV XIX XVIII

The in-situ reaction between $C_8F_{17}Li$ and diethyl oxalate (1:1 mole ratio) gave a high yield of the keto-ester XXI.

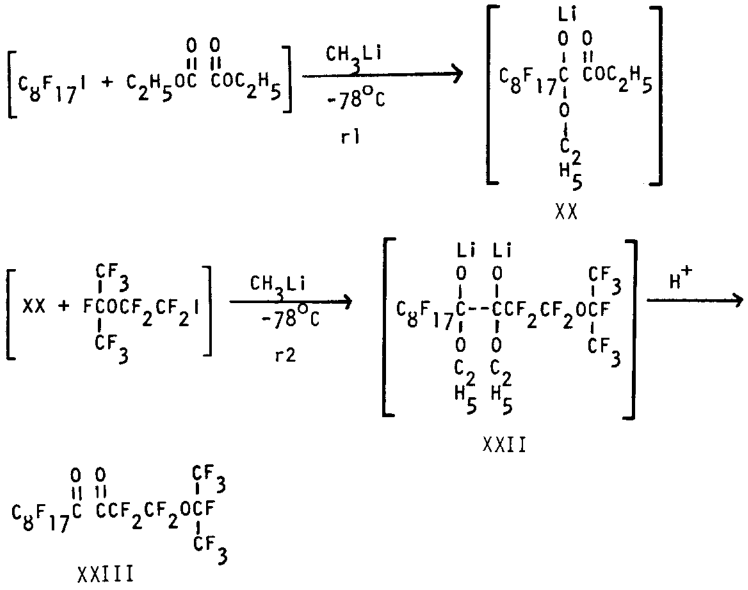


$$\mathrm{C_8F_{17}Li} + \mathrm{C_2H_5O\overset{O}{C}\overset{O}{C}OC_2H_5} \longrightarrow \left[\mathrm{C_8F_{17}\overset{OLi}{\underset{OC_2H_5}{C}}\overset{O}{C}OC_2H_5}\right] \xrightarrow{H^+} \mathrm{C_8F_{17}\overset{O}{C}\overset{O}{C}OC_2H_5}$$

XII XV XX XXI

In a 2:1 mole ratio of XII to XV, none of the symmetric diketone was formed. Apparently the rate of decomposition of XII is much faster than its reaction with the required intermediate XX. A GC/MS analysis of the reaction mixture indicated the ketoester compound XXI and products typical of $C_8F_{17}Li$ decomposition.

By using the above data, an asymmetric diketone (XXIII) can be prepared readily by the following sequential reactions.



$$R_fLi \xrightarrow{r3} LiF + \text{decomposition products}$$

From our observations, r2 is much slower than r1 and therefore a more stable R_fLi must be used in the second step. Since R_fLi decomposes at a rate dependent on reaction conditions (time, temperature, solvent) and structure of R_fLi, r3 must be slower than r1 and r2. Based on our studies of relative thermal stability of various R_fM compounds (M=MgX or Li) and their relative rates of reactions with diethyl oxalate, the asymmetric diketone XXIII was prepared in 84% yield. Two different R_fLi compounds were used representing two different orders of stability and reactivity. By these sequential reactions, utilizing the less stable R_fLi first and the more stable and reactive $R_f'Li$ in the second step, good yields of asymmetric diketones can be prepared.

