Journal of Fluorine Chemistry, *36* (1987) 123–139

Received: June 25, 1986; accepted: March 20, 1987

SOLVENT EFFECTS IN REACTIONS BETWEEN PERFLUOROALKYLIODIDES AND CADMIUM

GRACE J. CHEN

University of Dayton Research Institute, Dayton, OH 45469
(U.S.A.)

and CHRIST TAMBORSKI*

Air Force Wright Aeronautical Laboratories, Materials Laboratory,
Wright-Patterson Air Force Base, OH 45433 (U.S.A.)

SUMMARY

The interaction between perfluoroorgano iodides (R_fI where $R_f = F(CF_3)_2C(CF_2CF_2)_3$, n-$C_6F_{13}$, n-$C_8F_{17}$, $F(CF_3)_2COCF_2CF_2$, $F(CF_3)_2CO(CF_2CF_2)_4$ and $C_2H_5OC(O)(CF_2CF_2)_2OCF_2CF_2$) with cadmium in an acetonitrile solvent media produces primarily the coupled products (R_fR_f, 72-90% yield) in addition to minor quantities of the reduction products (R_fH). On the other hand ICF_2CF_2I and $ClCF_2CFClI$, by a 1,2-dehalogenation reaction, form the olefins $CF_2 = CF_2$ and $CF_2 = CFCl$, respectively, as the principal products. The interaction of R_fI compounds with cadmium in other solvent media, e.g. diethyl ether, tetrahydrofuran (THF), N,N-dimethylformamide (DMF), and bis(2-methoxyethyl)ether(diglyme) were examined and found to produce a different ratio of R_fR_f and R_fH products.

INTRODUCTION

Recently the synthesis of perfluoroaliphatic cadmium compounds by various means has been described. In 1980 Krause and Morrison [1] by means of a ligand-exchange reaction between $(CH_3)_2Cd$ and $(CF_3)_2Hg$ in glyme solvent prepared $(CF_3)_2Cd$ glyme

---

*Present address: Fluidics Inc., P.O.Box 1886, Dayton, OH 45429 (U.S.A.)

0022-1139/87/$3.50

complex. In 1984 Lange and Naumann reported that the interaction between perfluoroalkyl iodides and dialkyl cadmium compounds yield bis(perfluoroorgano)cadmium compounds in quantitative yields [2]. More recently Burton and Wiemers [3] and Heinze and Burton [4] prepared perfluoroorganocadmium compounds [$(R_f)_2Cd$ and R_fCdI] through the reaction between cadmium and perfluoroalkyl iodides or CF_2X_2 (X = Br or Cl) in DMF solvent. Although olefinic by-products were obtained in minor amounts, no coupling products, R_fR_f, were noted under their experimental conditions.

In our current studies we are examining the reactions between cadmium and longer chain R_fI in a variety of solvents. Although we have not determined the structure of the organocadmium compounds, we found that the solvent media plays an important role in determining the ratio and type of reaction products.

RESULTS AND DISCUSSION

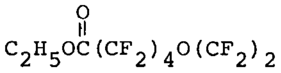
In our studies we have found that all the R_fI compounds were found to react with cadmium powder in solvents such as CH_3CN, $C_2H_5OC_2H_5$, THF, DMF, and diglyme at or below reflux temperature. Depending upon the structure of the R_fI, choice of solvent and reaction conditions, one or more products such as the coupled product R_fR_f, reduction product R_fH, olefin product, and small quantities of still unidentified products were obtained.

