FLUORO-KETONES.   II REACTIONS OF FLUOROCARBON GRIGNARDS AND

COPPER COMPOUNDS WITH PERFLUOROALKYLACID FLUORIDES

H. GOPAL* and C. TAMBORSKI**

Air Force Materials Laboratory, Wright-Patterson Air Force Base,

Ohio 45433 (U.S.A.)

SUMMARY

The reactions between C_6F_5MgBr (I), $p-BrC_6F_4MgBr$ (X),

C_6F_5Cu (XXI), $p-HC_6F_4Cu$ (XXII) and $p-BrC_6F_4Cu$ (XV) with primary

and secondary perfluoroalkylether acid fluorides were studied.

The Grignard compounds react very slowly with the secondary

acid halides $(R_fCF(CF_3)C(O)F)$ whereby competing reactions cause

undesirable by-products and reduction of ketone yields.

Primary acid halides $(R_fCF_2C(O)F)$ react much faster with

C_6F_5MgBr to give the ketone in improved yields. The organo-

copper compounds react with either primary or secondary acid

halides to give the ketone in excellent yields with no by-

product formation from competing secondary reactions. Solvent,

type of organometallic reagent and primary versus secondary

acid fluoride are variables that influence product yield and

product distribution.

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*National Research Council Resident Research Associate (1974-1976)

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  see reference (8).

INTRODUCTION

The reaction of C_6F_5MgBr (In diethyl ether solvent) with an acid halide, $CH_3C(O)Cl$ was first reported [1] to yield the product $C_6F_5C(O)CH_3$ in low yield (28%). This observation was confirmed by us in some of our later studies [2]. We had speculated that in a stoichiometric reaction between C_6F_5MgBr and $CH_3C(O)Cl$, the low yield of product was due to the consumption of the Grignard (protonation) by the product $C_6F_5C(O)CH_3$ which may exist in an enolic form $[C_6F_5C(OH)=CH_2]$. Enolic forms of $CH_3C(O)R_f$ compounds have been suggested [3] as a possible intermediates. More recently [4] the reaction between C_6F_5MgBr (in diethyl ether) with the primary acid halide $C_3F_7C(O)Cl$ to produce $C_6F_5C(O)C_3F_7$ in higher yields (66%) was reported. The completely fluorinated ketone, not having an enolizable hydrogen, could not protonate the Grignard and thus preserved the stoichiometry of the reaction.

In our current studies we have examined the reactions of C_6F_5MgBr (I), $p\text{-}BrC_6F_4MgBr$ (X), C_6F_5Cu (XXI), $p\text{-}BrC_6F_4Cu$ (XV) and $p\text{-}HC_6F_4Cu$ (XXII) with various primary and secondary acid fluorides e.g., $C_3F_7O[CF(CF_3)CF_2O]_nCF(CF_3)C(O)F$ [5] and $C_2F_5O(CF_2CF_2O)_nCF_2C(O)F$ [6] as a means of preparing various fluoro (arylalkylether) ketones ($Ar_fC(O)R_fOR_f$ where $Ar=$ polyfluoroaryl or bromoperfluoroaryl, R_fOR_f=perfluoroalkylether). Solvent (diethyl ether versus tetrahydrofuran, THF), structure of acid halide (primary versus secondary) and organometallic specie (Grignard versus organocopper) all have an effect on rate of reaction and product distribution.
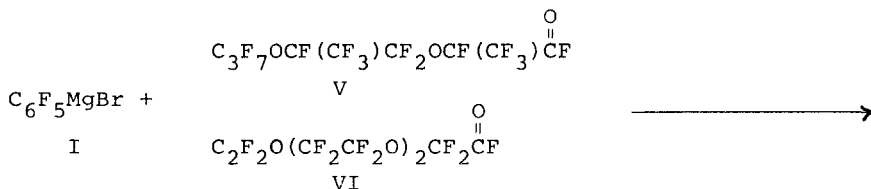
RESULTS AND DISCUSSION

