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Journal of Fluorine Chemistry 127 (2006) 1601–1605
JOURNAL OF FLUORINE CHEMISTRY
www.elsevier.com/locate/fluor

Short communication

Synthesis of fluorinated first generation starburst molecules containing a triethanolamine core and 1,2,4-oxadiazoles

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Received 27 June 2006; received in revised form 21 July 2006; accepted 21 July 2006
Available online 27 July 2006

Abstract

5-Pentafluorophenyl-1,2,4-oxadiazoles, differently substituted at C(3), have been synthesized and used to functionalize the aliphatic primary hydroxyl functionalities of triethanolamine, under mild conditions. UV–visible absorption and emission spectra are reported, for both tri- and difunctionalised molecules, showing their potential applications as light-emitters in optoelectronic devices.

Keywords: 1,2,4-Oxadiazoles; Starburst molecules; Fluoroarylation; PL spectra

1. Introduction

Electroluminescent (EL) devices based on organic thin layers have attracted much attention because of the potential application to large-area flat-panel displays and light-emitting diodes (LEDs) [1]. Considerable progress has been made on organic LEDs (OLEDs) using both low molecular weight organic materials and polymers. 1,3,4-Oxadiazole, 1,2,4-triazole, benzimidazole, benzothiazole benzothiadiazole, and several other heterocycles-based molecules and polymers are the most widely investigated emitting materials for OLEDs [2a].

Despite this wide use of electron-poor azoles, particularly 1,3,4-oxadiazoles, in electroluminescent organic materials [2], only one example of the use of 1,2,4-oxadiazoles in organic luminous devices is reported [3]. In this patent, Taguchi discussed the importance of 1,2,4-oxadiazoles as electron transporting material (ETM) and remarked the need of the presence of fluorine atoms to improve the stability and the electron transport capability [3]. In addition, amorphous materials, such as starburst molecules, have been highly employed for electroluminescence applications [2,4]. On these basis and in the mainframe of our studies on the synthesis and reactivity of oxadiazoles and their fluorinated derivatives [5], we decided to explore the possibility to functionalize a branched core molecule with fluorinated 1,2,4-oxadiazoles in order to obtain first generation starburst molecules as potential luminous materials.

2. Results and discussion

We previously reported that 3-amino-5-pentafluorophenyl-1,2,4-oxadiazoles easily undergo a classic nucleophilic aromatic substitution (with methanol or aliphatic amines) of the 4′-fluoro moiety under mild experimental conditions [5e]. To take advantage of such reactivity, we synthesized a series of 3-substituted-5-pentafluorophenyl-1,2,4-oxadiazoles to be used in the functionalization of the hydroxyl groups of triethanolamine (TEA) as model branched core. In planning the synthesis of the arylating reagents, we considered various C(3) substituents which may confer different electronic and physicochemical properties (Scheme 1).

The synthesis of 5-pentafluorophenyl-1,2,4-oxadiazoles **2a–e** was accomplished by refluxing, in toluene for 8 h, a mixture of amidoxime **1a–e**, pentafluorobenzoyl chloride and pyridine. In the case of the perfluoroalkylated derivative **1f** [6], a milder procedure yielded the open-chain *O*-pentafluorobenzoyl-amidoxime derivative **3** which was then heated at 160 °C for 2 h in a sealed tube to give oxadiazole **2f**.

Reaction of **2a–f** with TEA, in a 3:1 molar ratio, was performed in an acetonitrile suspension of K_2CO_3 continuosly stirred at 40 °C. Removal of solvent and chromatography of the

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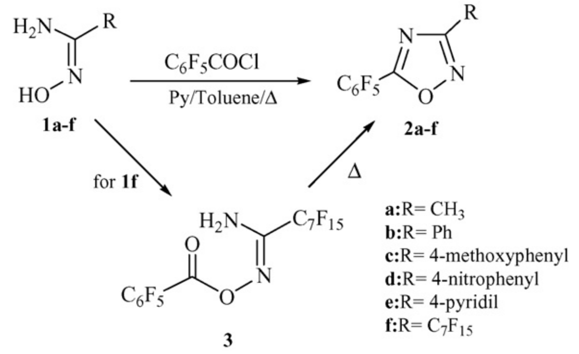
doi:10.1016/j.jfluchem.2006.07.012



Scheme 1.

Table 1
Recovered starting materials and yields of compounds **4** and **5** for the reaction the oxadiazoles **2a–f** with TEA (3:1 molar ratio)

Starting oxadiazole (% recovered)	Time (h)	Yield of **4** (%)	Yield of **5** (%)
2a (8)	4	77	15
2b (40)	24	47	9
2b[a] (7)	24	10	70
2c (–)	12	90	2
2d (12)	48	40	–
2e (36)	24	40	20
2f (20)	24	30	70
2f[a] (15)	24	13	60

[a] **2b** and **f**/TEA 2:1 molar ratio.

residue yielded trisubstituted compounds **4a–f** together with some amounts of disubstituted derivatives **5** and unreacted starting material, which was easily recovered (see Table 1). In the reaction of **2d**, the corresponding compound **5d** was not isolated and about 40% of reaction mixture was converted into unidentified products [7].