In CH_3CN solvent medium, R_fI(I) were found to react with cadmium at or below the reflux temperature to give the coupled products R_fR_f(II) in 72-90% yield. In addition, the reduction products R_fH(III) were found in minor yields. Under the same conditions n-$C_6F_{13}Br$ failed to yield any detectable quantity of products.

$$\underset{\text{I}}{R_fX} + Cd \xrightarrow{CH_3CN} \xrightarrow{H^+} \underset{\text{II}}{R_fR_f} + \underset{\text{III}}{R_fH} \qquad (1)$$

$X = I;$ $R_f =$ (a) $F(CF_3)_2C(CF_2CF_2)_3$, (b) $n\text{-}C_6F_{13}$

(c) $F(CF_3)_2CO(CF_2CF_2)_4$, (d) $F(CF_3)_2COCF_2CF_2$

(e) 

$C_2H_5O\overset{\overset{O}{\|}}{C}(CF_2)_4O(CF_2)_2$

$X = Br;$ $R_f = n\text{-}C_6F_{13}$

All the iodides (Ia,b,c,d) except Ie reacted very slowly with cadmium at room temperature in CH_3CN. At the reflux temperature the reaction rate was accelerated and the reactions were completed in several hours (see Table 1). On the assumption that the organocadmium compound is as shown in equation 2, a 1:1 mole ratio of reactants is required.

$$2Cd + \underset{\text{I}}{2R_fI} \xrightarrow{CH_3CN} \left[\underset{\text{IV}}{(R_f)_2Cd} + CdI_2 \longleftrightarrow \underset{\text{V}}{2R_fCdI}\right] \longrightarrow R_fR_f \qquad (2)$$

From Table 1 (Exp. 1 and 2) it can be seen that either a 1.1 or 0.54 mole ratio of reactants gives nearly the same results. This would indicate that either the organocadmium intermediate is not as shown in equation 2 or that as soon as either IV or V is formed, reaction occurs with R_fI to give the coupled product R_fR_f. It can be seen that a 1.1 mole ratio does accelerate the reaction.

An iodide Ie containing a functional group $C_2H_5OC(O)(CF_2)_4O(CF_2)_2I$ (see Table 1 Exp. 7) on reaction with cadmium in CH_3CN behaved somewhat differently from the other iodides (Ia→Id) in that more of the reduction product IIIe was formed. The product ratio was affected by the mole ratio of reactants. Apparently

TABLE 1

REACTIONS OF R_fI WITH CADMIUM IN CH_3CN

Exp.	R_fI	Molar Ratio Cd/R_fI	Temp. (°C)	Time (h)	Yield of[a]		M.P.(B.P.) (°C)
					R_fR_f	R_fH	
1	$F(CF_3)_2C(CF_2CF_2)_3I$	1.1	80[b]	0.5	-(85)	f	99-101
2	$F(CF_3)_2C(CF_2CF_2)_3I$	0.54	80[b]	3.5	-(89)	f	99-101
3	$n\text{-}C_6F_{13}I$	0.56	80[b]	2.0	96(74)	f	74-75
4	$F(CF_3)_2CO(CF_2CF_2)_4I$	0.62	80[b]	3.5	-(90)	f	92-93
5	$F(CF_3)_2CO(CF_2CF_2)I$	0.62	25[c]	119	5(-)	4	-
6	$F(CF_3)_2CO(CF_2CF_2)I$[g]	0.62	78[b]	5.0	91(75)	f	(136)
7	$C_2H_5OC(O)(CF_2)_4O(CF_2)_2I$[d]	0.55	25[c]	2.5	60(-)	10	-
	$C_2H_5OC(O)(CF_2)_4O(CF_2)_2I$[d]	0.55	80[b]	16.5	60(-)	12[e]	-
	$C_2H_5OC(O)(CF_2)_4O(CF_2)_2I$[d]	0.77	80[b]	2.0	72(-)	16[e]	-

[a] Yields based on R_fI, determined by GC area %, isolated yields in parentheses

[b] Reflux temperature; [c] Room temperature; [d] Ref. 8;

[e] In addition to unreacted R_fI, minor unidentified products were seen on GC/MS analyses

[f] Minor quantities of R_fH were detected in reaction mixture; [g] Ref. 9

the presence of a functional ester group affected either the type or stability of the organocadmium intermediate.