By comparison to the hydrogen analog C_6H_5MgBr, C_6F_5MgBr (I) is a weaker nucleophile in diethyl ether. For example C_6H_5MgBr on carbonation yields an acid, ketone or alcohol depending on experimental conditions. C_6F_5MgBr however yields only the acid [7]. We have found that C_6F_5MgBr reacts very slowly with the secondary acid fluoride $C_3F_7OCF(CF_3)C(O)F$ (II) as compared to the C_6H_5MgBr [8]. After 9 days at 0°, only 55% of the Grignard reacted to form two products $C_6F_5C(O)CF(CF_3)OC_3F_7$ (III) and $p-C_6F_5C_6F_4C(O)CF(CF_3)OC_3F_7$ (IV) in a ratio of 121:3 (G.C. area ratio). After an additional 7 days at ⌁20°, 88% of the Grignard reacted to form the same products in a ratio of 80:10. Since the rate of reaction between the Grignard compound and the secondary halide was slow, a competing reaction between the Grignard and the product $C_6F_5C(O)CF(CF_3)OC_3F_7$ (III) was observed.
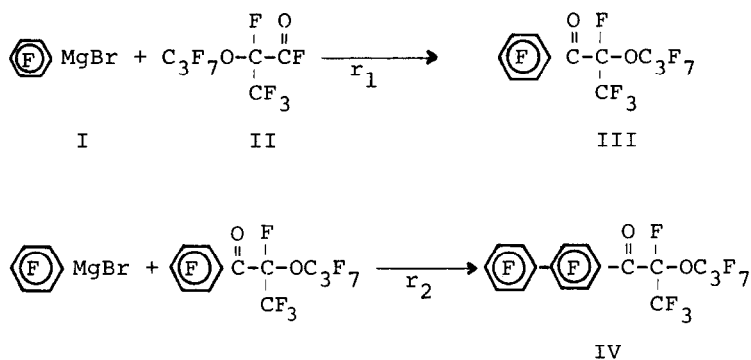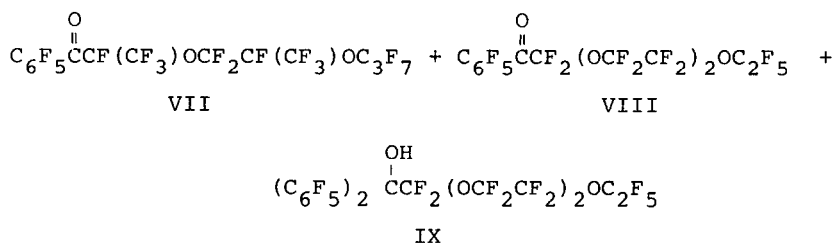

The perfluoroacyl group activates the p-fluorine toward nucleophilic reaction and since r_1 is slow, competition for the Grignard compound results. No other products, e.g., alcohol as a result of the ketone reacting further was observed.

In THF as a reaction medium, C_6F_5MgBr (I) is a more reactive nucleophile. Within 4 hours, the reaction between the Grignard and $C_3F_7OCF(CF_3)C(O)F$ (II) produced a multiplicity of products. Two major products III and IV were observed by gas chromatographic analysis (G.C.) in the ratio of 41:55. Some of the remaining minor products were partially characterized by gas chromatography-mass spectral analysis (GS-MS) and the results were consistent with the following structures: $C_6F_5C_6F_4H$, $(C_6F_5)_2C[CF(CF_3)OC_3F_7]OH$, $(C_6F_5)_2C[CF(CF_3)OC_3F_7]OC_2H_5$ and $p-C_6F_5C_6F_4C[CF(CF_3)OC_3F_7]H(OH)$. The higher yield of the biphenyl ketone IV indicates that in tetrahydrofuran C_6F_5MgBr (I) reacts preferentially with the para fluorine of III than the acid fluoride II.
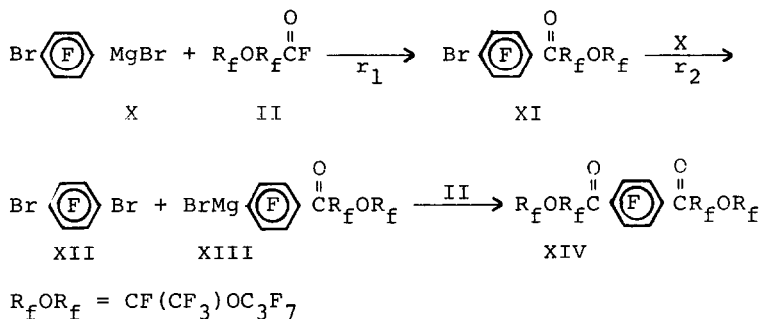
Previously [4] the primary acid chloride $C_3F_7C(O)Cl$ has been reported to react with C_6F_5MgBr (I) (diethyl ether) to give the ketone $C_6F_5C(O)C_3F_7$ in 66% yield (no by-products were mentioned). Since the secondary acid fluorides in our study may offer steric hindrance towards reaction with C_6F_5MgBr (I), it was of interest to examine the reactivity of the primary perfluoroalkylether acid fluorides. A competing reaction in diethyl ether solvent between C_6F_5MgBr (I) and an equivalent of the secondary acid fluoride (V) and a primary acid fluoride (VI) was performed.

