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Nitroarenes – the simple way to liquid crystalline fluoroalkyl–aryl ethers

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An inexpensive and simple method of synthesis of highly fluorinated alkyl–aryl ethers with nitro- and cyano-group at the *para*-position was described. Obtained ethers were converted to liquid-crystalline biphenyls, tolanes, esters and pyrimidines.

Keywords: aromatic nucleophilic substitution; smectic liquid crystals

1. Introduction

Liquid crystals (LCs) containing alkoxy tails partially substituted with fluorine play an important role as components of ferroelectric and antiferroelectric mixtures for fast response time displays [1]. Application of these classes of LCs is limited because of their difficult synthesis. The introduction of a partially fluorinated alkyl group can be realised only by a few methods. The alkylation of phenols with perfluoroalkylsulfonic acids esters of 1H,1H-perfluoroalkanols [2] gave good results, but these compounds are toxic. The appropriate iodides and bromides are unreactive. For 1H,1H-perfluoroalkanols the application of the Mitsunobu reaction [3] gave, in our hands, only traces of the required product. The 1H,1H,2H,2H-perfluoroalkanols were more reactive and the yield was ~40%. Introduction of a perfluorinated alkyl tail can be carried out by free radical addition of 1-iodoperfluoroalkanes to alkenes and a following reduction [4,5]. This method can be applied for the synthesis of compounds that contain three or more methylene groups between the oxygen atom and a perfluorinated part. The aromatic nucleophilic substitution reaction was used by Idoux [6] for the preparation of 4-(1H,1H-perfluoroalkoxy)benzonitriles from sodium salts of 1H,1H -perfluoroalkanols and 4-chlorobenzonitrile, but acceptable results were obtained only for derivatives of trifluoroethanol. The higher 1H,1H-perfluoroalkanols were unreactive or gave only a poor yield of desired products. Better results were obtained by Wang [7,8]. The reaction of 4-chloro-3-nitrotrifluoromethylbenzene with 1H,1H,ωH-perfluoroalkanols in dimethyl formamide (DMF) and the presence of potassium carbonate gave 3-nitro-4-(1H,1H,ωH-perfluoroalkoxy) trifluoromethylbenzenes.

2. Results and discussion

The last method seemed to be promising due to its simplicity and good yield of desired product, but disadvantages were the use of the expensive and difficult to obtain 4-chloro-3-nitrotrifluoromethylbenzene and the several steps needed to obtain the final desired materials as LCs. To simplify this synthesis it was decided to test the reactivity of two cheap and commonly available compounds 4-chloronitrobenzene and 4-chlorobenzonitrile. The obtained results were promising, but the yields of appropriate ethers did not exceed 57%. Prolongation of the reaction time and increase of temperature did not grow the yield. On the theoretical aspects of this reaction, it has been stated that the use of chlorine is not good [9,10]. Potassium alcoholate is a rather soft base but the carbon atom, when connected to chlorine, gives a rather hard centre. The 'softening' of the carbon atom by a change of leaving group could raise the yield. To test this hypothesis, the most commonly available and cheapest appropriate nitro derivatives were chosen. The first experiment was carried out with 1,4-dinitrobenzene and trifluoroethanol in the presence of anhydrous potassium carbonate in DMF and was successful. Conversion was quantitative after 1 h at 100–130°C. The experiment, when repeated with 4-nitrobenzonitrile, also gave quantitative conversion, but the reaction time increased to 4 h. In response to these results 4-nitroacetophenone was also checked. In this case, the reaction proceeded very slowly and after 6 h the conversion was less than 15%. Continuation of this reaction caused formation of tar and it was not possible to isolate the required product. Experiments with higher 1H,1H-perfluoroalkanols and 1,4-dinitrobenzene and 4-nitrobenzonitrile

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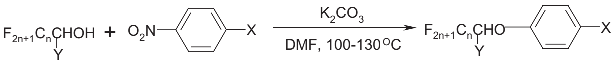
Table 1. Reactions of fluorinated alcohols with activated nitrobenzenes*.



n	Y	X	Conversion (%)	Isolated yield (%)	m.p. (°C)
1	H	$-CN$	100	–	–
1	H	$-NO_2$	100	–	–
1	$-CH_3$	$-NO_2$	100	–	–
3	H	$-CN$	100	98	Oil
3	H	$-NO_2$	100	79.5	47–48
7	H	$-CN$	100	96	Oil
7	H	$-NO_2$	100	75.2	47–49
7	H	$-COCH_3$	15	–	–
8	H	$-NO_2$	100	87.4	46–47
1	$-C_6H_{13}$	$-CN$	100	96	Oil

Note: *Alcohol 1 mmol; activated nitrobenzene 1, 2 mmol; potassium carbonate 4 mmol; DMF 4 ml (in the reactions carried out on a larger scale, volume of solvent can be reduced). m.p. melting point.

gave quantative conversion (estimated based on the GC peak area ratio of product to starting nitroderivatives) too. Products of the above reactions were isolated (Table 1) and then converted to final compounds (Schemes 1 and 2).

