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Various synthetic approaches to fluoroalkyl p-nitrophenyl ethers

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Abstract

Homologous 1H,1H-perfluoroalkyl p-nitrophenyl ethers (alkyl = C_2–C_8) were synthesized using different methods. The results are discussed in context with contradictory comments of the literature. The fluoroalkoxylation of p-chloronitrobenzene occurs in only one step, but it is limited to small fluoroalkyl groups. The fluoroalkylation of p-nitrophenol via sulphonic acid esters is a better synthetic route. Differences in reactivity and yield between tosylates, mesylates and triflates are found and discussed. The preferred synthesis includes the use of trifluoromethane sulphonic acid esters.

Keywords: Fluoralkyl p-nitrophenyl ethers; Triflates

1. Introduction

Recently we have synthesized fluorine-containing side-group liquid-crystalline polyacrylates as well as polymethacrylates [1] and investigated their mesophase behaviour [2]. For this, trifluoromethoxy-azobenzene was used as mesogen. The remarkable results obtained suggested a continuing investigation of the influence of a fluorinated alkoxy group with increased chain length on the liquid-crystalline properties of such polymers [3]. The synthesis of these polymers had to be started with p-fluoroalkoxy anilines. However, these products are not commercially available and we synthesized them from the corresponding fluoroalkyl p-nitrophenyl ethers.

We investigated different synthetic routes and synthesized some intermediate and final products, most of which have not been described previously. Only the 2,2,2-trifluoroethyl ether of p-nitrophenol has been reported [4–7]. In the present work, the syntheses of fluoroalkyl p-nitrophenyl ethers via sulphonic acid esters of fluoroalcohols (tosylates, mesylates, triflates) are described.

2. Experimental details

2.1. General techniques

^{1}H NMR spectra were run on a Bruker WP 200 SY (200 MHz) spectrometer, ^{13}C broad-band decoupled NMR spectra were recorded on a Varian Gemini 300 (75 MHz) spectrometer. Internal hexamethyldisilazane (HMDS) was used as the respective reference and the solvent used was always $CDCl_3$.

Infrared (IR) spectra were recorded on a Perkin–Elmer System 2000 spectrometer using $CHCl_3$ as solvent or films on NaCl.

Boiling and melting points are uncorrected.

Elemental analyses (for F) were carried out according to a standard method.

2.2. Starting materials

The following fluoroalcohols (**1**) were used for the syntheses (Scheme 1): **1a** (Merck), **1b** (Aldrich), **1c** (Fluka), **1d** and **1e** were synthesized by reduction of the perfluoropentanoic acid (Aldrich) and perfluorohexanoic acid (Hoechst) respectively using lithium aluminum hydride, **1f** (ABCR), **1g** (Riedel de Haen).

2.3. Synthesis

2.3.1. Preparation of the sulphonic acid 1H,1H-perfluoroalkyl esters (2–4)

Tosylates (**2**): 40 mmol 1H,1H-perfluoroalcohol were dissolved in 20 ml triethylamine (dried over KOH and distilled) in a dried flask equipped with a dropping funnel. Then, a solution of 50 mmol p-toluenesulphonic acid chloride in 20 ml $CHCl_3$ (dried over 4 Å molecular sieves and distilled) was slowly dropped under cooling by a water bath. The mix-

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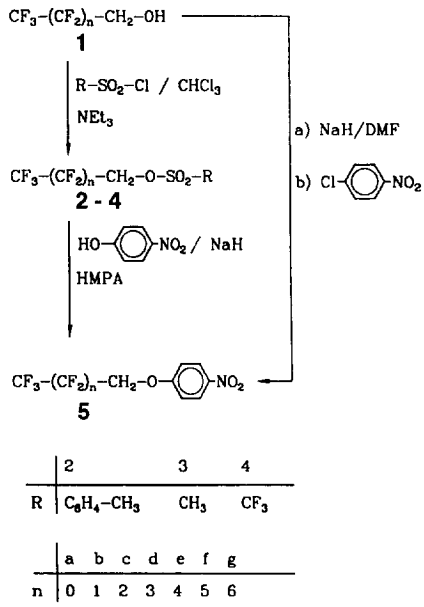

Scheme 1.

ture was stirred for 6 h at room temperature. After adding 100 ml $CHCl_3$ the solution was washed with 100 ml of 1 N HCl, 50 ml of aqueous saturated solution of $NaHCO_3$ and 50 ml of brine. The product was obtained after drying with $MgSO_4$, removing of the solvent and can be used without any further purification.

