New activated bisfluoroaromatic compounds

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Bis(*p*-fluorophenylethynyl) derivatives were obtained by the reaction of bisbromoaromatic compounds with *p*-fluorophenylacetylene in the presence of a Pd catalyst. Subsequent oxidation of these products using an I_2—DMSO system led to new bis(*p*-fluorophenylglyoxalyl)ketones, α-diketones, and heterocyclic compounds.

Key words: bisbromoaromatic compounds, *p*-fluorophenylacetylene, bisfluoroaromatic compounds, bis(*p*-fluorophenylethynyl) ketones, diazines, and imidazoles, cross-coupling reactions, bis(*p*-fluorophenylglyoxalyl) ketones, diazines, and imidazoles.

Bisfluoroaromatic compounds with activating electron-withdrawing groups at the *para*-positions with respect to the fluorine atoms are used for the preparation of aromatic polyethers.[1,2] In recent years, along with sulfonyl[2] and carbonyl[1,3,4] groups, ethynyl[5], quinoxaline[4—6] and other heterocyclic fragments[7] have come into use as activating electron-withdrawing groups.

In most cases, activated bisfluoroaromatic compounds are not easily available, which limits their practical application. In this connection, the preparation of activated bisfluoroaromatic compounds based on available products is of interest. In the present work, a series of compounds of this type based on chloral, a cheap starting reagent that is used, for example, for the preparation of condensation polymers,[8,9] was synthesized.

A reaction scheme based on 4,4'-dibromobenzophenone and 4,4'-dibromobenzyl[8,9] was chosen for the synthesis of the new bisfluoroaromatic compounds (Scheme 1). This involves: 1) transformation of α-diketone into quinoxaline, 6-carboxyquinoxaline, 2-phenylimidazole,[10] and 2,3-dicyanopyrazine derivatives; 2) interaction of bisbromoaromatic compounds with *p*-fluorophenylacetylene in the presence of a Pd catalyst (cross-coupling);[11] and 3) oxidation of the thus obtained bis(*p*-fluorophenylethynyl) compounds into bis(*p*-fluorophenylglyoxalyl) compounds.

The transformation of α-diketone into heterocycles occurs in yields close to quantitative, and leads to bisbromoaromatic compounds **2** of high purity.[10]

Cross-coupling reactions substantially depend on the ratio of the initial reagents, the catalyst, and solvents. The optimal molar ratio of dihalide, *p*-fluorophenylacetylene, and catalyst is 100 : 200 : 2.5, and the optimum solvent-to-base ratio is 1 : 1 (v/v). However, it is worth noting that the nature of the central groups in the bisbromoaromatic compounds exerts the largest effect on the rate and completeness of the cross-coupling reactions. Carbonyl groups are effective activators, and accordingly the cross-coupling reactions of **1a,b** are high-yielding (Table 1). Heterocyclic bridges are much less effective as activators of bromine atoms,[12] which results in a marked decrease in the yields of the target bis(fluorine-containing) compounds **3c—f**. The structures of compounds **3a—f** synthesized were confirmed by data from elemental analysis and Raman spectra.

An I_2—DMSO[13] system was used for oxidation of compounds **3a—f** into the corresponding bis(*p*-fluorophenylglyoxalyl) derivatives (**4a—f**). This system compares favorably with $KMnO_4$, due, in particular, to the mild reaction conditions. The reaction proceeds smoothly at 155 °C and is not accompanied by iodination or oxidation of the phenyl rings of substrates. The structures of the oxidation products were confirmed by the data from elemental analysis and IR spectroscopy.

The use of compounds **3a—f** and **4a—c,e** in the synthesis of aromatic polyethers provides a way to try some promising approaches. Thus, the introduction of arylethynyl fragments in polyethers allows the formation of liquid-crystalline domains in polymers and makes their cross-linking possible at high temperatures.

The use of compounds **4a—c,e** as monomers makes it possible to obtain polyethers containing α-diketone groups, which can be further transformed into the corresponding heterocycles (see Scheme 1) to give polyheteroarylenes, whose direct synthesis appears to be rather problematic.