Homo and cross-coupling of two different iodides yielded as one might expect a mixture of coupled products.

$$n\text{-}C_6F_{13}I + n\text{-}C_8F_{17}I + 2Cd \underset{\text{GC area \%}}{\xrightarrow{CH_3CN}} \underset{(26)}{n\text{-}C_{12}F_{26}} + \underset{(44)}{n\text{-}C_{14}F_{30}} + \underset{(28)}{n\text{-}C_{16}F_{34}} \tag{3}$$

In addition to the coupled products, GC/MS analyses indicated small quantities of $n\text{-}C_6F_{13}H$ and $n\text{-}C_8F_{17}H$. The diiodide $I(CF_2)_4I$ gave on reaction with cadmium in CH_3CN three different series of products (characterized by GC/MS only); $I(CF_2)_8I$, $I(CF_2)_{12}I$ and $I(CF_2)_{16}I$ as the major products and two additional series of minor products; $H(CF_2)_8H$, $H(CF_2)_{12}H$, $H(CF_2)_{16}H$, and $I(CF_2)_8H$, $I(CF_2)_{12}H$ and $I(CF_2)_{16}H$.

R_fI with beta halogens other than fluorine reacted with cadmium in CH_3CN to form olefins as the major products. Such observations have previously been noted, although in a different solvent system, using zinc dehalogenation of 1,2-dihalo (other than fluorine) perfluoroalkyl compounds [5,6,7].

$$\begin{array}{lcl} XCF_2CFYI + Cd & \longrightarrow & CF_2 = CFY \\ \text{VI; } X=I, Y=F & & \text{VIII; } Y=F \\ \text{VII; } X=Y=Cl & & \text{IX; } Y=Cl \end{array} \tag{4}$$

ICF_2CF_2I(VI) yielded only the 1,2-deiodinated product $CF_2 = CF_2$ (VIII) while $ClCF_2CFClI$(VII) yielded $CF_2 = CFCl$(IX) as the principal product in addition to a homologous series of products (determined by GC/MS only) which can be represented by a general formula $Cl(CF_2CFCl)_nCl$. These minor products may have formed from either a coupling reaction, telomerization reaction of

$CF_2 = CFCl$ or a combination of both. Studies on elucidating the formation and structure of these minor products are in progress.

The effect of several other solvents (see Table 2) on the interaction of R_fI with cadmium were also examined. In contrast to the slow reaction of R_fI (Ia and Ic) in CH_3CN, all the other solvents provided a faster reaction rate at room temperature. The reactions in diglyme, after hydrolysis of the reaction, yielded a mixture of R_fR_f and R_fH with small amounts of unidentified products (GC/MS). The reaction temperature did not exert a major effect on the products. At 80°C the distribution of products was slightly different from that at 25°C (see Table 2, Exp. 2 and 3).

In DMF as the solvent, $F(CF_3)_2CO(CF_2CF_2)_4I$ gave the following products R_fR_f (IIc, 31%), R_fH (IIIc, 43%), and a number of minor products one of which by GC/MS analysis is consistent with the structure $F(CF_3)_2CO(CF_2CF_2)_3CF{=}CF_2$.

The reactions in diethyl ether or THF, after hydrolysis yielded primarily the reduced product R_fH. In THF the reaction was exothermic and was completed in two hours, while in diethyl ether the reaction rate was considerably slower requiring two days for consumption of the starting R_fI. It is interesting to note that in THF as the solvent, only a mole ratio of 0.5 (Cd:R_fI) was required for producing the reduction product R_fH in near quantitative yield. The reduction product was produced as a result of the interaction of the R_fI, cadmium and the THF solvent prior to any hydrolysis of the reaction mixture. After the consumption of the R_fI and cadmium, a two-phase reaction mixture resulted. The bottom layer was identified by NMR analysis as primarily the R_fH with some THF, while the upper layer was