2a: Yield: 98%. M.P. 31 °C (32 °C [8]). Analysis: Calcd. for $C_9H_9F_3O_3S$ (254,02): F, 22.44%. Found: F, 22.42%. IR ($CHCl_3$): 1398 s ($ArSO_2OC$); 1291–1178 s (C–F and $ArSO_2OC$) cm^{-1}. ^1H NMR δ: 7.73 (2H, H–Ar, m, $J=8.4$ Hz); 7.31 (2H, H–Ar, m, $J=8$ Hz); 4.28 (2H, CH_2, q, $^3J(HF)=8$ Hz); 2.40 (3H, CH_3, s) ppm. ^{13}C NMR δ: 146, 132, 130, 128 (C–Ar, s); 122 (CF_3, q, $J(CF)=278$ Hz); 64.5 (CH_2, q, $^2J(CF)=38$ Hz); 22 (CH_3, s) ppm.

Mesylates (**3**): analogous to the tosylates, but with methanesulphonic acid chloride.

3a: Yield: 85%. n_D^{25}, 1.3654. Analysis: Calcd. for $C_3H_5F_3O_3S$ (178.13): F, 32.00%. Found: F, 32.15%. IR ($CHCl_3$): 1374 s (RSO_2OC); 1225–1185 s (C–F and RSO_2OC) cm^{-1}. ^1H NMR δ: 4.47 (2H, CH_2, q, $^3J(HF)=8$ Hz); 3.08 (3H, CH_3, s) ppm. ^{13}C NMR δ: 122 (CF_3, q, $J(CF)=277.5$ Hz); 64 (CH_2, q, $^2J(CF)=38$ Hz); 38 (CH_3, s) ppm.

3b: Yield: 80%. n_D^{25}, 1.3494. Analysis: Calcd. for $C_4H_5F_5O_3S$ (228.14): F, 41.64%. Found: F, 41.67%. IR ($CHCl_3$): 1374 s (RSO_2OC); 1230–1182 s (C–F and RSO_2OC) cm^{-1}. ^1H NMR δ: 4.61 (2H, CH_2, t, $^3J(HF)=12.6$ Hz); 3.14 (3H, CH_3, s) ppm.

3c: Yield: 80%. n_D^{25} 1.3454. Analysis: Calcd. for $C_5H_5F_7O_3S$ (278.14): F, 47.81%. Found: F, 47.91%. IR ($CHCl_3$): 1374 s (RSO_2OC); 1234–1183 s (C–F and RSO_2OC) cm^{-1}. ^1H NMR δ: 4.59 (2H, CH_2, t, $^3J(HF)=13.2$ Hz); 3.09 (3H, CH_3, s) ppm.

3f: Yield: 90%. n_D^{25}, 1.3366. Analysis: Calcd. for $C_8H_5F_{13}O_3S$ (428.16): F, 57.68%. Found: F, 58,49%. IR (neat): 1369 s (RSO_2OC); 1240–1145 s (C–F and RSO_2OC) cm^{-1}. ^1H NMR δ: 4.59 (2H, CH_2, t, $^3J(HF)=13.2$ Hz); 3.09 (3H, CH_3, s) ppm.

3g: Yield: 95%. M.P. 46–48 °C. Analysis: Calcd. for $C_9H_5F_{15}O_3S$ (478.17): F, 59.60%. Found: F, 59.66%. IR ($CHCl_3$): 1372 s (RSO_2OC); 1243–1183 s (C–F and RSO_2OC) cm^{-1}. ^1H NMR δ: 4.60 (2H, CH_2, t, $^3J(HF)=13.2$ Hz); 3.09 (3H, CH_3, s) ppm.

Triflates (**4**): analogous to the tosylates, but with trifluoromethanesulphonic acid chloride and CH_2Cl_2 as solvent instead of $CHCl_3$. Because of the higher volatility the trifluoromethanesulphonic acid chloride was introduced in the closed flask by a syringe using a rubber septum and it was cooled by an ice bath. After evaporation of the solvent the products were purified by fractionation (**4c–4d**) or by chromatography using a short column with silica gel and CH_2Cl_2 as solvent (**4e–4g**).