Experimental

The starting substances and solvents were purified according to known procedures. Raman spectra were obtained on a U-1000 spectrometer with excitation by the 5145 Å line of an

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Scheme 1

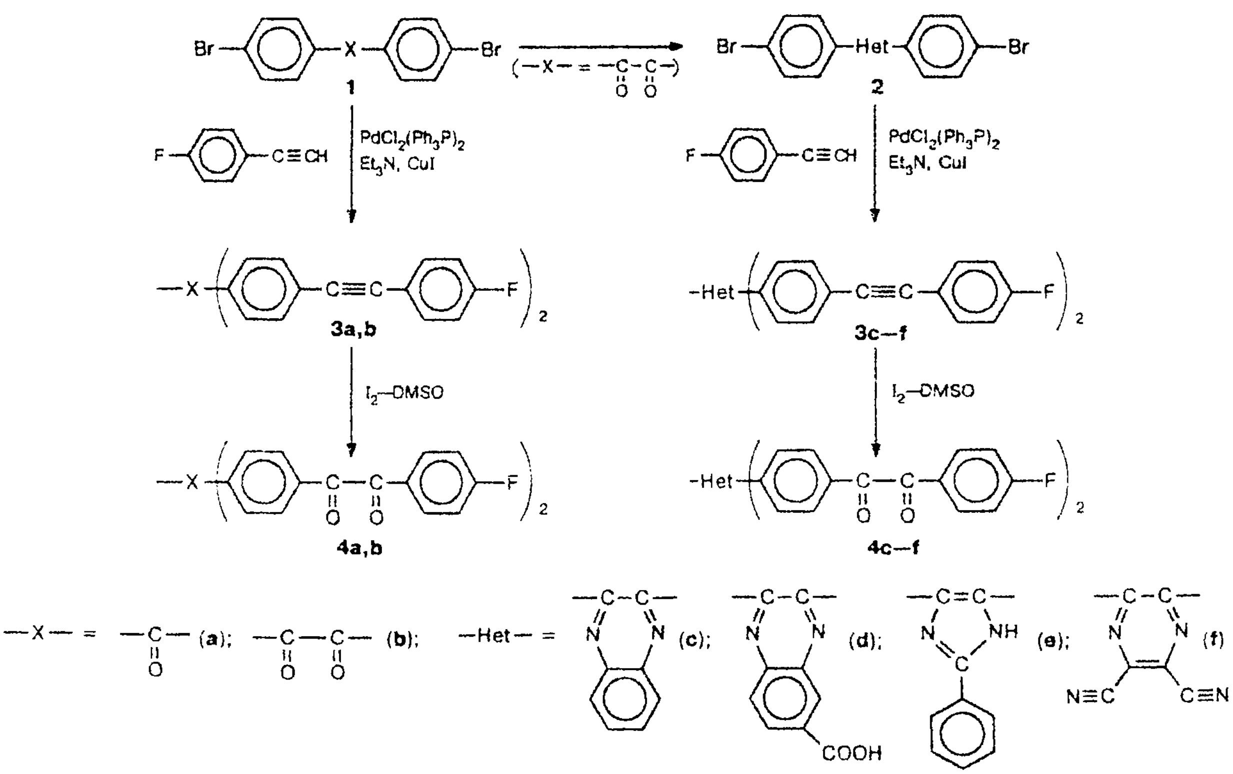
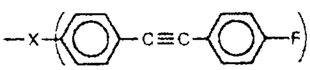


Table 1. The characteristics of compounds  (3a—f)

