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Short Communication

Polyphenyl fluorides

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Studies related to the chemistry of aromatic fluorine compounds have been carried out at the Illinois State Geological Survey since 1933. In our reference collection we have several compounds that have not previously been described. This communication records data on 18 biphenyl, three terphenyl and some benzene fluorinated derivatives that were obtained as by-products and/or by specific synthesis.

The accumulated by-product residues from many Balz–Schiemann[1,2] aryl fluoride syntheses proved to be a valuable source of polyphenyl fluorides. Although the amount and composition of the residues vary considerably among syntheses, the polyphenyl yield is usually about 5–10%.

Various direct syntheses were used to prepare authentic samples of polyphenyl fluoro derivatives for structural proof and for identification purposes. The pure compounds were used to prepare standard mixtures for ^{19}F NMR, infrared and mixed melting point determinations.

Table 1 lists the compounds studied, their physical constants, methods of preparation, reaction conditions and the purification procedure. Data on the pertinent intermediates are also included.

Experimental

Because by-product residues and small-scale syntheses were used, yield data are not reported. Melting and boiling points are uncorrected. Freezing points were determined with a toluene thermometer. Solid products were vacuum sublimed after recrystallization.

Identities of the individual compounds were established by elemental analysis and ^{19}F NMR and/or infrared spectra determinations.

Details of the modifications used for the diazotization of the anilines and for the diazonium group replacement by fluorine and iodine can be found in ref. 2.

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TABLE I POLYPHENYL FLUORIDES

		Synthesis			Aryl intermediate				Synthesis of intermediate		Analysis Calculated values ( )		
Ring substitution	M.p. °C	Method[a]	Time/temp. h/°C	Solvent[b]	Benzene derivative	B.p. °C/mm	Lit. ref.	Method[a]	Benzene intermediate	Lit. ref.	C	H	F
BIPHENYL													
($C_{12}H_3F_7$)											(51.45	1.08	47.47)
2,2',3,4',5,5',6F_7 *	123.5	A	0.5/85	1	1,2,4,5F_4	--	3	--	--	--	51.15	1.35	--
($C_{12}H_4F_6$)											(54.98	1.54	43.48)
2,2',4,4',5,5'F_6 *	120.5	B	3/210-250	2	2,4,5F_3-I	--	4	--	--	--	55.06	1.51	43.46
2,2',4,4',6,6'F_6 *	130.0	B	2/200	2	2,4,6F_3-I	--	--	--	--	--	55.13	1.55	--
					($C_6H_2F_3I$)						(27.94	0.78	22.09)
					2,4,6F_3-I *	165.0[c]	--	C	2,4,6F_3-NH_2	5	28.10	0.80	21.94
($C_{12}H_5F_5$)											(59.03	2.06	38.91)
2,2',4,5,5'F_5 *	100.0	D	--	2,3	2,5F_2-NH_2	--	6	--	--	--	59.08	2.24	39.16
	102.0[d]	E	--	2,3	2,4,5F_3-NH_2	--	3	--	--	--	--	--	--
					1,4F_2	--	7	--	--	--	--	--	--
2,3',4,5',6F_5 *	96.0	D	--	2	3,5F_2-NH_2	--	5	--	--	--	59.00	2.02	39.13
($C_{12}H_6F_2N_2O_4$)											(51.44	2.16	N,9.99)
2,2'(NO_2)$_2$5,5'F_2 *	121.0	B	2/170-200	2	2(NO_2)5F-I	--	--	--	--	--	51.74	1.99	N,10.00
					($C_6H_3FINO_2$)						(26.99	1.13	N,5.24)
					2(NO_2)5F-I *	148/20[e]	--	C	2(NO_2)5F-NH_2	8	27.19	1.12	N,5.06
($C_{12}H_6F_4$)											(63.73	2.67	33.60)
2,2',4,4'F_4 *	137.0	B	4/150-230	2	2,4F_2-I	--	9	--	--	--	63.88	2.75	--
2,2',5,5'F_4 *	78.5	B	0.25/180	2	2,5F_2-I	--	9	--	--	--	63.94	2.69	33.30
3,3',5,5'F_4 *	85.5	B	4/150-250	2	3,5F_2-I	--	9	--	--	--	63.59	2.67	--
($C_{12}H_7F_3$)											(69.23	3.39	27.38)
2,3',4F_3 *	40.0	D	--	2	3F-NH_2	--	10	--	--	--	69.28	3.45	27.30
2,2',3F_3 *	80.0	D	--	4	2F-NH_2	--	7	--	--	--	69.46	3.41	27.24
2,4',5F_3 *	51.0	D	--	2	4F-NH_2	--	10	--	--	--	--	--	--
	50.5[d,f]	E	--	2	4F-NH_2	--	10	--	--	--	69.45	3.57	27.12
					1,4F_2	--	7	--	--	--	--	--	--

