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FLUOROALKYLATION OF AROMATIC COMPOUNDS

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SUMMARY

Perfluoroalkylation of benzene, halobenzenes, pyridine, furan and thiophene has been accomplished through thermolysis of perfluoroalkyl iodides (CF_3I, n-$C_{10}F_{21}I$ and R_fOR_fI) in the presence of the appropriate aromatic compound. Yields of alkylated products vary depending on temperature, presence of an HI acceptor and reactants ratio. Isomeric mixtures are obtained with halobenzenes, pyridine and thiophene. Furan however yields only the alpha substituted product.

INTRODUCTION

In 1960, G.V.D. Tiers [1] described a general reaction for the direct introduction of a perfluoroalkyl group into benzene and other aromatic compounds. Perfluoroalkylation was accomplished by heating the R_fI in the presence of an aromatic substrate at 250°C (thermolysis reaction) in a closed vessel. Other investigators have extended the scope of this thermolysis reaction using a variety of aromatic compounds and perfluoroalkyl mono and di-iodides. It has been generally accepted that the thermolysis reaction generates perfluoroalkyl free radicals which are the reactive species in the alkylation of aromatic substrates. Alternate methods of generating the perfluoroalkyl free radicals by either photolysis, peroxides or other free radical initiators have also been reported [2].

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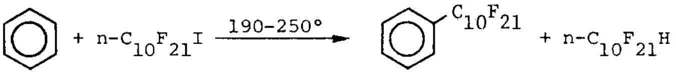
With the objective of extending the scope of the thermolysis reaction we have investigated R_fI compounds with aromatics under various experimental conditions. n-$C_{10}F_{21}I$ was used primarily since the products of reaction could easily be followed by gas chromatographic analysis. Other R_fI compounds were examined to a lesser extent and found to behave similarly to n-$C_{10}F_{21}I$.

RESULTS AND DISCUSSION

Perfluoroalkylation of Benzene

The perfluoroalkylation of benzene with n-$C_{10}F_{21}I$ proceeds readily at temperatures as low as 190°C yielding $C_6H_5C_{10}F_{21}$ and n-$C_{10}F_{21}H$ as the only major identifiable organic products. Analysis of the reaction mixture by gas chromatography however, indicated that other products were formed as well, though only in trace amounts. The distribution and yield of these products were found to depend on factors such as the benzene to iodide ratio,



the presence of base, reaction temperature, and even the construction of the reaction vessel (Table 1). In addition, a variable amount of insoluble black residue (mostly iodine and decomposition products) was also produced.

When benzene is present in a large excess, the yield of alkylated product obtained may be as great as 86%. In addition, 5-10% n-$C_{10}F_{21}H$ along with traces of the dialkylated product, $(C_{10}F_{21})_2C_6H_4$, are also produced. When benzene is not present in a large excess, lower yields of $PhC_{10}F_{21}$ and greatly increased amounts of n-$C_{10}F_{21}H$ are obtained. In this case, the addition of a base, such as sodium acetate [3] to the reaction mixture compensates for this and allows good yields of product to be maintained.

There are a number of advantages to performing the thermally induced reaction at 190°C as opposed to the 250°C which has been previously reported [1]. The yield of $PhC_{10}F_{21}$ is higher while the amounts of n-$C_{10}F_{21}H$ and (n-$C_{10}F_{21})_2Ph$ produced are lower. Also, at 190°C the addition of sodium acetate increases the yield of $PhC_{10}F_{21}$, while at 250°C it has no effect. Interestingly, the nature of the reaction vessel also exerted some influence on the course of the reaction. All other factors being equal, more n-$C_{10}F_{21}H$ was produced in reactions performed in glass tubes as opposed to stainless steel reaction vessels.

Also worth noting is that the presence of air appears to have little, if any, effect on the reaction. On the other hand, both copper (II), which is known to catalyze free radical arylations, and tertiary amines (such as NEt_3), which catalyze the free radical addition of perfluoroalkyl iodides to olefins, have a deleterious effect on the reaction [4,5].

