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FLUORO-KETONES IV.

SYNTHESIS OF PHENYLPERFLUOROALKYL KETONES - MECHANISM OF REACTION BETWEEN PHENYLLITHIUM AND FLUOROESTERS*

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SUMMARY

Although fluorine containing ketones ($R_fC(O)R_f$ and $R_fC(O)R$, R_f = perfluoroalkyl) have been prepared from the reaction between organolithium reagents and perfluoroalkyl esters, the reaction has not found general applicability. Variable yields of ketones and co-production of secondary and tertiary alcohol by-products have in most instances been experienced. We have examined in more detail the factors e.g., temperature, mode of addition and perfluoroalkyl ester structure which influence ketone product and by-products formation. By controlling experimental conditions excellent yields of $C_6H_5C(O)R_f$ compounds can be attained. A lithium salt of a hemiketal (II) has been isolated and shown to be the active intermediate in the production of the ketone. The stability of the salt and its potential reaction with the solvent dictates the type of reaction products. Low temperature favors stability of the lithium salt of the hemiketal whereby high yields of ketones are produced on hydrolysis.

INTRODUCTION

Organometallic compounds have been extensively used in the synthesis of fluorocarbon ketones [1,2]. The reactions between Grignard or organolithium reagents with fluorocarbon esters have been previously reported to yield fluorocarbon ketones in variable yields along with by-products e.g., secondary and tertiary alcohols.

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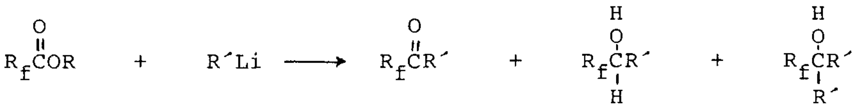


$$R_f\overset{\overset{O}{\|}}{C}OR \quad + \quad R'Li \longrightarrow R_f\overset{\overset{O}{\|}}{C}R' \quad + \quad R_f\overset{\overset{H}{O}}{\underset{H}{C}}R' \quad + \quad R_f\overset{\overset{H}{O}}{\underset{R'}{C}}R' \qquad (1)$$

For example, in earlier studies McBee, Roberts and Curtis [3] reported the reaction between n-C_3F_7Li and n-$C_3F_7CO_2C_2H_5$ to yield the ketone (n-$C_3F_7)_2C{=}O$ in yields ranging from 0% to 33% with by-product formation of the secondary alcohol, (n-$C_3F_7)_2CH(OH)$, ranging from 0% to 42%. Formation of the tertiary alcohol, (n-$C_3F_7)_3COH$, was not observed. McGrath and Levine [4] in their studies on the reaction between C_6H_5Li and a series of esters e.g., $CF_3CO_2CH_3$, $C_2F_5CO_2CH_3$ and n-$C_3F_7CO_2CH_3$ noted ketone, $R_fC(O)C_6H_5$, yields ranging from 18% to 64% and the by-product tertiary alcohols, $(R_f)_3COH$, yields ranging from 0% to 44%. The presence of the secondary alcohols, ($R_fCH(OH)C_6H_5$) was not reported. In both previous studies experimental conditions of reaction temperature, time and mode of addition were varied.

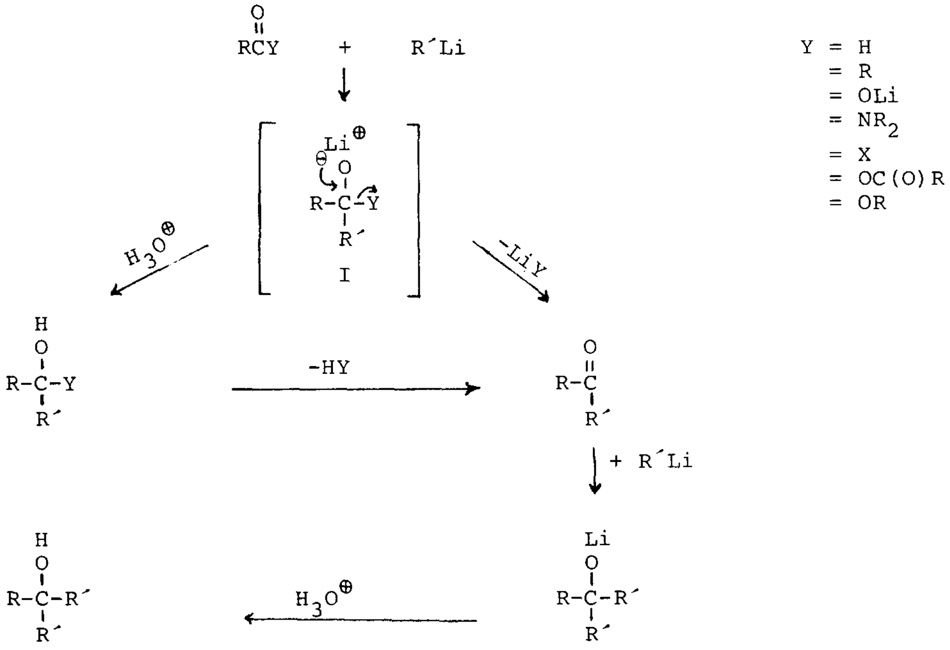
In our current studies we have reexamined in more detail than previously reported [4] the reactions between C_6H_5Li and perfluorocarbon esters with the objective of providing an improved and general synthesis procedure for perfluorocarbon ketones.