$$C_6F_5MgBr + \begin{array}{c} C_3F_7OCF(CF_3)CF_2OCF(CF_3)\overset{\overset{\displaystyle O}{\|}}{C}F \\ V \\ C_2F_2O(CF_2CF_2O)_2CF_2\overset{\overset{\displaystyle O}{\|}}{C}F \\ VI \end{array} \longrightarrow$$

I

$$\underset{\text{VII}}{C_6F_5\overset{\overset{\text{O}}{\|}}{C}CF(CF_3)OCF_2CF(CF_3)OC_3F_7} + \underset{\text{VIII}}{C_6F_5\overset{\overset{\text{O}}{\|}}{C}CF_2(OCF_2CF_2)_2OC_2F_5} +$$

$$\underset{\text{IX}}{(C_6F_5)_2\overset{\overset{\text{OH}}{|}}{C}CF_2(OCF_2CF_2)_2OC_2F_5}$$

Three products VII, VIII and IX were found in a G.C. area %
5.4, 71.7 and 8.7. The principal formation of compounds VIII
plus IX from the primary acid halide (VI) clearly indicates the
faster rate of reaction and that steric hindrance is an important
factor in effecting rates of reaction. The formation of the
tertiary alcohol IX from the ketone VIII and absence of any
tertiary alcohol from VII, likewise indicates a greater steric
hindrance offered by the secondary acyl fluoride (V).

In diethyl ether solution p-BrC$_6$F$_6$MgBr (X) also reacts
slowly with the secondary acid halides. After 12 days at 20°,
G.C. analysis of the reaction mixture from p-BrC$_6$F$_4$MgBr (X) and
C$_3$F$_7$OCF(CF$_3$)C(O)F (II) indicated the following compounds (in
G.C. area ratio) p-BrC$_6$F$_4$H (from hydrolysis of p-BrC$_6$F$_4$MgBr)
-36%, p-BrC$_6$F$_4$C(O)CF(CF$_3$)OC$_3$F$_7$ (XI) -48%, p-BrC$_6$F$_4$Br (XII) -8%
and p-C$_3$F$_7$OCF(CF$_3$)C(O)C$_6$F$_4$C(O)CF(CF$_3$)OC$_3$F$_7$ (XIV) -7%. These
results can be rationalized by considering the following:

$$\underset{X}{Br\langle\text{F}\rangle\,MgBr} + \underset{II}{R_fOR_f\overset{\overset{\text{O}}{\|}}{C}F} \xrightarrow{r_1} \underset{XI}{Br\langle\text{F}\rangle\overset{\overset{\text{O}}{\|}}{C}R_fOR_f} \xrightarrow{\;\; X \;\;}{r_2}$$

$$\underset{XII}{Br\langle\text{F}\rangle Br} + \underset{XIII}{BrMg\langle\text{F}\rangle\overset{\overset{\text{O}}{\|}}{C}R_fOR_f} \xrightarrow{II} \underset{XIV}{R_fOR_f\overset{\overset{\text{O}}{\|}}{C}\langle\text{F}\rangle\overset{\overset{\text{O}}{\|}}{C}R_fOR_f}$$
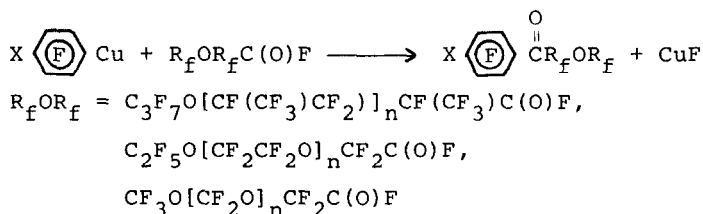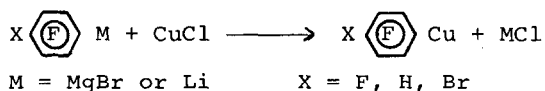
$$R_fOR_f = CF(CF_3)OC_3F_7$$

Since r_1 appears very slow and r_2 is fast, the intermediate Grignard XIII must react with II more rapidly than X in order to form the diketone XIV. When the same reaction is repeated in tetrahydrofuran, the nucleophilic character of X is increased and the rates of reactions are similarly increased. After only 2 hours at 0°, the reaction was complete. The two principal products XII and XIV were found in a 1:1 ratio (G.C. area ratio). In addition however 5 unidentified minor components were also indicated.