TABLE 1

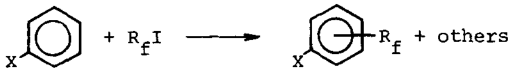
THERMAL PERFLUOROALKYLATION OF BENZENE WITH $n\text{-}C_{10}F_{21}I$

BENZENE/IODIDE (mole/ratio)	TEMPERATURE (°C)	TIME (h)	YIELD ($\%PhR_f^a$, R_fH^b)
165	110	168	0, 0
53	200	26	86, <10
32	200	36	77, <10
7	200	48	74, 10^c
1.6	190	60	70, 5^c
1.6	250	24	57, 37^c
13	200	22	75, $<10^d$
13	200	22	<10, $<10^e$
3	205	48	0^f

a. Isolated yield, b. yield estimated by GC, c. molar amount NaOAc added to the reaction mixture, d. reaction run in the presence of air, e. $CuCl_2$ and air added to the reaction mixture and f. NEt_3 added to reaction mixture.

Perfluoroalkylation of Halobenzenes

The alkylation of halobenzenes with perfluoroalkyl iodides has been previously reported by other investigators [3,7,8]. In addition, the isomeric composition of the product mixture obtained using CF_3I as the alkylating agent has also been determined [7,8].



X = F, Cl, Br, I $R_f = CF_3, n\text{-}C_3F_7, C_7F_{15}$

The results obtained in our study for the alkylation of halobenzenes with both $n\text{-}C_{10}F_{21}I$ and CF_3I are presented in Table 2. An examination of Table 2 also reveals a dramatic difference between the isomer distribution obtained with $n\text{-}C_{10}F_{21}I$ and CF_3I. Since the ratio of isomers produced with CF_3I is in good agreement with previously published data [7,8], the observed difference is most likely due to the nature of the radical, rather than some variance in the experimental parameters. The most straight forward explanation would be that the difference is due to steric hindrance - the large n-$C_{10}F_{21}$ radical has more difficulty attacking the ortho position than the smaller CF_3 radical. However, the fact that there is essentially no difference between the isomeric distribution from fluorobenzene (small X) to iodobenzene (very large X) makes it unlikely that this could be the entire explanation.

Perfluoroalkylation of Heterocyclic Compounds

The alkylation of nitrogen heterocycles depends greatly on whether they are activated towards electrophilic attack, such as pyrrole, or deactivated, such as pyridine. The alkylation of pyridine [9] with perfluoroalkyliodides has not been as intensively pursued as that of benzene. This is somewhat surprising since the results of our study indicate that pyridine may be alkylated as readily as benzene, in this case producing all three of the possible monosubstituted isomers (Table 3).

Though pyridine is readily alkylated by n-$C_{10}F_{21}I$, the reaction of n-$C_{10}F_{21}I$ with nitrogen heterocycles such as pyrrole, indole, and imidazole, which are activated towards electrophilic attack, yielded no alkylated product. However, in all cases the n-$C_{10}F_{21}I$ was consumed and large amounts of black tarry materials and n-$C_{10}F_{21}H$ were produced. This may indicate that under the conditions of the reaction, these heterocycles rapidly undergo polymerization which is perhaps initiated by the $C_{10}F_{21}$ radical.

In contrast to the reaction of n-$C_{10}F_{21}I$ with pyrrole described above, the reaction of n-$C_{10}F_{21}I$ with other 5-membered heterocycles such as furan and thiophene produced the desired alkylated products (Table 3).

The alkylation of furan with n-$C_{10}F_{21}I$ yields <u>only</u> the 2-isomer, while the alkylation of thiophene produces predominantly the 2-isomer (92%), thus providing a convenient and direct route for the preparation of 2-fluoroalkyl derivatives of these heterocycles. The high specificity for the 2-position is, however, surprizing since both halobenzenes and pyridine yield significant amounts of all the possible monosubstituted isomers. In addition to the alkylated product; n-$C_{10}F_{21}H$ and large amounts of insoluble black residues are also produced. Both furan and thiophene were more reactive towards n-$C_{10}F_{21}I$ than benzene, which might consequently lead to greater susceptibility to other side reactions and account for the lower yields of alkylated product as compared to benzene or pyridine.