TABLE 1

Characterization of new compounds

Product	b.p./mm (m.p.) °C	IR, (C=O) cm^{-1}	M.S.	Combustion Data (Calc'd/Found) C	H
$n\text{-}C_8F_{17}\overset{O}{\overset{\|}{C}}OC_2H_5$ (IV) (n.c.)	158/760	1780	492 (M^+)	$\frac{26.84}{26.65}$	$\frac{1.02}{1.01}$
$(n\text{-}C_8F_{17})_2C=O$ (V) (n.c.)	(57)	1788	866 (M^+)	$\frac{23.57}{23.09}$	$\frac{0}{0.23}$
$(CF_3)_2CFOCF_2CF_2\overset{O}{\overset{\|}{C}}OC_2H_5$ (VII) (n.c.)	110/760	1787	358 (M^+)	$\frac{26.83}{26.91}$	$\frac{1.41}{1.39}$
$\left[(CF_3)_2CFOCF_2CF_2\right]_2C=O$ (VIII) (n.c.)	130/760	1786	579 $(M\text{-}F)^+$	$\frac{22.09}{21.94}$	$\frac{0}{0.12}$
$n\text{-}C_8F_{17}\overset{O}{\overset{\|}{C}}CF_2CF_2OCF(CF_3)_2$ (XIV) (n.c.)	104/19	1790	713 $(M\text{-}F)^+$	$\frac{22.96}{22.84}$	$\frac{0}{0.07}$
$(CF_3)_2CFOCF_2CF_2\overset{O}{\overset{\|}{C}}\overset{O}{\overset{\|}{C}}OC_2H_5$ (XVII) (n.c.)	150/760	1751 1770 (shoulder)	386 (M^+)	$\frac{27.99}{27.78}$	$\frac{1.31}{1.20}$
$\left[(CF_3)_2CFOCF_2CF_2\overset{O}{\overset{\|}{C}}\text{-}\right]_2$ (XVIII) (n.c.)	156/760	1758	607 $(M\text{-}F)^+$	$\frac{23.02}{22.89}$	$\frac{0}{0.02}$
$n\text{-}C_8F_{17}\overset{O}{\overset{\|}{C}}\overset{O}{\overset{\|}{C}}OC_2H_5$ (XXI) (n.c.)	76/4.6	1753 1772 (shoulder)	520 (M^+)	$\frac{27.71}{27.58}$	$\frac{0.97}{0.77}$
$n\text{-}C_8F_{17}\overset{O}{\overset{\|}{C}}\overset{O}{\overset{\|}{C}}CF_2CF_2OCF(CF_3)_2$ (XXIII) (n.c.)	83/4.6	1757	741 $(M\text{-}F)^+$	$\frac{23.70}{23.35}$	$\frac{0}{0.03}$

TABLE 2

Reactions with $C_2H_5O\overset{O}{C}OC_2H_5$ (DEC)

Organometallic (RM)	Mole Ratio RM/DEC	Temp. °C	Time (hours)	Products		% Yield	
				Ester	Ketone	GC area	Isolated
1 R_fMgBr	1.05/1	-78	0.25	IV		2	
					V	-	
		-78	4.5	IV		63	
					V	-	
		-60	20	IV		94	86
					V	2	-
2 R_fOR_fMgBr	1.05/1	-78 to	4.25	VII		98	88
		-40			VIII	2	
3 R_fOR_fMgBr	2/1	-40	0.25	VII		98	
					VIII	2	
		0	3.0	VII		75	
					VIII	25	
4 R_fOR_fLi	1.05/1	-78	1	VII		16	
					VIII	45	
	1.05/1	-110	1	VII		99	
					VIII	0	

5 R_fOR_fLi	2.1/1	-78	1.5	VII		8	6
					VIII	86	84
6 R_fLi	2.3/1	-78	0.5	IV		16	-
<u>(in situ)</u>					V	55	38

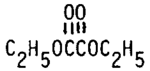
Reactions with $R_fCO_2C_2H_5$ or $R_fOR_fCO_2C_2H_5$

Organometallic (RM)	Mole Ratio $RM/R_fCO_2C_2H_5$	Temp ^oC	Time (hours)	Products Ester	 Ketone	% Yield GC area	Isolated
7 R_fLi	1/1.03	-78	0.5	IV		3	--
<u>(in situ)</u>	$RM/R_fCO_2C_2H_5$				V	94	--
8 R_fLi	1/1.03	-78	0.75	XIV		96	84
<u>(in situ)</u>	$RM/R_fOR_fCO_2C_2H_5$				VII	1.5	--

$R_f = n\text{-}C_8F_{17}$

$R_fOR_f = F(CF_3)_2COCF_2CF_2\text{-}$

TABLE 3



Reactions with $C_2H_5O\overset{O}{\overset{\|}{C}}\overset{O}{\overset{\|}{C}}OC_2H_5$ (DEO)