DISCUSSION

With hydrocarbon compounds, the reaction between an organolithium reagent, RLi and an acyl derivative RC(O)Y has been suggested [5] to proceed according to the reactions shown in Scheme 1.

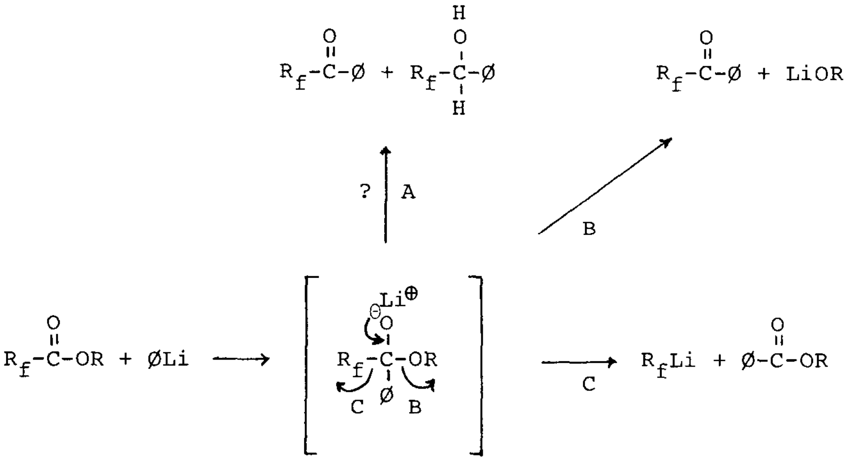
The final products of the reaction are a function of ease of expulsion of group Y from the intermediate lithium salt I. The group Y leaving capacity is related to the thermal stability of the lithium salt I. In the various reported studies on reaction of organolithium compounds with acyl derivatives, Y can be H (aldehydes), R (ketones), OLi (from acids), NR_2 (secondary amides), X (acid halides), OC(O)R (acid anhydrides) or OR (esters).

In our present study we have examined thus far the following variations (in Scheme 1) where Y is $-OCH_3$ and $-OC_2H_5$, R'Li is C_6H_5Li and R is CF_3, C_2F_5, n-C_3F_7, i-C_3F_7, n-$C_3F_7O[CF(CF_3)CF_2O]_nCF(CF_3)$ and $C_2F_5O(CF_2CF_2O)_nCF_2$. The reactions were carried out under various experimental conditions of time, temperature, mode of addition and variation of ester structure. Table 1 is a summation of the reaction products found based on variations of the above mentioned experimental conditions.



SCHEME 1

On the assumption that the reaction between C_6H_5Li and a perfluorocarbon ester yields an intermediate lithium salt of a hemiketal II, (see Scheme 1 where Y=OR) a similar and expanded suggested mechanism explaining the reaction products of Table 1 is shown in Scheme 2.