Since the reactions between C_6F_5MgBr (I) and $p-BrC_6F_4MgBr$ (X) with secondary acid fluorides, does not appear as a convenient synthesis procedures, due to competing reactions, other perfluorophenyl organometallic compounds were investigated. C_6F_5Cu[9] $p-HC_6F_4Cu$[10] and $p-BrC_6F_4Cu$ (XV) [10] in some respects undergo different reactions than their Grignard analogs. The possibility of an intermediate transient C_6F_5Cu (XXI) was suggested [11] in the reaction between C_6F_5MgBr (I) (diethyl ether) and $ClC(O)[CF_2]_4C(O)Cl$ catalyzed by CuCl, to yield the diketone $C_6F_5C(O)[CF_2]_4C(O)C_6F_5$ in 75-80% yields.

Pentafluoro or substituted perfluorophenylcopper compounds can be conveniently prepared through the reaction of the Grignard or lithium compounds with CuX. We have found that the reaction between these organocopper compounds and either primary or secondary acid fluorides give only one ketone product in improved isolated yields of 75-92% (See Table I). The reaction is not contaminated (as determined by G.C. analysis and product isolation) with undesirable by-products from competing reactions. Although detailed studies on specific rates have not

been determined, the reaction qualitatively appears to be more
rapid than the Grignard compounds regardless of whether primary
or secondary acid halides are used. In one example (Compound
III, Table I), CuCl in only 10% of stoichiometric quantity was
used. The yield of ketone product was 92% and no by-product
formation was noted. These results corroborate the previous
suggestion [11] of an intermediate transient organocopper inter-
mediate. Use of smaller quantities of CuX than stoichiometry
also facilitates isolation of the ketone product from the other-
wise large quantities of copper salts.

$$X \langle F \rangle\ M\ +\ CuCl\ \longrightarrow\ X \langle F \rangle\ Cu\ +\ MCl$$

$$M = MgBr\ or\ Li \qquad X = F,\ H,\ Br$$

$$X \langle F \rangle\ Cu\ +\ R_fOR_fC(O)F\ \longrightarrow\ X \langle F \rangle\ \overset{\overset{O}{\|}}{C}R_fOR_f\ +\ CuF$$

$$R_fOR_f\ =\ C_3F_7O[CF(CF_3)CF_2)]_nCF(CF_3)C(O)F,$$

$$C_2F_5O[CF_2CF_2O]_nCF_2C(O)F,$$

$$CF_3O[CF_2O]_nCF_2C(O)F$$

EXPERIMENTAL

General Comments

Reactions involving organometallic reagents were carried out
under dry nitrogen with usual precautions for rigorous exclusion
of moisture and air. Tetrahydrofuran was dried by refluxing
over metallic sodium followed by distillation from calcium
hydride prior to use. Anhydrous diethyl ether (Mallinckrodt)
was used without further purification. All new compounds were
characterized by NMR (^{19}F and ^{1}H), IR, mass spectral and
combustion analysis (except VII, IX). GC analysis were per-

formed on an F&M Model 700 instrument using 6 ft. and 12 ft.,
10% SE-30 on Chromosorb W and a 10% Apiezon L on Chromosorb W
columns. Yields of products were determined by GC analysis.
Isolated yields were always lower and depended on the complexity
of the reaction mixture. Mass spectral analysis were performed
using an electron impact or chemical ionization spectrometer.