Organometallic (RM)	Mole Ratio RM/DEO	Temp. oC	Time (hours)	Products		% Yield	
				Ketoester	Ketone	GC area	Isolated
1 R_fOR_fMgBr [a]	2.08/1	-78	2	XVII		b	76
2 R_fOR_fLi	2.04/1	-78	2	XVII		9	--
					XVIII	88	77
3 R_fLi (in situ)	1.03/1	-78	1	XXI		94 c	84
4 R_fLi (in situ)	1.02/1	-78	0.5	XXI		95	--
R_fOR_fLi (in situ)	2.04/1	-78	2.0	XXI		15	11
					XXIII	84	70

[a] diethyl ether/THF solvent

[b] solvent peaks interfered with product identification

[c] no diketone detected, however $C_8F_{17}C(O)C(O)CH_3$ (4%) was detected by GC/MS

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. Diethyl carbonate and diethyl oxalate were distilled from CaO prior to use. All melting and boiling points are uncorrected. Gas chromatographic analyses (GC) were performed on a Perkin-Elmer Sigma I using 6' stainless steel columns (1/4" d.) packed with 10% SE-30 on Chromosorb W. Yields of product are reported as GC area percent and isolated yields (see Tables 2 and 3). The isolated yields were always lower due to isolation procedures by distillation. The GC area percent yields correlated within 2-3% of GC yields determined using an internal standard in the reaction mixture. 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.

Synthesis of $n\text{-}C_8F_{17}C(O)OC_2H_5$ (IV) *via* Grignard intermediate I

Into a diethyl ether (250 ml) solution of $n\text{-}C_8F_{17}I$ (10 g, 18.3 mmol) was slowly added C_6H_5MgBr (6.2 ml of a 3M diethyl ether solution, 18.3 mmol) at -78°C over a period of 3 min. After an additional 30 min., $(C_2H_5O)_2C{=}O$ (2.05 g, 17.4 mmol) was added to the above Grignard I at -78°C. After 4.5 h., the reaction mixture was allowed to warm to -60°C. After an additional 20 h., the reaction mixture was hydrolyzed with conc. HCl (5ml) at -78°C and then poured over 2N HCl (100 ml). The organic layer was separated and dried ($MgSO_4$). A GC/MS analysis of the reaction mixture showed IV (94 GC area %) and some ketone V (2 GC area %). Distillation yielded the pure product IV, 7.35 g (86%). See Table 1 and 2.

Synthesis of $(CF_3)_2CFOCF_2CF_2C(O)OC_2H_5$ (VII) *via* Grignard intermediate VI

Into a diethyl ether solution (1000 ml) of $(CF_3)_2$ $CFOCF_2CF_2I$ (50 g, 121 mmol) was slowly added C_2H_5MgBr (40.5 ml of a 3M diethyl ether solution, 121 mmol) at -78°C over 15 min. After 30 min., the $(C_2H_5O)_2C=O$ (13.9 g, 115 mmol) in diethyl ether (40 ml) was added dropwise to the above Grignard (VI) at -70°C over 6 min. The reaction mixture was allowed to warm to -40°C. After 2 h., the reaction mixture was hydrolyzed with 2N HCl (500 ml), phase separated and dried ($MgSO_4$). A GC/MS analysis of the reaction mixture indicated VII (98 GC area %), VIII (~2 GC area %) and a trace of $(CF_3)_2CFOCF_2CF_2H$. Distillation yielded 36.2 g of VII (88%). See Tables 1 and 2.

Synthesis of $(CF_3)_2CFOCF_2CF_2C(O)OC_2H_5$ (VII) *via* organolithium intermediate IX

Into a diethyl ether (250 ml) solution of $(CF_3)_2CFOCF_2CF_2I$ (10 g, 24.3 mmol) was slowly added CH_3Li (15.2 ml of a 1.6M diethyl ether solution, 24.3 mmol) at -78° over a period of 8 min. After an additional 30 min., $(C_2H_5O)_2$ C=O (2.72 g, 23.1 mmol) in diethyl ether (10 ml) was added dropwise to the above organolithium intermediate (IX) at -78°C. After 1 h., the reaction mixture was hydrolyzed with conc. HCl (4 ml) at -78°C and then the reaction mixture poured into 2N HCl (100 ml). The organic layer was separated and dried ($MgSO_4$). GC/MS analysis of the solution indicated VII (16 GC area %), VIII (45 GC area %) and unreacted $(C_2H_5O)_2$ C=O (32 GC area %). See Tables 1 and 2.