TABLE 2

PERFLUOROALKYLATION OF C_6H_5X WITH $n\text{-}C_{10}F_{21}I$ AND CF_3I^a

X	R_fI	PhX/R_fI (mole ratio)	TIME (h)	TEMP (°C)	% ISOMER COMPOSITION			YIELD
					O	M	P	
F	$n\text{-}C_{10}F_{21}I$	14	40	210	19	48	33	63^b
Cl	$n\text{-}C_{10}F_{21}I$	12	40	210	14	47	39	43^b
Cl	$n\text{-}C_{10}F_{21}I$	12	72	210	18	44	37	79^b
Cl	CF_3I	4	48	190	52	25	23	27^c
Br	$n\text{-}C_{10}F_{21}I$	25	27	210	8	54	38	79^b
Br	$n\text{-}C_{10}F_{21}I$	1.6	60	188	--	--	--	55^b
Br	$n\text{-}C_{10}F_{21}I$	25	60	185	10	49	41	65^b
Br	CF_3I	4	48	190	48	30	22	61^c
I	$n\text{-}C_{10}F_{21}I$	12	24	210	13	49	38	50^b

a. Method, thermal decomposition of R_fI in steel tubes with added NaOAc, b. isolated yield, isomeric composition determined via GC, c. yield determined by GC using an internal standard.

TABLE 3

PERFLUOROALKYLATION OF HETEROCYCLIC COMPOUNDS WITH $n\text{-}C_{10}F_{21}I$

AROMATIC	AROMATIC $n\text{-}C_{10}F_{21}I$ (mole ratio)	TEMP (°C)	TIME (h)	ISOMER COMPOSITION (%)^a			YIELD (isolated)
				2	3	4	
Furan	18	175	42	100	--	--	39
Furan	18	180	4	100	--	--	48
Furan	9	190	24	100	--	--	58
Thiophene	16	185	40	--	--	--	34
Thiophene	8	175	24	92	8	--	32
Pyridine	32	210	20	47	43	10	58
Pyridine	61	200	20	--	--	--	51
Pyridine	25	200	26	51	40	9	65
Pyridine	2	188	60	--	--	--	44

a. Isomer composition determined by GC.

Perfluoroalkylation With Other Iodides

In addition to n-$C_{10}F_{21}I$, a number of reactions were performed with other iodides as well (Table 4). Perfluoroalkylether iodides (R_fOR_fI) had essentially the same reactivity as n-$C_{10}F_{21}I$. Iodopentafluorobenzene (C_6F_5I) is unreactive under conditions which give good yields of alkylated product using n-$C_{10}F_{21}I$. The diiodide, $I(CF_2)_2O(CF_2)_5O(CF_2)_2I$, produced the disubstituted compound $C_6H_5(CF_2)_2O(CF_2)_5O(CF_2)_2C_6H_5$ as the principal product. Some of the monosubstituted compound $C_6H_5(CF_2)_2O(CF_2)_5O(CF_2)_2H$ (GC/MS analysis) was also formed in minor quantity.

TABLE 4

PERFLUOROALKYLATION OF BENZENE WITH OTHER R_fI

IODIDE	BENZENE/IODIDE (mole ratio)	OTHER	TIME (h)	TEMP (°C)	YIELD[a] (%)
$(CF_3)_2CFOCF_2CF_2I$	4	--	40	210	55
$C_3F_7O(CF(CF_3)CF_2O)_2C_2F_4I$	20	NaOAc	24	184	73
$IC_2F_4O(CF_2)_5OC_2F_4I$	60	--	25	200	68[b]
C_6F_5I	3	--	72	210	no reaction

a. Isolated yield, b. Product is $C_6H_5(CF_2)_2O(CF_2)_5O(CF_2)_2C_6H_5$.

EXPERIMENTAL

Large scale reactions (those greater than 30 ml of reactants) were performed in a stainless steel (316 SS) high pressure reactor (Parr Instrument Co.). Smaller scale reactions were generally performed in stainless steel (304 SS) tubes fitted with Swagelok caps at both ends. In a few cases, the reactions were performed in sealed glass ampules. No attempt was made to trap any volatile components which might have been formed in the reaction. Generally, no release of pressure was observed when the vessels were opened.

The crude reaction mixtures were analyzed by GC/MS analysis (1/4" x 6' 10% SE-30 or 1/4" x 12' 10% Carbowax 20M). In the case of substrates which gave mixtures of ortho, metal, and para isomers; when using n-$C_{10}F_{21}I$, total yield was that of isolated product while the isomeric composition was determined by GC. With CF_3I, both total yield and the isomeric composition were determined by GC analysis since $CF_3C_6H_4X$ and C_6H_5X (X=Cl,Br) are not readily separable. The procedure used for the identification of the isomers of $CF_3C_6H_4Cl$ and $CF_3C_6H_4Br$, which has been previously reported [7] was based on a comparison of GC retention times of the peaks in the isomeric mixture to those of authentic samples.