Reaction Between C_6F_5MgBr (I) and $C_3F_7OCF(CF_3)C(O)F$ (II) in
Diethyl Ether

   C_2H_5MgBr (50ml of 1.71M, 90 mmol) was added to 250ml diethyl
ether solution of C_6F_5Br (22.2g; 90 mmol) at 0°. After ~30 min,
$C_3F_7OCF(CF_3)C(O)F$ (II) (30.0g; 90 mmol) was added. The course
of the reaction was followed by G.C. analysis (10% SE 30, 0.25"x
6' with n-C_8H_{18} as internal standard) of aliquot samples removed
periodically and hydrolyzed with 6NHCl. After 9 days at 0°, 45%
C_6F_5H (from hydrolysis of C_6F_5MgBr) remained in addition to the
products $C_6F_5C(O)CF(CF_3)OC_3F_7$ (III) and p-$C_6F_5C_6F_4C(O)CF(CF_3)$
OC_3F_7 (IV) in a ratio of 121:3 (G.C. area ratio). After an
additional 7 days at ~20°, 12% C_6F_5H remained and the ratio of
III to IV was 80:10. No additional compounds e.g., tertiary
alcohol from the reaction between C_6F_5MgBr and III were noted.

Reaction Between C_6F_5MgBr (I) and $C_3F_7OCF(CF_3)C(O)F$ (II) in THF

   C_2H_5MgBr (84.2 ml of 1.71 M diethyl ether solution; 144 mmol)
was added to 250 ml of THF solution of C_6F_5Br (35.3g; 144 mmol)
at 0°. After ~30 min, $C_3F_7OCF(CF_3)C(O)F$ (II) (48.0g; 144 mmol)
was added. The reaction was followed by G.C. analysis (a 0.25" x
12' Apiezon L on Chromosorb W column and a 0.25" x 12' SE 30 on
Chromosorb W column with n-$C_{12}H_{26}$ as an internal standard).
After 4h the reaction was completed and hydrolyzed by the addition
of methanol followed by a 25% solution of NH_4Cl. The upper

organic layer was separated and the lower aqueous layer was further extracted with diethyl ether. The combined organic layers were washed with H_2O repeatedly and dried ($MgSO_4$). The solvent was removed by distillation and the remaining crude product mixture was analyzed by G.C. Two major products $C_6F_5C(O)CF(CF_3)OC_3F_7$ (III) and p-$C_6F_5C_6F_4C(O)CF(CF_3)OC_3F_7$ (IV) were found in a ratio of 41:55 (G.C. area ratio). In addition minor components were also formed which were identified and assigned tentative structures based on their mass spectral (GC-MS analysis) fragmentation pattern as $C_6F_5C_6F_4H$, $(C_6F_5)_2C[CF(CF_3)OC_3F_7]OH$, $(C_6F_5)_2C[CF(CF_3)OC_3F_7]OC_2H_5$ and p-$C_6F_5C_6F_4C[CF(CF_3)OC_3F_7]H(OH)$. From the crude product mixture III, b.p. 94°/36mm and IV b.p. 145-146°/10mm were isolated by fractional distillation.

Competition Reaction Between C_6F_5MgBr (I), $C_3F_7OCF(CF_3)CF_2OCF$ $(CF_3)C(O)F$ and $C_2F_5O(CF_2CF_2O)_2CF_2C(O)F$ (VI)

To a diethyl ether solution (100 ml) of C_6F_5MgBr (I) (15 mmol) at 0° was added a mixture of $C_3F_7OCF(CF_3)CF_2OCF(CF_3)C(O)F$ (V) (7.47g; 15 mmol) and $C_2F_5O(CF_2CF_2O)_2CF_2C(O)F$ (VI) (6.96g; 15 mmol) dissolved in diethyl ether (20 ml). After 3.5h, a sample analyzed by G.C. indicated ~75% of the C_6F_5MgBr remained unreacted and two new product peaks A and B. The reaction mixture was allowed to warm to room temperature and stirred an additional 48h. The reaction mixture was quenched with CH_3OH and subsequently with 3N·HCl and analyzed by G.C. The G.C. area % of the follow-ing products was indicated; C_6F_5H (from hydrolysis of C_6F_5MgBr) -

14.2%, products A-71.7%; B-5.4% and C-8.7%. G.C. - M.S. analysis
of the reaction mixture indicated the following:

    A - $C_2F_5O(CF_2CF_2O)_2CF_2C(O)C_6F_5$ (VIII)

    B - $C_3F_7OCF(CF_3)CF_2OCF(CF_3)C(O)C_6F_5$ (VII)
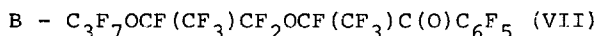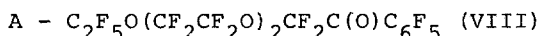
    C - $(C_6F_5)_2C(OH)CF_2(OCF_2CF_2)_2OC_2F_5$ (IX). By fractional

distillation compound A was isolated, b.p. 95-96°/12mm (see Table I)