The reaction of both optically active (R)- and (S)-1,1,1-trifluorooctan-1-ol with 4-nitrobenzonitrile gave a very good yield of desired ether but full racemisation occurred. This was probably caused by the acidity of a hydrogen atom adjacent to a perfluoroalkyl group.

Isolation of pure nitro-ether is difficult on a large scale. Dinitrobenzene can be removed by fractional crystallisation from methanol, but it was not necessary. Reduction of the nitro group proceeds quickly under very mild conditions. The *p*-phenylenediamine, a product of the reduction of dinitrobenzene, can be removed simply by crystallisation from hexanes due to its very low solubility.

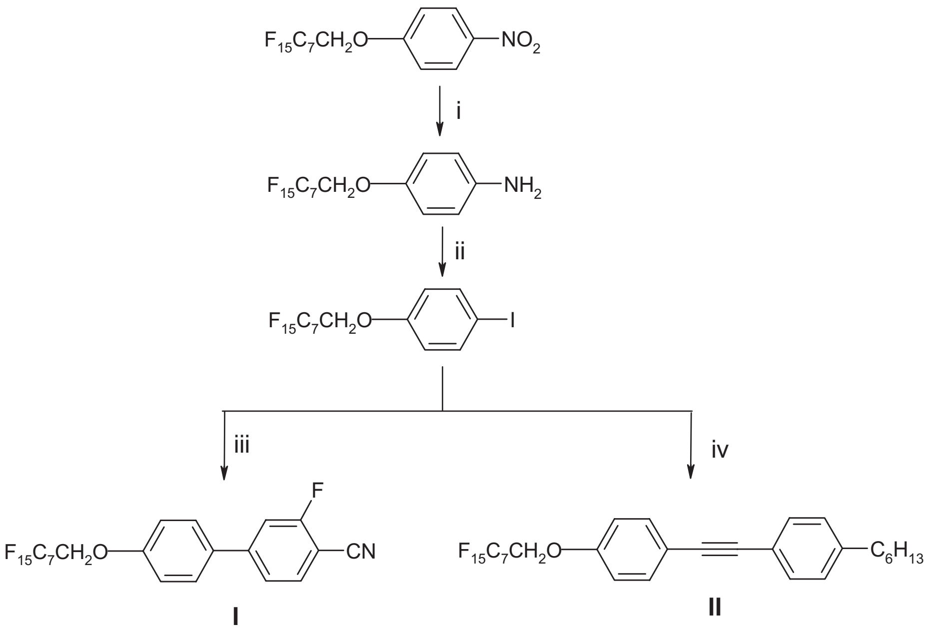
Transformation to iodide was carried out under standard conditions. The dioxane was added throughout the reaction to prevent formation of foam.

Synthesis of biphenyl **I** was carried out in the presence of palladium acetate (0.1 mole percent). The reaction was exothermic and proceeded very quickly, about 2 h. The obtained product was contaminated with colloidal palladium, which was removed by filtration through silica-gel in dichloromethane and finally purified by crystallisation from a methanol–acetone mixture.

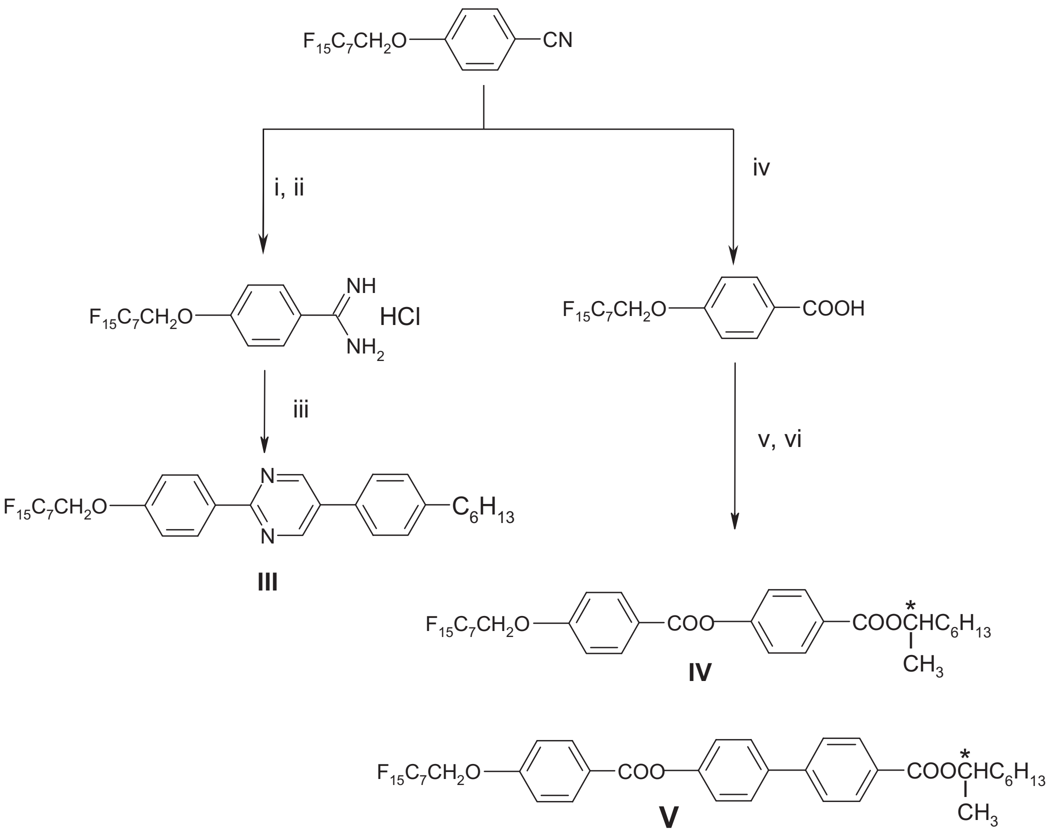
Tolane **II** was prepared according to the procedure proposed by Thonard and Krause [12].