$(C_{12}H_8F_2)$													
$2,4'F_2$*	49.5	B	1/200-250	2	2F-I	--	11	--	--	--	75.99	4.41	--
					4F-I	--	15	--	--	--	--	--	--
$(C_{14}H_{12}F_2O_2)$											(67.20	4.83	15.18)
$4,4'(OCH_3)_23,3'F_2$*	153.5	B	6/190-215	2	$4(OCH_3)3F$-I	--	2	--	--	--	67.08	4.63	15.00
$2,2'(OCH_3)_25,5'F_2$*	121.0	B	3.5/190-210	2	$2(OCH_3)5F$-I	--	2	--	--	--	67.25	4.63	14.97
$(C_{14}H_6F_8)$											(51.55	1.85	46.60)
$2,2'(CF_3)_24,4'F_2$*	61.5	B	1.5/250	2	$2(CF_3)4F$-I	--	--	--	--	--	51.35	1.85	--
					$(C_7H_3F_4I)$						(28.99)	1.04	I,43.76)
					$2(CF_3)4F$-I*	83/25[g]	--	C	$2(CF_3)4F-NH_2$	12	28.98	1.30	I,43.58
$(C_{14}H_{10}F_4O_2)$											(58.75	3.52	26.55
$2,2'(OCH_3)_23,3',5,5'F_4$*	49.5	B	3/200-210	2	$2(OCH_3)3,5F_2$-I	--	--	--	--	--	58.84	3.38	26.35
					$(C_7H_5F_2IO)$						(31.14	1.87	14.07)
					$2(OCH_3)3,5F_2$-I*	60/3[h]	--	C	$2(OCH_3)3,5F_2-NH_2$	--	31.31	1.81	14.28
					$(C_7H_7F_2NO)$						(52.83	4.43	N,8.80)
					$2(OCH_3)3,5F_2-NH_2$*	104/22[i]	--	F	$2(OCH_3)3,5F_2-NO_2$	13	52.95	4.43	N,8.88
$(C_{18}H_{18}F_4)$											(69.67	5.85	24.48)
$2,2',4,4',6,6'(CH_3)_63,3',5,5'F_4$*	161	B	4/170-220	2	$2,4,6(CH_3)_33,5F_2$-I	--	--	--	--	--	69.90	5.63	--
					$(C_9H_9F_2I)$						(38.32	3.22	13.47)
					$2,4,6(CH_3)_33,5F_2$-I*	64[j]	--	C	$2,4,6(CH_3)_33,5F_2-NH_2$	14	38.31	3.19	--
p-TERPHENYL													
$(C_{18}H_{13}F)$											(87.07	5.28	7.65)
2F*	173.5	B	2/220-270	2	2F-I	--	11	--	--	--	87.33	5.10	--
					4-Iodobiphenyl	--	--	--	--	--	--	--	--
3F*	174.0	B	3/210-275	2	3F-I	--	11	--	--	--	86.99	5.24	--
					4-Iodobiphenyl	--	--	--	--	--	--	--	--
4F*	160.0	B	3.5/200-230	2	4F-I	--	15	--	--	--	86.95	5.41	7.85
					4-Iodobiphenyl	--	--	--	--	--	--	--	--

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[a] Methods: (A) Modified Friedel-Craft reaction using $AlCl_3$ and ethyl bromide (B) Ullmann Reaction using copper bronze (C) Sandmeyer Reaction (D) Balz-Schiemann Reaction (E) Gomberg-Bachman-Hey Reaction (F) Reduction with iron-ammonium chloride.

[b] Recrystallization solvents: (1) petroleum ether b.p. 90-110° (2) ethanol (3) petroleum ether b.p. 30-60° (4) benzene (5) carbon tetrachloride.

[c] F.p. 28°

[d] No depression in m.p. with Schiemann product.

[e] n_D^{20} 1.6223.

[f] B.p. 87°/0.5 mm.

[g] B.p. 175° (micro. cap); f.p. 17°; n_D^{20} 1.5100.

[h] n_D^{20} 1.5493.

[i] Acetyl derivative m.p. 78° (N,6.96); N,6.89.

[j] M.p.

* New compound.

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