4c: Yield: 55%. B.P. 87 °C (300 mbar). Analysis: Calcd. for $C_5H_2F_{10}O_3S$ (332.12): F, 57.20%. Found: F, 56.63%. IR (neat): 1432 s (F_3CSO_2OC); 1240–1144 s (C–F and F_3CSO_2OC) cm^{-1}. ^1H NMR δ: 4.79 (2H, CH_2, t, $^3J(HF)=12.2$ Hz) ppm.

4d: Yield: 38%. B.P. 90 °C (80 mbar). n_D^{25}, 1.3085. Analysis: Calcd. for $C_6H_2F_{12}O_3S$ (382.13): F, 59.66%. Found: F, 59.59%. IR (neat): 1433 s (F_3CSO_2OC); 1235–1140 s (C–F and F_3CSO_2OC) cm^{-1}. ^1H NMR δ: 4.76 (2H, CH_2, t, $^3J(HF)=12.4$ Hz) ppm.

4e: Yield: 62%. n_D^{25}, 1.3101. Analysis: Calcd. for $C_7H_2F_{14}O_3S$ (432.13): F, 61.55%. Found: F, 61.56%. IR (neat): 1432 s (F_3CSO_2OC); 1247–1142 s (C–F and F_3CSO_2OC) cm^{-1}. ^1H NMR δ: 4.82 (2H, CH_2, t, $^3J(HF)=12.2$ Hz) ppm.

4f: Yield: 85%. n_D^{25}, 1.3088. Analysis: Calcd. for $C_8H_2F_{16}O_3S$ (482.10): F, 63.05%. Found: F, 63.04%. IR (neat): 1432 s (F_3CSO_2OC); 1250–1145 s (C–F and F_3CSO_2OC) cm^{-1}. ^1H NMR δ: 4.82 (2H, CH_2, t, $^3J(HF)=12.3$ Hz) ppm.

4g: Yield: 90%. n_D^{25}, 1.3084. Analysis: Calcd. for $C_9H_2F_{18}O_3S$ (532.15): F, 64.26%. Found: F, 64.27%. IR (neat): 1432 s (F_3CSO_2OC); 1245–1144 s (C–F and F_3CSO_2OC) cm^{-1}. ^1H NMR δ: 4.82 (2H, CH_2, t, $^3J(HF)=12.4$ Hz) ppm.

2.3.2. p-Nitrophenyl-ether (5)

Method 1: To 30 mmol NaH in a dried flask purged with nitrogen was slowly added a solution of 50 mmol 1H,1H-perfluoroalcohol in 30 ml DMF at room temperature. When the evolution of hydrogen was finished 30 mmol p-chloronitrobenzene were added at room temperature. The reaction mixture was stirred for 10 h at 130 °C, after cooling poured into 100 ml diluted HCl and extracted by diethyl ether. The ether extracts are washed neutral with brine, dried over $MgSO_4$ and the solvent distilled off in vacuum. Purification was possible by reprecipitation of a solution in DMF with water (for **5a**) or by column chromatography on aluminum oxide using CH_2Cl_2 as solvent.

Method 2: A solution of 21 mmol p-nitrophenol in 40 ml HMPA was slowly added to 26 mmol sodium hydride at room temperature under nitrogen. When evolution of hydrogen was finished a solution of 23.5 mmol sulphonic acid 1H,1H-perfluoroalkyl ester in 5 ml HMPA was slowly added to the stirred solution at room temperature. The reaction mixture was stirred vigorously for 8 h at 110 °C. Then, after cooling, ice and 100 ml water were added and the reaction product extracted three times with 100 ml of diethylether. The ether extract was washed once by 100 ml diluted sodium hydroxide and twice by 50 ml of brine, dried over $MgSO_4$ and the solvent distilled off. The p-nitrophenyl ether obtained was purified by column chromatography on silica gel using CH_2Cl_2 as solvent.