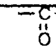
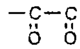
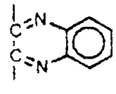
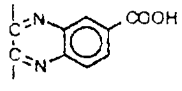
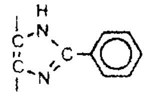
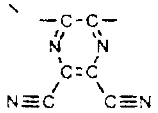
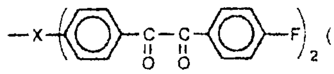
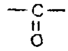
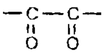
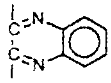
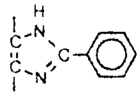
Compound	—X—	Yield (%)	M.p. /°C	Raman spectra, $\nu(C{\equiv}C)/cm^{-1}$	Found/Calculated (%)				Molecular formula
					C	H	N	F	
3a	 $-\underset{\overset{\Vert}{O}}{C}-$	93	267—269	2218	82.94 83.24	3.68 3.82		8.98 9.08	$C_{29}H_{16}F_2O$
3b	 $-\underset{\overset{\Vert}{O}}{C}-\underset{\overset{\Vert}{O}}{C}-$	83	226—228	2214	80.03 80.70	3.48 3.61		8.48 8.51	$C_{30}H_{16}F_2O_2$
3c		42	215—216	2221	83.33 83.38	4.06 3.88	5.26 5.40	6.51 6.64	$C_{36}H_{20}F_2N_2$
3d		39	282—283	2219	79.17 78.99	3.48 3.58	4.84 4.98	6.84 6.75	$C_{37}H_{21}F_2N_2O_2$
3e		31	295—296	2220	83.71 83.43	3.91 4.16	4.98 5.26	7.09 7.13	$C_{37}H_{22}F_2N_2$
3f		32	237—239	2217	78.55 78.75	3.03 3.11	10.01 10.80	7.18 7.32	$C_{34}H_{16}F_2N_4$

Table 2. The characteristics of compounds  (**4a—c,e**)

Com-pound	—X—	Yield (%)	M.p. /°C	Found/Calculated (%) C	H	N	F	Molecular formula
4a	 $-\overset{\overset{}{}}{\underset{\|\|}{C}}-$ (C=O)	87	183—184	72.01 72.19	3.61 3.31		7.73 7.88	$C_{29}H_{16}F_2O_5$
4b	 $-C(=O)-C(=O)-$	89	217—218	70.46 70.58	3.09 3.16		7.31 7.44	$C_{30}H_{16}F_2O_6$
4c		89	228—230	74.4 74.21	3.34 3.46	4.61 4.80	6.46 6.52	$C_{36}H_{20}F_2N_2O_4$
4e		71	195—196	73.85 74.48	3.80 3.71	4.48 4.69	6.21 6.36	$C_{37}H_{22}F_2N_2O_4$

Ar$^+$-laser ILA-2 (100 mW). IR spectra were recorded on a UR-20 instrument (Vaseline oil).

4,4'-Bis(4-fluorophenylethynyl)benzophenone (3a). *p*-Fluorophenylacetylene (2.4 g, 20 mmol), triphenylphosphine (0.066 g, 0.25 mmol), and copper iodide (0.067 g, 0.35 mmol) were added under argon to a solution of bromide **1a** (3.68 g, 10 mmol) in 160 mL of a mixture of dimethylacetamide and triethylamine (1 : 1) and stirred for 15 min. Bis(triphenylphosphine)palladium dichloride (0.07 g, 0.1 mmol) was added, and the reaction mixture was heated at 80 °C for 10 h (TLC monitoring) and then cooled to -20 °C. The precipitate that formed was filtered off, washed with 10% HCl and water to neutral pH, and dried *in vacuo* at 100 °C. Compound **3a** (3.89 g, 93%) was obtained, m.p. 267—269 °C. Compounds **3b—f** were obtained analogously. Their characteristics are given in Table 1.

4,4'-Bis(4-fluorophenylglyoxalyl)benzophenone (4a). I_2 (2.54 g, 10 mmol) was added to a solution of compound **3a** (2.09 g, 5 mmol) in 50 mL of DMSO. The reaction mixture was stirred at 155 °C for 22 h, then cooled to -20 °C, and poured into 500 mL of water. The precipitate was filtered off, washed with a 1% $Na_2S_2O_3$ solution and ethanol, and dried *in vacuo* at 100 °C. Compound **4a** (2.10 g, 87%) was obtained, m.p. 183—184 °C. Compounds **4b,c,e** were obtained analogously. Their characteristics are given in Table 2.

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