Reaction Between $p-BrC_6F_4MgBr$ (X) and $C_3F_7OCF(CF_3)C(O)F$ (II) in

Diethyl Ether

    To a diethyl ether (131 ml) solution of $p-BrC_6F_4Br$ (X) (20.1g;
65.3 mmol) was added C_2H_5MgBr (21.8 ml of 3.0 M diethyl ether;
65.4 mmol) at 0°. After ~30 min $C_3F_7OCF(CF_3)C(O)F$ (II) (21.8g;
65.6 mmol) in diethyl ether (100 ml) was added. The temperature
was allowed to rise to ~20° and the reaction was followed bv G.C.
analysis (0.25" x 6' SE 30 on Chromosorb W column using nC_8H_{18}
as an internal standard). Analysis of the reaction mixture after
12 days showed the following products in G.C. area %:

    $p-BrC_6F_4H$(from hydrolysis of $p-BrC_6F_4MgBr$) 36%.

    $p-BrC_6F_4C(O)CF(CF_3)OC_3F_7$(XI) 47.5%, $p-BrC_6F_4Br$ (XII) 8% and

    $p-C_3F_7OCF(CF_3)C(O)C_6F_4C(O)CF(CF_3)OC_3F_7$ (XIV) 7%.

Reaction Between $p-BrC_6F_4MgBr$ (X) and $C_3F_7OCF(CF_3)C(O)F$ (II) in

THF

    To a THF (80 ml) solution of $p-BrC_6F_4Br$ (6.37g; 20.7 mmol)
was added C_2H_5MgBr (16.2 ml of 1.28M diethyl ether; 20.7 mmol) at
0°. After ~30 min $C_3F_7OCF(CF_3)C(O)F$ (II) (7.0g; 21.0 mmol) was
added and the reaction was followed by G.C. analysis (0.25" x 6'

SE 30 on Chromosorb W column using nC_8H_{18} as an internal stand-
ard). After 2h the reaction was completed and hydrolyzed by the
addition of methanol followed by a 25% solution of NH_4Cl. The
upper organic layer was separated and the lower aqueous layer
extracted with diethyl ether. The combined organic layers were
washed with H_2O repeatedly and dried ($MgSO_4$). After removing
the solvent the remaining crude reaction mixture was analyzed by
G.C. indicating two major components $p-BrC_6F_4Br$ (XII) and
$p-C_3F_7OCF(CF_3)C(O)C_6F_4C(O)CF(CF_3)OC_3F_7$ (XIV) in a 1:1 ratio
(G.C. area ratio). In addition 5 minor unidentified components
were indicated. On cooling the reaction mixture most of the
$p-BrC_6F_4Br$ (XII) crystallized and was separated by filtration.
Because of the remaining complex mixture, the diketone (XIV) was
isolated by preparative G.C.

Reaction Between $p-BrC_6F_4Cu$ (XV) and $C_3F_7OCF(CF_3)C(O)F$ (II)

To a THF (800 ml) solution of $p-BrC_6F_4Br$ (63.3g; 205 mmol)
was slowly added C_2H_5MgBr (117 ml of 1.75 M diethyl ether; 205
mmol) at 0°. After 1h, CuCl (25.2g; 254 mmol) was added and the
reaction allowed to stir for 1h. To this mixture, $C_3F_7OCF(CF_3)$
$C(O)F$ (II) (68.0g; 205 mmol) in diethyl ether (100 ml) was added
and the mixture was allowed to warm to ~20°. After 18h, the
reaction was hydrolyzed with 3N HCl. The organic layer was
phase separated and the aqueous layer was extracted with diethyl
ether. The combined organic and diethyl ether extracts were
further washed repeatedly with 3N HCl and H_2O to remove the
copper salts. The dried ($MgSO_4$) diethyl ether solution was
distilled leaving a crude product (98g; 88.5% yield, ~96% pure).