The isomers of n-$C_{10}F_{21}C_6H_4Cl$ were identified by independent synthesis, via a copper coupling reaction [10] of IC_6H_4Cl and n-$C_{10}F_{21}I$, of the meta and para isomers, followed by a comparison of GC retention times. The ortho isomer was identified by difference. (All of the GC and GC/IR work [see below] carried out with the isomers of $C_{10}F_{21}C_6H_4X$ was performed on a 1/4" x 12' 10% Carbowax 20M column). The isomers were further confirmed by GC/IR analysis. All assignments were consistent with reported literature values [11, 12] for ortho, meta and para isomers. (See Table 6). The isomers of n-$C_{10}F_{21}C_6H_4Br$ were identified by GC/IR analysis of the isomeric mixture and shown to elute in the same order as the those of n-$C_{10}F_{21}C_6H_4Cl$: that is meta, para, and finally ortho. The isomers of n-$C_{10}F_{21}C_6H_4F$ and n-$C_{10}F_{21}C_6H_4I$ were identified assuming a similar order of elution to the isomers of their chloro and bromo analogs.

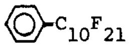
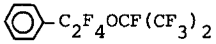
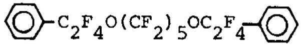
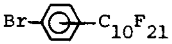
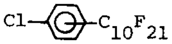
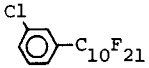
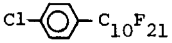
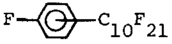
The isomers obtained from the alkylation of pyridine ($C_5H_4NC_{10}F_{21}$), furan ($C_4H_3OC_{10}F_{21}$), and thiophene ($C_4H_3SC_{10}F_{21}$) via n-$C_{10}F_{21}I$ were identified by GC/IR analysis. In each case, the IR spectrum obtained from each peak eluting from the GC column allowed the identification of the specific isomer by comparison with both literature values and the spectra of model compounds. (See Table 6).

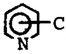
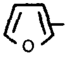
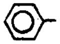
Alkylation of Benzene with n-$C_{10}F_{21}I$ and other Iodides

General Procedure: Into a stainless steel bomb (316 SS) equipped with Swagelok caps were placed n-$C_{10}F_{21}I$, benzene, and in some cases a molar amount of sodium acetate. After being sealed the vessel was then brought to the desired reaction temperature (for specific experimental details see Tables 1 and 4). At the end of the given length of time, the vessel was allowed to cool to room temperature, opened, and the contents poured into a separatory funnel. The vessel was then rinsed several times with diethyl ether and the extracts also placed in the separatory funnel. The diethyl ether solution was then analyzed via GC (6' x 1/4", 10% SE-30, 60-250° at 10°/min) to determine both the amount of n-$C_{10}F_{21}I$ remaining (if any) and the amount of n-$C_{10}F_{21}H$ and $PhC_{10}F_{21}$ produced in the reaction. The organic layer was then washed with solutions of sodium bisulfite, and sodium bicarbonate, water, and then a saturated sodium chloride solution, and finally it was dried over magnesium sulfate. After removal of the solvents, the residue was dried in vacuo, and then recrystallized from ethanol yielding $PhC_{10}F_{21}$ a white microcrystalline solid (see Table 5 for analyses). In a typical experiment benzene (30 ml) and n-$C_{10}F_{21}I$ (10.0 g, 15.5 mmole) yielded $PhC_{10}F_{21}$ (7.05 g, 11.8 mmole, 77%).