SCHEME 2 Lithium Salt of a Hemiketal II

TABLE 1

C_6H_5Li ADDED TO ESTER

EXPERIMENT	R_f	TEMP/TIME[a]	$R_f-\overset{O}{\overset{\|}{C}}-\emptyset$	$R_f-\overset{\overset{H}{O}}{\underset{H}{C}}-\emptyset$	$R_f-\overset{\overset{H}{O}}{\underset{\emptyset}{C}}-\emptyset$	$\emptyset\overset{O}{\overset{\|}{C}}OCH_3$	$R_f'O\overset{F}{C}=\overset{F}{C}F$	OTHERS[c]
1	CF_3	-78°/10 MIN	98	0	2			
2	CF_3	-40°/10 MIN	98	0	2			
		↓ RT/4 DAYS	96	2	2			
3	CF_3	RT/10 MIN	82	0	18			
		↓ RT/8 DAYS	79	3	18			
4	C_2F_5	-78°/10 MIN	98	0.5	1.5			
5	C_2F_5	-40°/10 MIN	88	0.5	11.5			
		↓ RT/6 DAYS	1	87	12			
6	$n-C_3F_7$	-78°/10 MIN	98	0.5	1.5			
7	$n-C_3F_7$	-40°/10 MIN	86.5	0.5	13			
		↓ RT/5 DAYS	0	87	13			

8	i-C_3F_7	-78°/10 MIN	TRACE	0	0	b,d	b	
9	i-C_3F_7	-110°/10 MIN	89	0	0	b,d	b	
10	$C_3F_7O\overset{F}{\underset{CF_3}{C}}$	-78°/10 MIN	99	0				
		↓ -30°/30 MIN	99			1d		
		↓ 0°/30 MIN	59			36d	b	5
		↓ RT/24 HRS	5			90d	b	5
11	$C_2F_5O(CF_2CF_2O)_3CF_2$	-78°/10 MIN	99					1
		↓ 0°/30 MIN	99					2
		↓ RT/26 HRS	96	3.5				0.5
		↓ RT/6 DAYS	76	18				6
		↓ RT/12 DAYS	55	17				27

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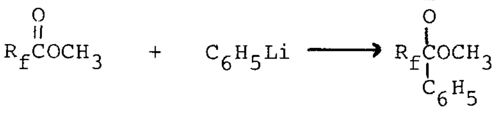
[a] The ↓ indicates the reaction was allowed to increase in reaction temperature.
[b] Products were identified by GC/MS and IR, no attempt was made to determine yield.
[c] Minor products were not characterized completely.
[d] $C_6H_5CO_2C_2H_5$

The stability of the lithium salt of a hemiketal II seems to be the major factor in determining the reaction products to be formed. Attempts to independently synthesize II and thus prove its existence met with partial success. The addition of C_6H_5Li to a series of esters, $CF_3CO_2CH_3$, $C_2F_5CO_2CH_3$ and $n\text{-}C_3F_7CO_2CH_3$ produced the proposed II at -78°C. Isolation of pure lithium salt II at room temperature however was successful only with the first member of the series (R_f=CF_3).



$$R_fC(=O)OCH_3 + C_6H_5Li \longrightarrow R_fC(OLi)(C_6H_5)OCH_3 \qquad (2)$$

II

During the attempted isolation of the C_2F_5 and $n\text{-}C_3F_7$ substituted II at room temperature, the C_2F_5 member decomposed at a slower rate than the $n\text{-}C_3F_7$ member. The CF_3 derivative, however, was thermally stable (under nitrogen) at room temperature and decomposed on heating to 150°C to produce $C_6H_5C(O)CF_3$. Acid hydrolysis of each of the above lithium salt of hemiketals (II) at -78°C produced the ketones.

The relative stability of the intermediate II governs the subsequent formation of products. From the data in Tables 1, 2 and the synthesis of II, the following conclusions have been reached in regard to the various experimental conditions:

Temperature (C_6H_5Li added to R_fCO_2R)- at low temperature (-78°C) with the exception of the $i\text{-}C_3F_7$ derivative (Exp. 8 and 9), all the lithium salt of hemiketals (II) are stable. On acid hydrolysis at -78°C they all produce high yields of the ketones. At temperatures above -78°C the CF_3 and $C_2F_5O(CF_2CF_2O)_3CF_2$ substituted II are stable for at least 24 hours at room temperature (Exp. 1 and 11). Only after many additional hours does the formation of the secondary alcohol begin. The C_2F_5 and $n\text{-}C_3F_7$ substituted II on warming to room temperature yield secondary alcohols at a much faster rate. As the length of the perfluoroalkyl group increases the rate of transformation of II to secondary alcohol increases (Exp. 2,5,7). The $i\text{-}C_3F_7$ substituted II is unstable at -78°C and decomposes to yield as the final products $CF_3CF{=}CF_2$ and $C_6H_5CO_2C_2H_5$ (Exp. 8). At -110°C, however, the $i\text{-}C_3F_7$ substituted II is sufficiently stable such that on acid hydrolysis at -110°C an 89% yield of ketone was obtained in addition to $CF_3CF{=}CF_2$ and $C_6H_5CO_2C_2H_5$. The $C_3F_7OCF(CF_3)$ substituted II, which is stable at -78°C (EXP. 10), begins to decompose above -30°C by the same mechanism as the $i\text{-}C_3F_7$ derivative to yield $n\text{-}C_3F_7OCF{=}CF_2$ and $C_6H_5CO_2C_2H_5$.

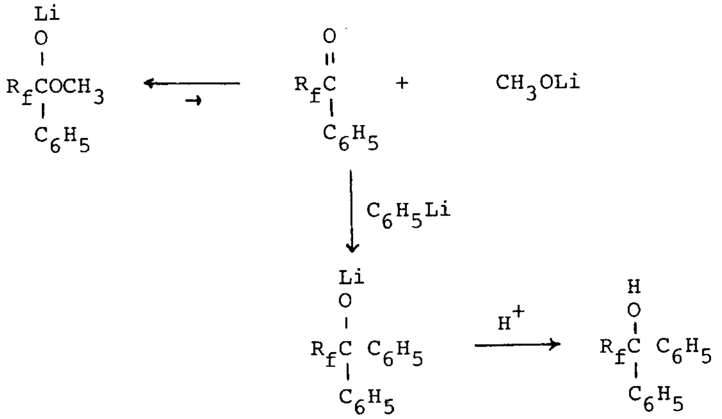
$$R_fC(OLi)(C_6H_5)OR \longrightarrow R_fLi + C_6H_5CO_2R \qquad (3)$$

$$R_fLi \longrightarrow LiF + R_f'CF = CF_2 \qquad (4)$$

where R_f = i-C_3F_7; R_f' = CF_3

R_f = n-$C_3F_7OCF(CF_3)$; R_f' = n-C_3F_7O

Mode of Addition ($R_fCO_2CH_3$ added to C_6H_5Li)- Since the rate of reaction at -78°C between the ester and C_6H_5Li is fast, the mode of addition is very important. By adding C_6H_5Li to the ester, the reaction products are present in the excess ester. Conversely by adding the ester to C_6H_5Li the reaction products are present in the excess C_6H_5Li. From the data in Table 2, addition of ester to C_6H_5Li, it can be seen that by varying the reaction temperature, -40°C, and room temperature, the stability of II varies. At -40°C, the three lithium salts of the hemiketals (II) (EXP. 12,14,16) decompose at different rates, where the order of stability is $CF_3 > C_2F_5 >$ n-C_3F_7. This was determined by hydrolyzing the reaction mixtures at -40°C to yield the ketones in 96%, 53% and 37% respectively. The other major products of reaction were the tertiary alcohols, $R_fC(OH)(C_6H_5)_2$ which were formed through the reaction of the ketone with the C_6H_5Li present in excess during the addition of the ester. At room temperature, the major products of the reaction (EXP. 13,15, 17) are the tertiary alcohols $R_fC(OH)(C_6H_5)_2$ which are produced in 98% yield. These observations suggest that the lithium salts of the hemiketals (II) in the reaction medium must be in equilibrium with the ketone and CH_3OLi, e.g.



(5)

TABLE 2

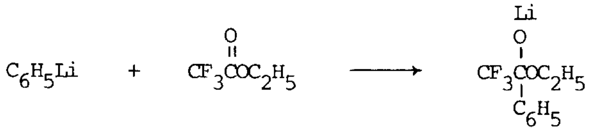
ESTER ADDED TO C_6H_5Li

EXPERIMENT	R_f	TEMP/TIME[a]	$R_f\overset{\overset{O}{\|}}{C}-Ø$	$R_f\underset{H}{\overset{\overset{H}{O}}{C}}-Ø$	$R_f\underset{Ø}{\overset{\overset{H}{O}}{C}}-Ø$
12	CF_3	-40°/10 MIN	96	0	4
		↓			
		RT/3 DAYS	94	2	4
13	CF_3	RT/10 MIN	1	1	98
14	C_2F_5	-40°/10 MIN	53	1	46
		↓			
		RT/3 DAYS	4	49	47
15	C_2F_5	RT/10 MIN	0	2	98
16	$n\text{-}C_3F_7$	-40°/10 MIN	37	0.5	62.5
		↓			
		RT/6 DAYS	0	37.5	62.5
17	$n\text{-}C_3F_7$	RT/10 MIN	0	2	98

[a] The ↓ indicates the reaction was allowed to increase in reaction temperature.