TABLE 2

REACTIONS OF R_fI WITH CADMIUM IN OTHER SOLVENTS

Exp.	R_fI	Solvent	Molar Ratio Cd/R_fI	Time (h)	Temp. (°C)	Products (GC area %)			
						R_fH	R_fR_f	R_fI	Others
2	$F(CF_3)_2CO(CF_2CF_2)_4$	diglyme	1.27	2	-5→25[a]	36	60	0	4
3	$F(CF_3)_2CO(CF_2CF_2)_4$	diglyme	1.10	2	80	51	43	0	6
4	$F(CF_3)_2CO(CF_2CF_2)_4$	THF	1.10	1	25[a]	98	trace	0	∿1
4a	$F(CF_3)_2CO(CF_2CF_2)_4$	THF	0.56	1	25[a]	96	trace	trace	∿2
5	$F(CF_3)_2CO(CF_2CF_2)_4$	DMF	1.10	0.5	25[a]	25	19	52	4
	$F(CF_3)_2CO(CF_2CF_2)_4$	DMF	1.10	1.5	25[a]	26	20	48	6
	$F(CF_3)_2CO(CF_2CF_2)_4$	DMF	1.10	2	80	43	31	0	26[b]
6	$F(CF_3)_2COCF_2CF_2$	CH_3CN	0.62	119	25[a]	4	5	89	2
7	$F(CF_3)_2CO(CF_2CF_2)_4$	diethyl ether	1.39	2.5	25[a]	40	trace	56	4
	$F(CF_3)_2CO(CF_2CF_2)_4$	diethyl ether	1.39	4.25	25[a]	45	trace	50	5
	$F(CF_3)_2CO(CF_2CF_2)_4$	diethyl ether	1.39	21.0	25[a]	72	trace	23	5
	$F(CF_3)_2CO(CF_2CF_2)_4$	diethyl ether	1.39	45.0	25[a]	90	trace	1	9
8	$F(CF_3)_2C(CF_2CF_2)_3$	diethyl ether	2.04	2	25[a]	46	trace	52	2
	$F(CF_3)_2C(CF_2CF_2)_3$	diethyl ether	2.04	23	25[a]	94	trace	0	6

[a] Room temperature; [b] By GC/MS one of the products was identified as $F(CF_3)_2C(CF_2CF_2)_3CF{=}CF_2$ (8%)

TABLE 3

ANALYSES OF PRODUCTS

Compound	Number	M.S.	Combustion Data Calc'd/Found	
			C	H
$[(CF_3)_2CF(CF_2)_6]_2$ (nc)	IIa	$919(M-F)^+$	23.05/22.90	0/0
$[C_6F_{13}]_2$	IIb	$619(M-F)^+$	22.59/22.34	0/0
$[(CF_3)_2CFO(CF_2)_8]_2$ (nc)	IIc	-	22.58/22.37	0/0
$[(CF_3)_2CFO(CF_2)_2]_2$ (nc)	IId	$551(M-F)^+$	21.07/20.90	0/0
$[C_2H_5OC(O)(CF_2)_4O(CF_2)_2]_2$[e]	IIe	$778(M-F)^+$		
$(CF_3)_2CF(CF_2)_6H$ (nc)[a]	IIIa	$451(M-F)^+$	23.00/22.95	0.21/0.24
$(CF_3)_2CFO(CF_2)_8H$ (nc)[b]	IIIc	567(M-F)	22.54/22.53	0.17/0.21
$(CF_3)_2CFO(CF_2)_2H$[c]	IIId	267(M-F)	21.00/20.88	0.35/0.36
$C_2H_5OC(O)(CF_2)_4O(CF_2)_2H$[d]	IIIe			

[a] b.p. 135 C; [b] b.p. 166 C; [c] b.p. 46 C; [d] b.p. 156 C, see Ref. 8 and 10; [e] see Ref. 8

primarily THF with some R_fH. The fact that the R_fH was formed prior to hydrolysis indicates a proton abstraction from the solvent. GC/MS analysis of the reaction mixture prior to hydrolysis or after hydrolysis indicated the presence of the reduction product R_fH as well as the deprotonated THF product C_4H_6O. The presence of the dihydrofuran (C_4H_6O) product clearly indicates the THF solvent participation in forming the R_fH rather than hydrolysis of the R_f-Cd by minor quantities of water present in the solvent.