In the case of **2b** and **f**, representative experiments conducted with a 2:1 oxadiazole/TEA molar ratio, a part the prevalent formation of disubstituted compounds **5b** and **f**, show the formation of some amounts of trisubstituted derivatives **4b** and **f** (see Table 1) (Scheme 2).

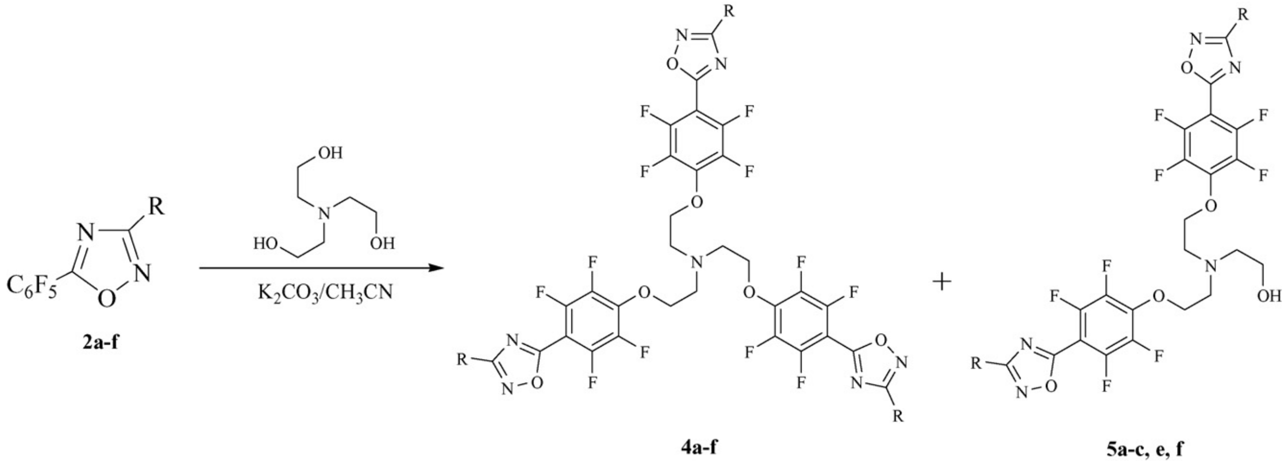
Interestingly, compounds **5** could represent useful building blocks in convergent dendrimeric synthesis [8,9]. Despite the fact that electron withdrawing substituents on the oxadiazole could increase the reactivity towards the nucleophilic substitution on the fluoroaryl ring, lower yields in trisubstituted products have been obtained for compounds **4d–f** in all tested conditions. This behaviour could be ascribed to the enhanced electron-poor character of the oxadiazoles **2d–f**, wich are more susceptible to ring opening [10] or decomposition. The lower yield of **4f** could also be due to some steric effects exerted by the long perfluoroalkyl chain in the disubstituted precursor **5f**.

The structures proposed for **4** and **5** have been confirmed by spectroscopic data; ^1H NMR spectra clearly show the tri- or disubstitution of the triethanolamine arms; ^{19}F NMR analyses, unequivocally proves the entry of the oxygen nucleophile in the *para* position of the pentafluorophenyl-ring. In the spectra of all compounds **4** and **5**, in facts, the two *ortho* positioned pairs of fluorine atoms, were as present two doublets, but with line broadening or few splittings, resulting from *para* and *meta* couplings [5e,11].

3. Spectroscopic studies

In order to asses photoluminescent properties of the title compounds, for potential applications in organic luminous devices, a preliminary spectroscopic study was done. UV–vis absorption and photoluminescence (PL) spectra of compounds **4**, **5** and of their precursors **2**, have been recorded in acetonitrile solutions and are reported in Table 2.

Along the whole series, absorbition maxima of substituted compound **4** or **5**, showed a red-shift of the maxima compared to starting oxadiazole. Photoluminescence in the UV or blue region was observed for **2**, **4** and **5** derivatives. Trisubstituded compounds **4a–f** showed PL spectra similar to those of the corresponding disubstituded derivatives **5**, while their maxima resulted shifted compared to starting oxadiazoles **2**. In some trisubstituted derivatives (for instance **4a** and **b** and **4f**) emission is very weak or not observed at all. This could be due to intramolecular self-quenching by photoinduced electron transfer between the tertiary amino and the oxadiazole moieties



Scheme 2.