As the ketone is formed it reacts with the C_6H_5Li present and forms the $R_fC(OLi)(C_6H_5)_2$ which after hydrolysis yields the $R_fC(OH)(C_6H_5)_2$. From the data at -40°C and room temperature the presence of the excess C_6H_5Li shifts the equilibrium to the right by reacting with the equilibrium concentration of $R_fC(O)C_6H_5$ to form the non-equilibrium product $R_fC(OLi)(C_6H_5)_2$. The stability of the lithium salt of the hemiketals which effects their equilibrium concentration, therefore, is $CF_3 > C_2F_5 > n\text{-}C_3F_7$ and is in identical order to their observed isolation attempts.

Nature of the -OR Group - The above lithium salts of the hemiketals which were prepared by addition of C_6H_5Li to the esters $R_fCO_2CH_3$. If, however, the OC_2H_5 derivative is prepared by addition of C_6H_5Li to $CF_3CO_2C_2H_5$ the lithium salt formed behaves differently than the OCH_3 analog.



$$C_6H_5Li + CF_3\overset{\overset{O}{\|}}{C}OC_2H_5 \longrightarrow CF_3\underset{C_6H_5}{\overset{\overset{Li}{O}}{C}}OC_2H_5 \qquad (6)$$

III

When III is prepared at -40°C and acid hydrolyzed at this temperature the ketone $CF_3C(O)C_6H_5$ is formed in 99% yield and less than 1% of the alcohol $CF_3C(OH)(C_6H_5)_2$ is also formed. If the reaction mixture is then allowed to warm to room temperature and acid hydrolyzed, the percent ketone decreases with time (27h, 18%) with the concurrent formation of the secondary alcohol $CF_3C(OH)H\ C_6H_5$ (27h, 61%) and other products in minor quantities. This observation is contrary to the $-OCH_3$ derivative of II which is stable up to 150°C.

The secondary alcohol formation as shown by route A, Scheme 2 is not well understood at this time and requires further study. It is noted, however, not only in the case of the lithium salt of the hemiketal III but also as the main decomposition product at higher temperatures of the II where $R_f = C_2F_5$, and $n\text{-}C_3F_7$ and as minor decomposition products where $R_f = CF_3$ and $C_2F_5O(CF_2CF_2O)_3CF_2$. Although other investigators [3,6,7] have previously noted the secondary alcohol formation, a satisfactory mechanistic interpretation covering all type of R_f and OR substituents has not been established as yet.

Nature of the R_f - From the above, the nature of the R_f group which stabilizes II is $CF_3 > C_2F_5O(CF_2CF_2O)_3CF_2 > C_2F_5 > n\text{-}C_3F_7 > C_3F_7OCF(CF_3) > i\text{-}C_3F_7$.

The thermal stability of the II must be a function of the R_f substituent. It does not appear that steric factors alone could be the principal reason (see EXP. 5 vs. 11). Electronic effects of the R_f substituent therefore must be a more important consideration. Since the lithium salt of the hemiketals could not be conveniently studied spectroscopically at room temperature, the stable ketone precursors $R_fC(O)C_6H_5$ were investigated by infrared analysis. The effect of the R_f substituent on the C=O frequency was determined and the results are shown in Table 3.

It is well known that highly electronegative groups adjacent to the carbonyl group increase its vibrational frequency [8]. There is a close correlation between the observed order of stability of II and the carbonyl stretching frequencies of their ketone precursors. The ketones exhibiting the highest carbonyl frequencies provide the most stable II while the ketones with the lowest carbonyl frequencies provide the least stable II.