From the above observations, it appears quite clearly that the solvent media plays an important role in the reaction between R_fI compounds and cadmium. A variety of products are formed indicating a number of different reaction mechanisms that may be taking place. Some experimental conditions did, however, produce high yields of principal products, e.g. R_fR_f or R_fH, while other conditions produced a variety of products which may not offer good laboratory preparations for such compounds. This study indicates that further, more detailed effort must be expended in this area in order to develop these perfluoroorganocadmium compounds as intermediates as has been done for the organolithium, organomagnesium, and organocopper compounds. The conversion of some perfluorocadmium compounds to other perfluoroorganometallic intermediates useful as synthons has already been initiated and reported by Burton and Weimers [3].

EXPERIMENTAL

All reactions were carried out in an atmosphere of dry nitrogen with the usual precautions for vigorous exclusion of moisture and air. All the solvents were dried and redistilled before use. Cadmium (powder, 100 mesh) was purchased from

Aldrich Chemical Company, Inc., U.S.A., and was used directly. Gas chromatographic analyses were performed on a Perkin Elmer Sigma I with 10% SE-30 on 80-100 mesh Supelcoport packed 6 ft. column. The GC/MS analyses were performed on a Finnigan 4021 mass spectrometer using either chemical ionization or electron impact mode or both if necessary. Infrared spectra were recorded on a Perkin Elmer 683 spectrophotometer. Yields of product are reported as isolated yields or GC area percent yields. Since sufficient quantities of all products were not isolated, GC detector response factors could not be determined (see Table 1).

Synthesis of $F(CF_3)_2C(CF_2CF_2)_6C(CF_3)_2F$(IIa) in CH_3CN

$F(CF_3)_2C(CF_2CF_2)_3I$(Ia) (10.0 g, 16.8 mmol) was added dropwise (2 min.) to a stirred mixture of cadmium (2.02 g, 18.0 mmol) and anhydrous CH_3CN (30 ml) at room temperature. After 30 min. no observable reaction occurred, and therefore the reaction mixture was heated to reflux temperature (ca. 80°C) for an additional 30 minutes. During this time a considerable amount of precipitate formed. The reaction mixture was cooled to room temperature, hydrolyzed with 2N HCl (30 ml) and $CF_2ClCFCl_2$ (30 ml) was added. The mixture was centrifuged, the aqueous (upper) and organic layers were decanted from the solid (unreacted Cd plus undissolved R_fR_f). This solid was extracted with additional $CF_2ClCFCl_2$ (3x30 ml). The remaining gray solid (excess Cd, 1.10 g) was discarded. The organic extracts were combined with the previous organic layer and washed with 2N HCl (1x20 ml) and water (2x30 ml). On evaporation of the solvent, a crude white product (7.20 g) resulted. The crude product was sublimed under vacuum (~140°C/0.03 mm) to yield a pure product (6.70 g, 85%) (see Table 1, Exp. 1).

Another experiment using one-half the amount of cadmium gave essentially the same results. In both experiments small quantities of the R_fH product were seen in the $CF_2ClCFCl_2$ organic extracts and confirmed by GC/MS analysis.

The other coupled R_fR_f compounds IIb, IIc, and IId were synthesized by a similar procedure as described above except the mole ratio of reactants and reaction time and temperatures were varied (see Tables 1 and 2). The reactions were assumed completed when the GC analyses of aliquot samples indicated maximum product formation. In each case minor quantities of the reduced products were detected (GC/MS).