When the above reaction was repeated at a temperature of -110°C, the product VII was obtained in 99 GC area %. See Tables 1 and 2.

Synthesis of $[(CF_3)_2CFOCF_2CF_2]_2$ C=O (VIII) *via* organolithium intermediate IX

When the reaction between $(CF_3)_2CFOCF_2CF_2Li$ and $(C_2H_5O)_2$ C=O in a 2:1 mole ratio was performed as described above at -78°C, the perfluoroketone VIII was prepared in a 86 GC area % yield. See Tables 1 and 2.

Synthesis of $(n\text{-}C_8F_{17})_2$ C=O (V)

Via $n\text{-}C_8F_{17}Li$ and $(C_2H_5O)_2$ C=O

To a diethyl ether solution (250 ml) of $n\text{-}C_8F_{17}I$ (15 g, 27.5 mmol) and $(C_2H_5O)_2$ C=O (1.4 g, 11.9 mmol) was slowly added CH_3Li (18.2 ml of 1.5M diethyl ether solution, 27.3 mmol) at -78°C over a period of 15 min. After an additional 30 min., the reaction mixture was hydrolyzed with conc. HCl (10 ml) at -78°C and then poured into 2N HCl (200 ml). The organic layer was separated and dried ($MgSO_4$). GC/MS analysis of the solution showed the perfluoroketone V in 55 GC area %, the perfluoroester IV in 16 GC area %, $n\text{-}C_8F_{17}C(O)CH_3$ in 14 GC area % and $C_6F_{13}CF{=}CF_2$ in 5 GC area %. Distillation of the mixture gave V, 3.92 g, 38% isolated yield. See Table 1 and 2.

Via $n\text{-}C_8F_{17}Li$ and $n\text{-}C_8F_{17}C(O)OC_2H_5$

To a diethyl ether solution (150 ml) of $n\text{-}C_8F_{17}I$ (4.6 g, 8.42 mmol) and $n\text{-}C_8F_{17}C(O)OC_2H_5$ (4.0 g, 8.13 mmol) was slowly added CH_3Li (6.3 ml of 1.4M diethyl ether solution, 8.82 mmol) at -78°C over a period of 5 min. After an additional 30 min., the reaction mixture was hydrolyzed with conc. HCl (2.0 ml) and then it was poured into 2N HCl (100 ml). A GC/MS analysis of the solution indicated the perfluoroketone V in 94 GC area %.

Synthesis of $n\text{-}C_8F_{17}C(O)CF_2CF_2OCF(CF_3)_2$ (XIV)

To a diethyl ether solution (500 ml) of $n\text{-}C_8F_{17}I$ (15.0 g, 27.5 mmol) and $(CF_3)_2CFOCF_2CF_2C(O)OC_2H_5$ (VII) (9.34 g, 26.1 mmol) was slowly added CH_3Li (19.3 ml of 1.4M diethyl ether solution, 27.1 mmol) at -78°C over a period of 15 min. After an additional 40 min., the reaction mixture was hydrolyzed with conc. HCl (5 ml) and then poured into 2N HCl (200 ml). The organic layer was separated and dried ($MgSO_4$). GC/MS analysis of the solution indicated the asymmetric ketone XIV in 96 GC area % plus the unreacted ester VII, ~ 1.5 GC area %. Distillation of the mixture gave the product XIV, 16.1 g (84% isolated yield). See Table 1 and 2.