CONCLUSION

The reaction between C_6H_5Li and various esters R_fCO_2R appear to proceed through a transient lithium salt of the hemiketal (II). At -78°C, the II is sufficiently stable (the exception is the $i\text{-}C_3F_7$ substituted II where

TABLE 3

R_f	STRETCHING FREQUENCY $\overset{O}{\overset{\|}{C}}$ (cm^{-1}) in $R_f\overset{O}{\overset{\|}{C}}C_6H_5$
CF_3	1724.1
$C_2F_5O(CF_2CF_2O)_3CF_2$	1725.4
C_2F_5	1709.4
n-C_3F_7	1711.1, 1716.3 (minor)
$C_3F_7OCF(CF_3)$	1711.9
i-C_3F_7	1700.9, 1724.1 (minor)

-110°C is required) such that acid hydrolysis at the low temperature produces high yields of the ketones $C_6H_5C(O)R_f$. At higher temperature than -78°C, the stability of II varies depending on the nature of R_f, OR, and temperature whereby a variety of products may be obtained resulting from at least three different modes of decomposition of the lithium salt of a hemiketal (II). Formation of the secondary alcohol $C_6H_5C(OH)HR_f$ at higher temperatures and longer reaction times has not been rationalized from the available data.

EXPERIMENTAL

General Comments

All reactions were carried out in anhydrous solvents and under an atmosphere of dry nitrogen. Most isolated compounds have been previously reported [4,9,10,11] and have been characterized by GC/MS, IR and GC retention time (with known compounds). Compounds n-$C_3F_7C(OH)HC_6H_5$, i-$C_3F_7C(O)C_6H_5$ and $CF_3C(OLi)(OCH_3)C_6H_5$ however, are new compounds (see experimental). GC analysis and separation (for analytical purposes) were performed on a 1/4' x 6', 10% SE-30 on chromosorb W column. GC/MS analyses were carried out on a du Pont 490 mass spectometer modified for chemical ionization, using a 1/8" x 6' SE-30 chromosorb W column. IR analyses were performed on Digilab FTS-20C spectometer in CCl_4 solution or as neat samples. N.M.R. analyses were performed on an XL-100 spectometer using $CDCl_3$ solvent and TMS and $CFCl_3$ as internal standards.

Synthesis of $CF_3C(OLi)(OCH_3)C_6H_5$(n.c.)

Into 250ml three-necked flask with a low temperature thermometer, a magnetic stirrer and maintained under a nitrogen atmosphere, were placed anhydrous diethyl ether (90ml), n-octane (internal GC standard, 0.51g, 4.47mmol) and $CF_3CO_2CH_3$ (2.56g, 20.0mmol). Phenyllithium (19.4ml of 1.03M in anhydrous diethyl ether, 20.0mmol) was added over a period of 30 min to the above rapidly stirred solution at -40°C. The solution was stirred at -40°C for an additional 10 min, an aliquot sample removed, hydrolyzed with 2N HCl and analyzed by GC. The reaction mixture was then allowed to warm to room temperature and then stirred at room temperature for 7 days during which time aliquot samples were removed periodically and analyzed by GC. The results were given in Table 1 (EXP. 1).

While stirring at room temperature for 7 days, a white solid precipitated from the reaction mixture. It was filtered and washed with anhydrous diethyl ether to yield 1.8g (42%) of product. On heating the solid to ∿150°C it decomposed to $CF_3C(O)C_6H_5$ plus a white solid suspected to be CH_3OLi. Its molecular weight was determined by acid-base titration (neutral equivalent); Found, M.W. 212± 1, Calc'd, 212. Analysis: Calc'd for $C_9H_8F_3OLi$; C, 50.96%; H, 3.77%; Li, 3.27%; Found: C, 50.72%; H, 3.55% and Li, 3.2%. On acid hydrolysis the solid produced $CF_3C(O)C_6H_5$.

Addition of C_6H_5Li to $R_fC(O)OCH_3$

These experiments were performed in an identical manner to the one described above. Results from periodic removal of aliquot samples and GC analysis using an internal standard (n-octane) are listed in Table 1.