Reaction of $C_2H_5OC(O)(CF_2)_4O(CF_2)_2I$ (Ie) in CH_3CN

The iodoester Ie (10.0 g, 19.4 mmol) was added dropwise (8 min.) to a mixture of cadmium (1.20 g, 10.7 mmol) and CH_3CN (30 ml). A rapid exothermic reaction (25°C→36°C) occurred which lasted for several minutes. Aliquot samples were analyzed periodically by GC (see Table 1). After 2.5 hours at room temperature, the reaction mixture was heated to reflux temperature for 16.5 hours. The GC analysis showed the results to be almost identical to the one after 2.5 hours at room temperature. An additional quantity of cadmium (0.48 g, 4.3 mmol) was added. The reaction mixture was again heated to reflux temperature for two hours, cooled, hydrolyzed with 2N HCl (20 ml) and phase separated. The bottom layer was washed with 2N HCl (4x15 ml), water, and yielded the crude product (6.6 g). A GC/MS analysis of the crude product indicated the starting iodoester (1%), coupled product IIe [8] as the major product (72%), the R_fH product (16%) (see Table 1, Exp. 7).

Reaction of n-$C_6F_{13}I$ and n-$C_8F_{17}I$ in CH_3CN

The n-$C_6F_{13}I$ (5.0 g, 11.2 mmol) and n-$C_8F_{17}I$ (6.12 g, 11.2 mmol) were added to the cadmium (1.76 g, 15.7 mmol) and CH_3CN (30 ml) mixture. The heterogeneous mixture was stirred and heated at reflux temperature (*ca.* 80°C) for 3.5 hours. Workup was accomplished as described for the synthesis of IIa. The crude white solid (7.5 g) was dissolved in $CFCl_2CF_2Cl$ and analyzed by GC and GC/MS. The analysis indicated $C_{12}F_{26}$ (26%), $C_{14}F_{30}$ (44%) and $C_{16}F_{34}$ (28%) with trace amounts of $C_6F_{13}H$ and $C_8F_{17}H$.

Attempted Reaction of n-$C_6F_{13}Br$ in CH_3CN

The n-$C_6F_{13}Br$ (8.94 g, 22.4 mmol) was added to cadmium (1.45 g, 12.9 mmol) and CH_3CN (30 ml). The heterogeneous mixture was heated at refluxing temperature (*ca.* 70°C) for five hours. During this time no observable reaction occurred. A GC analysis of the reaction mixture showed only the unreacted n-$C_6F_{13}Br$.

Reaction of ICF_2CF_2I in CH_3CN

The ICF_2CF_2I (10.0 g, 28.2 mmol) was added dropwise (5 min.) to a mixture of cadmium (0.79 g, 7.03 mmol) and CH_3CN (20 ml). A rapid exothermic reaction occurred with evolution of a gas which was identified as $CF_2 = CF_2$ by infrared analysis. After stirring for two hours, an aliquot sample was hydrolyzed, washed, and analyzed by GC which indicated only the presence of

ICF_2CF_2I. An additional quantity of cadmium (0.79 g, 7.03 mmol) was added which again caused an exothermic reaction. The evolved gas was identified as $CF_2 = CF_2$. A hydrolyzed aliquot sample of the reaction mixture indicated only unreacted ICF_2CF_2I.