Isolation of pure cyanoethers on a large scale required the removal of nitrobenzonitrile. This can be realised by reduction of the nitrocompound to aniline with zinc dust in methanol–acetic acid solution. The mixture was diluted with hot hexane and passed through silica-gel and hot hexanes. The product was crystallised from methanol.

Compound **III** was obtained by conversion of nitrile first to amidine hydrochloride (not isolated),



Scheme 1. Conversion of 1H,1H-perfluoroalkoxynitrobenzenes.i: H_2/10% Pd-C/EtOH, r.t.; ii: (a) HCl, H_2O-dioxane, $NaNO_2$, 5–10°C; (b)KI, r.t.; iii: $(HO)_2BPh(F)CN$, $Pd(OAc)_2$, K_2CO_3, H_2O-acetone [11]**;** iv: $HCCPhC_6H_{13}$, $(Ph_3P)_2PdCl_2$, Cu_2I_2, Et_3N, THF [12].



Scheme 2. Conversion of 1H,1H-perfluoroalkoxybenzonitriles.i: HCl, MeOH, ether; ii: NH_3, MeOH; iii: 1,3-bis-dimethylamino-2-(4-hexylyphenyl) propenium perchlorate, MeONa, MeOH; iv: H_2SO_4, AcOH, H_2O, reflux; v: ClCOCOCl, toluene, DMF (cat), r.t. to b.p.; vi: phenol, Py, toluene, 60–80°C, 3 days.

which was next condensed with 1,3-bis-dimethylamino-2-(4-hexylyphenyl)propenium perchlorate in the presence of sodium methoxide in methanol.

The hydrolysis of 4-(1H,1H- perfluoroalkoxy)benzonitrile to the acid was carried out in a mixture of concentrated sulphuric acid (3 parts), glacial acetic acid (10 parts) and water (1 part; v/v). The reaction proceeded rather quickly, and after 12 h was completely finished. The acid was crystallised from butanone.

Experimentally it was checked that basic hydrolysis (20% KOH, reflux) caused the total decomposition of the ether linkage. After acidification it was isolated using a mixture of starting alcohol, 4-hydroxybenzoic acid, 4-hydroxybenzamide and cyanophenol.

The obtained acid was converted first to acid chloride by reaction with oxalyl chloride in toluene in the presence of *N*,*N*-dimethylformamide as a catalyst at room temperature. The excess oxalyl chloride was removed by distillation with toluene. Acylation of the phenols in the presence of excess pyridine gave appropriate esters **IV** and **V**. The reaction proceeded under mild conditions with a good yield. The above esters were purified by filtration through silica-gel using dichloromethane as solvent and then by crystallisation from ethanol or an ethanol–acetone mixture.

Transformation of 4-(1H,1H- perfluoroalkoxy)iodobenzenes to boronic acid by treatment with buthyllithium and then with tripropylborate failed. The starting iodobenzene was recovered.

The purity of the obtained compounds was checked by thin layer chromatography (TLC) and GC. The structure was confirmed by MS and infrared (IR) spectra. The properties of the final liquid crystalline products are compared in Table 2.

Analogues of **I** (Cr 44 (N 39.3) Iso) and **IV** [13] exhibit only the monotropic nematic phase. An

Table 2. Properties of final compounds.

Compound	Phase transitions temperature (°C)
I	Cr 83.0 SmA 120.0 Iso
II	Cr 90.3 SmC 125.3 Iso
III	Cr 116 SmC 188.5 SmA 255.3 Iso
IV	Cr 67 Iso
V	Cr 140.4 SmA 182.2 Iso

analogue of **V** (MHPOBC) exhibits the same range of mesophase, but the temperature of melting and clearing points are about 50° lower and show rich polymorphism [14]. The compound with two less fluorine atoms (1H,1H,2H,2H-perfluorooctyl chain) exhibits a lower melting point (89.1°C) and almost the same clearing point (183.6°C) and the presence of a smectic C* phase. Analogues of **II** and **III** are unknown.

3. Conclusions

The reaction of 1H,1H-perfluorinated alcohols with activated nitrobenzenes in the presence of potassium carbonate is a practical method for the preparation of ethers in view of its simplicity and applicability to large-scale operations. The compounds obtained, 4-(1H,1H- perfluoroalkoxy)nitro- and cyanobenzenes, are very valuable substrates for the synthesis of many groups of LCs.

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