TABLE 5

ANALYTICAL DATA FOR ALKYLATED PRODUCTS[d]

COMPOUND	YIELD (%)	mp(b.p)°C	MS calc found	IR(cm^{-1})	COMBUSTION ANALYSIS C calc found	H calc found
	77	44-45	596 596	3080, 3050 (ArH) 1610, 1500, 1455 (C=C) 1300-1100 (C-F) 760, 700 (ArH)	32.21 32.24	0.84 0.48
	55	157-158	362 362	3090, 3060 (ArH) 1570, 1550, 1460 (C=C) 1300-1100 (C-F) 770, 700 (ArH)	36.46 36.50	1.38 1.22
	68	(140°/20mm)	636 636	3070, 3040 (ArH) 1600, 1500, 1450 (C=C) 1300-1100 (C-F) 760, 690 (ArH)	39.62 39.62	1.57 1.27
	79[a]	52-57	674,676[b] 674,676	3090 (ArH) 1300-1100 (C-F)	28.40 28.30	0.59 0.20
	79[a]	45-47	630[b] 630	3090 (ArH) 1300-1100 (C-F)	30.48 30.74	0.63 0.76
	55	63-64	630 630	3090 (ArH) 1300-1100 (C=C)	30.48 30.43	0.63 0.40
	87	56-57	630 630	3090 (ArH) 1300-1100 (C-F)	30.48 30.33	0.63 0.33
	63[a]	41-43	614[b] 614	3100 (ArH) 1300-1100 (C-F) 890, 850, 770 (ArH)	31.27 31.33	0.65 0.68

I$C_{10}F_{21}$	50[a]	60-64	722[b] 772	3100 (ArH) 1300-1100 (C-F)	26.59 26.47	0.55 0.45
$C_{10}F_{21}$	58[a]	58-63	598[b] 598	3070, (ArH) 1300-1100 (C-F)	30.10 30.14	0.67 0.34
$C_{10}F_{21}$	34[a]	30-31	602[c] 602	3130 (ArH) 1300-1100 (C-F)	27.91 27.80	0.50 0.58
$C_{10}F_{21}$	48	(221-223)	586 586	3160 (ArH) 1300-1100 (C-F)	28.87 29.06	0.52 0.26
$C_2F_4[OCF_2(CF_3)CF]_2OC_3F_7$	73	(66-68/0.05mm)	694 694	3000-3100 (ArH) 1600, 1500, 1450 (C=C) 1300-1100 (C-F) 750, 690 (ArH)	29.39 29.41	0.72 0.62

a. Yield and analyses based on the isomeric mixtures, b. GC/MS gives three peaks each with the calculated M/e, c. GC/MS gives two peaks each with the calculated M/e, d. all new compounds.

TABLE 6

ASSIGNMENT OF ISOMERS FROM THE ALKYLATION OF AROMATIC COMPOUNDS WITH $n\text{-}C_{10}F_{21}I^{a}$

COMPOUND	ABSORBANCE (CM^{-1})					
	AROMATIC C-C STRETCH				AROMATIC C-H BEND	
$\underline{o}\text{-}BrC_6H_4C_{10}F_{21}$	--	--	1474	1439	756	
$\underline{o}\text{-}ClC_6H_4C_{10}F_{21}$	1597	1580	1478	1443	760	
Reported for ortho isomer	1607±9	1577±4	1510-1460	1447±10	751+7	
$\underline{m}\text{-}BrC_6H_4C_{10}F_{21}$	--	1578	1478	1424	787	
$\underline{m}\text{-}ClC_6H_4C_{10}F_{21}$	1600	1582	1482	1428	791	
Reported for meta isomer	1600-1620	1586±5	1495-1470	1465-1431	782±9	
$p\text{-}BrC_6H_4C_{10}F_{21}$	1597	--	1493	1401	826	
$p\text{-}ClC_6H_4C_{10}F_{21}$	1605	1580	1497	1408	830	
Reported for para isomer	1606±6	1579±6	1520-1480	1409±8	817±13	
$2\text{-}C_5H_4NC_{10}F_{21}$	1590	1474	1439		745	
Reported for 2-isomer	1590	1475	1440		750	
$3\text{-}C_5H_4NC_{10}F_{21}$	1593	1486	1428		779	714
Reported for 3-isomer	1590	1480	1425		790	720
$4\text{-}C_5H_4NC_{10}F_{21}$	1597	--	1412		818	737
Reported for 4-isomer	1600	1500	1420		795	725
$2\text{-}C_4H_3OC_{10}F_{21}$	1593	1501	1393		749	
Reported for 2-isomer	1605-1570	1510-1475	1400-1380		727	
$2\text{-}C_4H_3SC_{10}F_{21}$	1532	1431	1354		710	
Reported for 2-isomer	1534-1515	1454-1430	1361-1347		690	
$3\text{-}C_4H_3SC_{10}F_{21}$	1539	1416	1362		733	
Reported for 3-isomer	1530	1410	1370		758	

a. Frequencies used for comparison were taken from Ref. 11, spectra for comparison from Ref. 12.