TABLE I[(a)]

Product	B.P./mm	I.R.(C=O) cm^{-1}	M.S.	Combustion Data $\dfrac{\text{Calc'd}}{\text{Found}}$ C	
$C_6F_5\overset{O}{\overset{\|}{C}}CF(CF_3)OC_3F_7$ (III) (e)(f)	94°/36	1744	480(M)⁺	$\dfrac{30.02}{29.79}$	
$p\text{-}C_6F_5C_6F_4\overset{O}{\overset{\|}{C}}CF(CF_3)OC_3F_7$ (IV)(f)	145-146°/10	1755	628(M)⁺	$\dfrac{34.42}{34.65}$	
$p\text{-}C_3F_7O(CF_3)CF\overset{O}{\overset{\|}{C}}C_6F_4\overset{O}{\overset{\|}{C}}CF(CF_3)\text{-}$ OC_3F_7 (XIV)(f)	(b)	1748	774(M)⁺	$\dfrac{27.26}{27.36}$	
$C_6F_5\overset{O}{\overset{\|}{C}}CF(CF_3)OCF_2CF(CF_3)OC_3F_7$ (VII) (e)(f)	(b)	1744	646(M)⁺	--	
$C_6F_5\overset{O}{\overset{\|}{C}}CF_2(OCF_2CF_2)_2OC_2F_5$ (VIII) (e)(f)	95-96°/12	1750	612(M)⁺	$\dfrac{27.45}{27.63}$	
$(C_6F_5)_2\overset{OH}{\overset{\|}{C}}CF_2(OCF_2CF_2)_2OC_2F_5$ (IX) (f)	(b)	(c)	763(M-OH)⁺(d)	--	
$p\text{-}BrC_6F_4\overset{O}{\overset{\|}{C}}CF(CF_3)OC_3F_7$ (XI)(e)	89/8.5	1750	540-542(M)⁺	$\dfrac{26.64}{26.57}$	$\dfrac{14.77}{14.61}$

Compound	b.p.	I.R.	M.S.		
p-BrC$_6$F$_4$$\overset{=}{\text{C}}$CF(CF$_3$)OCF$_2$CF(CF$_3$)-OC$_3F_7$ (XVI) (e)	83–85°/0.3	1750	706–708(M)$^+$	25.49 / 25.20	11.25 / 11.45
p-BrC$_6$F$_4$$\overset{\text{O}}{\overset{|}{\text{C}}}$CF(CF$_3$)$\{OCF_2$CF(CF$_3$)$\}_4$-OC$_3F_7$ (XVII) (e)	124–126°/0.02	1750	1204–1206(M)$^+$	23.92 / 23.91	6.63 / 6.62
p-HC$_6$F$_4$$\overset{\text{O}}{\overset{|}{\text{C}}}$CF(CF$_3$)OCF$_2$CF(CF$_3$)-OC$_3F_7$ (XVIII) (e)	97°/10	1744	628(M)$^+$	28.68 / 28.45	--
p-BrC$_6$F$_4$$\overset{\text{O}}{\overset{|}{\text{C}}}CF_2$(OCF$_2$)$_3OCF_3$ (XIX) (e)	96°/7	1750	558–590(M)$^+$	24.27 / 24.40	13.57 / 13.57
p-BrC$_6$F$_4$$\overset{\text{C}}{\overset{|}{\text{C}}}CF_2$(OCF$_2CF_2$)$_2OC_2F_5$ (XX) (e)	95°/7	1750	672–674(M)$^+$	24.98 / 24.95	11.87 / 11.86

(a) All new compounds.

(b) Isolated by gas chromatography.

(c) I.R. (film), OH(unbonded) – 3620 cm^{-1} C$_6$F$_5$(ring stretch) – 1500; 1530 and 1650 cm^{-1}.

(d) Chemical ionization mass spectral analysis – m/e 763(M–OH)$^+$, 613(M–C$_6$F$_5$)$^+$, 195(C$_6$F$_5$C=O)$^+$, 119(C$_2$F$_5$)$^+$.

(e) Prepared from the arylcopper and perfluoroalkylether acid fluorides.

(f) Prepared from the arylGrignard and perfluoroalkylether acid fluoride.

The crude product was distilled to give the pure ketone XI b.p. 89°/8.5mm (82g; 74% yield, >99% pure).

In the reactions where the aryl copper was prepared from stoichiometric quantities of CuCl, large quantities of cuprous salts were precipitated when the reaction was hydrolyzed. These salts and the relative insolubility of these highly fluorinated compounds made quantitative separation of ketone products difficult. Much better isolation procedures were experienced when less than stoichiometric (10%) amounts of CuCl were used in the synthesis of the aryl copper intermediate. Isolated yields as high as 92% were realized by this procedure. The above general procedures were used in the synthesis of the other ketones (III, VII, VIII, XI, XVI, XVII, XVIII, XIX and XX) (see Table I).

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