Addition of C_6H_5Li to $i\text{-}C_3F_7C(O)OC_2H_5$(-110°C)

Into a 250ml three-necked flask fitted with a low temperature thermometer, stirrer and an addition buret was added anhydrous diethyl ether (100ml) and $i\text{-}C_3F_7CO_2C_2H_5$ (2.01g, 8.31mmol). The contents were cooled to -110°C (EtOH-liquid N_2 bath) and phenyllithium (8.37ml of 0.993M in anhydrous diethyl ether 8.31mmol) was added over a period of 12 min. The rate of addition was controlled so as to keep the reaction temperature of -110°C. After stirring the reaction for 30 min at -110°C, a cooled (∿-60°C) solution of conc. HCl (2ml) and methanol (5ml) was slowly added in order to hydrolyze the reaction mixture. The mixture was then poured into 2M HCl (200ml), phase separated and dried over $MgSO_4$. GC analysis using an internal standard (n-octane) indicated i-$C_3F_7C(O)C_6H_5$ in 89% yield and smaller quantities of $C_6H_5CO_2C_2H_5$ and $CF_3CF{=}CF_2$. Distillation of the reaction mixture yielded 1.42g (65% yield), b.p. 76-78°C/15mm; IR (C=O at 1700.9, 1724.1 cm^{-1}); M.W. (mass spectral) calc'd 274, found 274; NMR(ppm): H, ∿8.0 (multiplet, 2.3Hz, ortho H split by ≡CF), and ∿7.5 (multiplet). F, -73.8 (doublet, 7.0Hz, $2CF_3$) and -179.1 (multiplet - septet - 7Hz, triplet - 2.3Hz, CF); Analysis: calc'd for $C_{10}H_5F_7O$; C, 43.81; H, 1.84; found: C, 43.72; H, 1.68.

Addition of C_6H_5Li to $C_3F_7OCF(CF_3)C(O)OC_2H_5$

Phenyllithium (27.9ml of 1.00M in anhydrous diethyl ether, 27.9mmol) was added over 12 min to a precooled solution of $C_3F_7OCF(CF_3)C(O)OC_2H_5$ (10.0g, 27.9mmol) in 400ml of anhydrous diethyl ether at -78°C (Dry Ice-isopropanol bath). After an additional 10 min, an aliquot sample was removed, hydrolyzed with 2N HCl and analyzed by GC. The reaction mixture was allowed to warm up to -30°C over 18 min and kept at this temperature for 30 min, then to 0°C over 30 min period for 30 min and then to R.T. for 24 h. During these various temperatures, aliquot samples were removed and analyzed by GC. See Table 1 (Exp. 10).

Synthesis of n-$C_3F_7C(OH)HC_6H_5$(n.c.)

The secondary alcohol was prepared in the same manner as described for the synthesis of $CF_3C(OLi)(OCH_3)C_6H_5$ except that n-$C_3F_7CO_2CH_3$ (4.56g; 20.0mmol) and phenyllithium (19.4ml of 1.03M in anhydrous diethyl ether; 20.0mmol) were used and the reaction was carried out at -78°C. After warming the reaction mixture to room temperature, it was allowed to stir an additional 5 days during which time periodic aliquot samples were removed and analyzed by GC. During this time the analysis indicated a gradual decrease of the ketone n-$C_3F_7C(O)C_6H_5$ and a concurrent increase in the secondary alcohol G.C. analysis after 5 days indicated a 91% yield of the secondary alcohol (using n-octane as an internal G.C. standard). Distillation of the reaction mixture yielded 3.6g (65%), b.p. 42°C/0.03mm. Analysis: infrared data (OH at 3620.6 cm^{-1}); M.W. (mass spectral) calc'd. 276; found 276; Analysis: calc'd for $C_{10}H_7F_7O$: C, 43.49; H, 2.55; found: C, 43.2; H, 2.29.

Addition of $R_fC(O)OCH_3$ to C_6H_5Li (R_f=n-C_3F_7; -40°C to R.T.)

$C_3F_7CO_2CH_3$ (4.56g, 20.0mmol), dissolved in mixture of anhydrous diethyl ether (20ml) and n-octane (internal GC standard, 0.50g) was added over a 30 min period to rapidly stirred phenyllithium (19.4ml of 1.03M in diethyl ether, 20.0mmol) in 70ml of anhydrous diethyl ether cooled to -40°C (Dry Ice-isopropanol bath). The solution was stirred at -40°C for an additional 5 min, an aliquot sample removed, hydrolyzed and analyzed by G.C. The reaction mixture was then allowed to warm to room temperature, and then stirred at room temperature for 6 days during which time aliquot samples were removed periodically and analyzed by G.C. See Table 2.

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