Alkylation of Halobenzenes with n-$C_{10}F_{21}I$

The alkylation of halobenzenes via n-$C_{10}F_{21}I$ was performed as described above for the alkylation of benzene (for experimental details see Table 2). In this case however, the product obtained as a white powder, consisted of a mixture of ortho, meta, and para isomers. The isomers could be separated and relative ratios obtained via GC analysis (12' x 1/4", 10% Carbowax 20M, at 110° ($FC_6H_4R_f$), 145° ($ClC_6H_4R_f$), 160° ($BrC_6H_4R_f$), and 180° ($IC_6H_4R_f$). Identification was accomplished via GC/IR, see Table 6. For example, from bromobenzene (20.0 ml, 29.9 g, 190 mmole) and n-$C_{10}F_{21}I$ (5.00 g, 7.75 mmole) was obtained a mixture of ortho, meta and para-$BrC_6H_4C_{10}F_{21}$ (4.12 g, 6.10 mmole, 79%) (for analyses see Tables 5 and 6).

Reaction of Chloroiodobenzenes with n-$C_{10}F_{21}I$

The procedure used to couple meta- and para- ClC_6H_4I with n-$C_{10}F_{21}I$ was adapted from literature [10]. Into a four-necked flask equipped with gas inlet and outlet tubes, a thermometer, and a rubber serum cap were added ClC_6H_4I (0.476 g, 2.00 mmole), n-$C_{10}F_{21}I$ (1.29 g, 2.00 mmole), and copper bronze (0.252 g, 4.00 mmole). The flask was purged with nitrogen and deoxygenated DMSO (15 ml) was added via syringe. The contents of the flask were then heated to 130°C and the mixture was stirred overnight under nitrogen. At the end of this time, the mixture was allowed to cool to room temperature, and diethyl ether (100 ml) was added. The extract was then filtered, washed several times with water, and finally dried over magnesium sulfate. Removal of the solvent afforded a solid which was recrystallized from ethanol yielding $ClC_6H_4C_{10}F_{21}$ as a semi-crystalline white solid. From the above mixture using meta-ClC_6H_4I was obtained meta-$ClC_6H_4C_{10}F_{21}$ (0.700 g, 1.11 mmole, 55%). Use of the para isomer gave para-$ClC_6H_4C_{10}F_{21}$ (1.10 g, 1.75 mmole, 87%) (see Table 5 and 6 for analyses).

Alkylation of Heteroaromatics with n-$C_{10}F_{21}I$

The alkylation of pyridine, furan, and thiophene by n-$C_{10}F_{21}I$ was carried out as described above for the alkylation of benzene (see Tables 3, 5 and 6). Pyridine: The crude product was distilled followed by recrystallization from hexane yielding a white solid. For example, from pyridine (20.0 ml, 19.6 g, 248 mole) and n-$C_{10}F_{21}I$ (5.00 g, 7.75 mmole) was obtained $C_5H_4NC_{10}F_{21}$ (2.66 g, 4.45 mmole, 58%). Furan and Thiophene: In both cases, the crude product was purified by distillation. For example, from furan (20.0 ml, 18.7 g, 275 mmole) and n-$C_{10}F_{21}I$ (10.0 g, 15.5 mmole) was obtained $C_4H_3OC_{10}F_{21}$ (4.40 g, 7.51 mmole, 48%) as a clear liquid. From thiophene (20.0 ml, 21.2 g, 252 mmole) and n-$C_{10}F_{21}I$ (10.0 g, 15.5 mmole) was obtained $C_4H_3SC_{10}F_{21}$ (3.20 g, 5.32 mmole, 34%) as a white semisolid. In both cases analytical samples were obtained by passage through a silica gel column (6") eluted with hexane. Analytical data for $C_5H_4NC_{10}F_{21}$, $C_4H_3OC_{10}F_{21}$, and $C_4H_3SC_{10}F_{21}$ are presented in Tables 5 and 6.

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