Reaction of $ClCF_2CFClI$ in CH_3CN

The $ClCF_2CFClI$ (10.0 g, 35.8 mmol) was added (15 min.) to a cooled (~0°C) mixture of cadmium (2.5 g, 22.2 mmol) and CH_3CN (50 ml). A slight exothermic reaction was noted with formation of a white precipitate and a gas evolution which was identified as $CF_2 = CFCl$ by an infrared analysis. The reaction mixture was then warmed to room temperature. After 30 minutes an aliquot sample was hydrolyzed, washed (2N HCl and H_2O) and analyzed by GC/MS (relative GC area %) as $CF_2 = CFCl$ (3%), $ClCF_2CFClI$ (61%), $C_4F_6Cl_4$ (21%), $C_6F_9Cl_5$ (10%) and $C_8F_{12}Cl_6$ (3%). An additional quantity of cadmium (2.0 g, 17.8 mmol) was added to the reaction at room temperature. An exothermic reaction occurred with evolution of a gas identified as $CF_2 = CFCl$ (infrared). After 25 minutes an aliquot sample, without hydrolysis, was analyzed by GC and showed at least four components which were the same as above except that no starting material $ClCF_2CFClI$ was present. $CF_2 = CFCl$ was the major component (60%; GC relative area). After one hour the reaction mixture was hydrolyzed with 2N HCl (30 ml) and $CFCl_2CF_2Cl$ (10 ml) was added. The reaction mixture was centrifuged, the bottom organic layer was washed with 2N HCl (2x2 ml) and concentrated to yield a residue (0.6 g). GC analysis (Hewlett Packard 5830A with a fused silica capillary Supelcowax 10, 60 meter column) and a GC/MS analysis showed at least five products (GC area % and number of isomers), $C_4F_6Cl_4$ (37%, 2), $C_6F_9Cl_5$ (31%, 4-5), $C_8F_{12}Cl_6$ (18%, 7), $C_{10}F_{15}Cl_7$ (4%, multiple peaks) and an unidentified component (1%, multiple peaks) suspected to be $C_{12}F_{18}Cl_8$.

A second reaction was carried out under slightly different conditions using cadmium (8.46 g, 75.3 mmol), CH_3CN (40 ml), CH_2Cl_2 (120 ml) and $ClCF_2CFClI$ (20.0 g, 71.7 mmol). A dry-ice condenser was used so as to condense the evolved gas $CF_2 = CFCl$. After complete addition of the $ClCF_2CFClI$ to the cooled (ca. 0°C) reaction mixture, the temperature was allowed to rise to room temperature. After two hours an aliquot sample was hydrolyzed, analyzed by GC and showed no $ClCF_2CFClI$ and the same components as in the previous experiment except for different ratios. $CF_2 = CFCl$ was still the major product. The reaction mixture was stirred at room temperature for 65 hours and hydrolyzed with 2N HCl (40 ml). The unreacted cadmium was isolated (1.34 g, 11.9 mmol). The organic layer was separated, washed with 2N HCl (2x50 ml) and concentrated to yield a residue (3.8 g). GC analysis on a capillary column (see above) showed at least five homologous products, each containing a number of isomers, $C_4F_6Cl_4$ (44%, at least two isomers), $C_6F_9Cl_5$ (22%, 4-5 isomers), $C_8F_{12}Cl_6$ (21%, at least seven isomers), $C_{10}F_{15}Cl_7$ (5%, multiple isomers) and an unidentified homolog (1%, multiple peaks) suspected to be $C_{12}F_{18}Cl_8$.

Reaction of $F(CF_3)_2CO(CF_2CF_2)_4I$ in Diglyme

The $F(CF_3)_2CO(CF_2CF_2)_4I$ (10.0 g, 14.0 mmol) was added (2 min.) to a mixture of cadmium (1.74 g, 15.5 mmol) and diglyme (30 ml) and heated for two hours at 80°C. The reaction mixture was worked up as described above for compound IIc. The excess cadmium (0.56 g) was isolated. The combined organic layers were analyzed by GC, and the results are shown in Table 2, Exp. 3. Another reaction was carried out at -5°C for 30 minutes and allowed to warm to room temperature for 1.5 hours, and gave a higher yield of the coupled product and a lower yield of the reduction product (see Table 2, Exp. 2).

Reaction of $F(CF_3)_2CO(CF_2CF_2)_4I$ in DMF

The $F(CF_3)_2CO(CF_2CF_2)_4I$ (10.0 g, 14.0 mmol) was added to a mixture of cadmium (1.74 g, 15.5 mmol) and DMF (30 ml). A slight exothermic reaction was noted. Aliquot samples were removed periodically, hydrolyzed and extracted with $CF_2ClCFCl_2$ and analyzed by GC (see Table 2, Exp. 5). After stirring the reaction at room temperature for 1.5 hours, GC analysis showed no further reaction, and therefore the reaction mixture was heated to reflux (*ca.* 80°C). After two hours the reaction mixture was hydrolyzed with 2N HCl (20 ml) and $CF_2ClCFCl_2$ (30 ml) added. A GC analysis showed consumption of the starting iodide and a higher yield of the coupled and reduced products. In addition a number of other byproducts were formed in small quantities. One of these was characterized by GC/MS analysis as $F(CF_3)_2CO(CF_2CF_2)_3CF{=}CF_2$ (8%) (see Table 2, Exp. 5).