Synthesis of $(CF_3)_2CFOCF_2CF_2\overset{O}{\overset{\|}{C}}\overset{O}{\overset{\|}{C}}OC_2H_5$ (XVII) via Grignard intermediate VI

To a diethyl ether solution (500 ml) of $(CF_3)_2CFOCF_2CF_2I$ (41.2 g, 100 mmol) was slowly added C_2H_5MgBr (33.3 ml of a 3M diethyl ether solution, 100 mmol) at -78°C over a period of 7 min. After an additional 30 min., a $C_2H_5OC(O)C(O)OC_2H_5$ (7.01 g, 48.0 mmol) solution in THF (60 ml) was added at -78°C over a period of 12 min. After an additional 2 h., the reaction mixture was hydrolyzed with conc. HCl (15 ml) at -78°C and then poured into 2N HCl (200 ml). The organic layer was separated and dried ($MgSO_4$). A GC analysis of the reaction mixture was not informative since the product XVII could not be separated clearly from the solvent peaks. Distillation from P_2O_5 however yielded 14.0 g (76%) of the product XVII. See Tables 1 and 3.

Synthesis of $[(CF_3)_3CFOCF_2CF_2C(O)]_2$ via organolithium lithium intermediate IX

To a diethyl ether solution (750 ml) of $(CF_3)_2CFOCF_2CF_2I$ (40 g, 97.1 mmol) was slowly added n-C_4H_9Li (43.3 ml of a 2.2M hexane solution, 95.2 mmol) at -78°C over a period of 28 min. After an additional 30 min., the $C_2H_5OC(O)C(O)OC_2H_5$ (6.95 g, 47.6 mmol) solution in diethyl ether (10 ml) was added dropwise over 30 min. After 2 h. the reaction mixture was hydrolyzed with conc. HCl (15 ml) and then poured into 2N HCl (200 ml). The organic layer was separated and dried ($MgSO_4$). A GC/MS analysis of the solution indicated the following products XVIII (88 GC area %), XVII (9 GC area %) and unreacted XV (2 GC area %). Distillation yielded the perfluorodiketone XVIII, 22.9 g (77%). See Tables 1 and 3.

Synthesis of n-$C_8F_{17}C(O)C(O)OC_2H_5$ (XXI) via organolithium intermediate XII

To a diethyl ether solution (500 ml) of n-$C_8F_{17}I$ (10 g, 18.3 mmol) and $C_2H_5OC(O)C(O)OC_2H_5$ (2.60 g, 17.8 mmol) was slowly added CH_3Li (10.1 ml of a 1.8M diethyl ether solution, 18.2 mmol) at -78°C over 20 min. After an additional 1h., the reaction mixture was hydrolyzed with conc. HCl (10 ml) and poured into 2N HCl (100 ml). The organic layer was separated and dried ($MgSO_4$). GC/MS analysis of the diethyl ether solution indicated the following products: XXI (94 GC area %), n-$C_8F_{17}C(O)C(O)CH_3$ (4 GC area %) and unreacted n-$C_8F_{17}I$ (2 GC area %).

Distillation gave the ketoester product XXI, 7.8 g (84%). See Table 1 and 3.

When the above reaction was repeated except an excess of n-$C_8F_{17}Li$ was used, no bis substituted diketone n-$C_8F_{17}C(O)C(O)$n-C_8F_{17} was produced. The major product identified by GC/MS was XXI in addition to the typical decomposition products of n-$C_8F_{17}Li$.

Synthesis of n-$C_8F_{17}C(O)C(O)CF_2CF_2OCF(CF_3)_2$ (XXIII)

To a diethyl ether solution (800 ml) of n-$C_8F_{17}I$ (20.0 g, 36.6 mmol) and $C_2H_5OC(O)C(O)OC_2H_5$ (5.2 g, 35.6 mmol) was slowly added CH_3Li (26 ml of a 1.4M diethyl ether solution, 36.4 mmol) over a period of 15 min. After an additional 30 min., $(CF_3)_2CFOCF_2CF_2I$ (30.2 g, 73.3 mmol) was added to the above mixture at -78°C. CH_3Li (52 ml of a 1.4M diethyl ether solution, 72.8 mmol) was then added slowly over a 15 min. period. After an additional 10 min., the reaction was allowed to warm to -50°C. After 2 h., the reaction mixture was hydrolyzed with conc. HCl (300 ml). The organic layer was separated and dried ($MgSO_4$). A GC/MS analysis of the diethyl ether solution indicated the following major products, XXIII (84 GC area %) and XXI (15 GC area %). Distillation yielded the asymmetric diketone XXIII, 16.1 g (70%). See Tables 1 and 3.

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