Reaction of $F(CF_3)_2CO(CF_2CF_2)_4I$ in THF

The $F(CF_3)_2CO(CF_2CF_2)_4I$ (10.0 g, 14.0 mmol) was added to a mixture of cadmium (1.74 g, 15.5 mmol) and tetrahydrofuran (30 ml) over a period of 15 minutes. A small exothermic reaction (25°→31°C) was noted. After stirring for one hour at room temperature, an aliquot sample was hydrolyzed and analyzed by GC indicating a 98 area % of the reduced product $F(CF_3)_2CO(CF_2CF_2)_4H$ and a trace amount (~0.2%) of the coupled product R_fR_f plus some unidentified products (~1%). After filtration of the reaction mixture under an atmosphere of nitrogen to remove unreacted cadmium (0.93 g, 8.30 mmol), two layers separated. The bottom layer was analyzed by ^1H and ^{19}F NMR and indicated the presence of only the reduced product $F(CF_3)_3CO(CF_2CF_2)_4H$ and tetrahydrofuran. The bottom layer was washed with 2N HCl (3x2 ml) to remove the dissolved THF to yield the R_fH compound (5.2 g, 63%). The upper organic layer was similarly analyzed by NMR and indicated predominantly THF with some R_fH compound. This layer was then added to 2N HCl (20 ml) to dissolve the THF and yielded more R_fH as a separate lower layer (2.6 g, 30%).

A similar reaction as described above was performed using one-half the amount of cadmium (0.868 g, 7.72 mmol). Workup of the reaction mixture produced the R_fH in 96% yield. In addition the recovered cadmium was 0.126 g (1.12 mmol). The products from both of the above experiments were combined and distilled to yield the pure product $F(CF_3)_2CO(CF_2CF_2)_4H$, 13.6 g, bp 166°C.

Reaction of $F(CF_3)_2CO(CF_2CF_2)_4I$ in Diethyl Ether

The reactions of the $F(CF_3)_2CO(CF_2CF_2)_4I$ in diethyl ether were carried out in the same manner as described for THF (see Table 2, Exp. 7 and 8).

ACKNOWLEDGEMENT

We would like to thank Dr. Chi-Kuen Yu of Technical Services Group, Dayton, Ohio for performing the mass spectral analysis.

REFERENCES

1 L. J. Krause and J. A. Morrison, J. Chem. Soc. Chem. Commun. (1980) 671.

2 H. Lange and D. Naumann, J. Fluorine Chem., 26 (1984) 1; 26 (1984) 93.

3 D. J. Burton and D. M. Wiemers, J. Am. Chem. Soc., 107 (1985) 5014.

4 P. L. Heinze and D. J. Burton, J. Fluorine Chem., 29 (1985) 359.

5 A. L. Henne and W. Postelneck, J. Am. Chem. Soc., 77 (1955) 2334.

6 W. T. Miller, Jr., E. Bergman, and A. H. Fainberg, J. Am. Chem. Soc., 79 (1957) 4159.

7 T. M. Keller and P. Tarrant, J. Fluorine Chem., 6 (1975) 105.

8 E. J. Soloski, C. Tamborski, and T. Psarras, J. Fluorine Chem., 11 (1978) 601.

9 H. R. Nychka and L. G. Anello, U.S.P. 3,435,078 (25 March 1969, Allied Chemical Company, U.S.A.).

10 L. S. Chen, G. J. Chen, M. T. Ryan, and C. Tamborski, J. Fluorine Chem., 34 (1987) 299.