5a: Yield: 92% (method 1), 70% (method 2 via tosylate), 98% (method 2 via mesylate). M.P. 69–74 °C (76–77 °C [4]). Analysis: Calcd. for $C_8H_6F_3NO_3$ (221.13): F, 25.77%. Found: F, 25.73%. IR ($CHCl_3$): 1595 m (Ar); 1521 s (NO_2); 1498 m (Ar); 1347 s (NO_2); 1114 m (C–O–C) cm^{-1}. ^1H NMR δ: 8.18 (2H, H–Ar, m, $J=7.2$ Hz); 6.97 (2H, H–Ar, m, $J=9.2$ Hz); 4.40 (2H, CH_2, q, $^3J(HF)=7.8$ Hz) ppm. ^{13}C NMR δ: 162, 143, 126, 115 (C–Ar); 123 (CF_3, q, $J(CF)=278$ Hz); 66 (CH_2, q, $^2J(CF)=36$ Hz) ppm.

5b: Yield: 55% (method 1), 23% (method 2 via mesylate). M.P. 53–55 °C. Analysis: Calcd. for $C_9H_6F_5NO_3$ (271.14): F, 35.03%. Found: F, 30.13%. IR($CHCl_3$): 1597 m (Ar); 1522 s (NO_2); 1498 m (Ar); 1347 s (NO_2); 1115 m (C–O–C) cm^{-1}. ^1H NMR δ: 8.22 (2H, H–Ar, m, $J=10$ Hz); 6.99 (2H, H–Ar, m, $J=9$ Hz); 4.47 (2H, CH_2, q, $^3J(HF)=12$ Hz) ppm.

5c: Yield: 85% (method 2 via triflate). M.P. 44–47 °C. Analysis: Calcd. for $C_{10}H_6F_7NO_3$ (321.15): F, 25.77%. Found: F, 41.40%. IR ($CHCl_3$): 1597 m (Ar); 1523 s (NO_2); 1497 m (Ar); 1347 s (NO_2); 1106 m (C–O–C) cm^{-1}. ^1H NMR δ: 8.19 (2H, H–Ar, m, $J=9.4$ Hz); 6.98 (2H, H–Ar, m, $J=9.4$ Hz); 4.49 (2H, CH_2, tt, $^3J(HF)=12.5$ Hz) ppm.

5d: Yield: 80% (method 2 via triflate). n_D^{25}, 1.4234. Analysis: Calcd. for $C_{11}H_6F_9NO_3$ (371.16): F, 46.07%. Found: F, 41.09%. IR (neat): 1596 m (Ar); 1523 s (NO_2); 1498 m (Ar); 1346 s (NO_2); 1114 m (C–O–C) cm^{-1}. ^1H NMR δ: 8.20 (2H, H–Ar, m, $J=9$ Hz); 6.98 (2H, H–Ar, m, $J=9$ Hz); 4.51 (2H, CH_2, t, $^3J(HF)=12.7$ Hz) ppm.

5e: Yield: 98% (method 2 via triflate). n_D^{25}, 1.4026. Analysis: Calcd. for $C_{12}H_6F_{11}NO_3$ (421.17): F, 49.62%. Found: F, 54.01%. IR (neat): 1596 m (Ar); 1523 s (NO_2); 1498 m (Ar); 1348 s (NO_2); 1115 m (C–O–C) cm^{-1}. ^1H NMR δ: 8.19 (2H, H–Ar, m, $J=9$ Hz); 6.99 (2H, H–Ar, m, $J=9$ Hz); 4.52 (2H, CH_2, t, $^3J(HF)=12.4$ Hz) ppm.

5f: Yield: 90% (method 2 via triflate). M.P. 47–49 °C. Analysis: Calcd. for $C_{13}H_6F_{13}NO_3$ (471.17): F, 52.41%. Found: F, 50.73%. IR (neat): 1595 m (Ar); 1522 s (NO_2); 1499 m (Ar); 1347 s (NO_2); 1113 m (C–O–C) cm^{-1}. ^1H NMR δ: 8.19 (2H, H–Ar, m, $J=9$ Hz); 6.99 (2H, H–Ar, m, $J=9$ Hz); 4.52 (2H, CH_2, t, $^3J(HF)=12.6$ Hz) ppm.

5g: Yield: 95% (method 2 via triflate). M.P. 42–45 °C. Analysis: Calcd. for $C_{14}H_6F_{15}NO_3$ (521.18): F, 54.68%. Found: F, 54.51%. IR (neat): 1596 m (Ar); 1521 s (NO_2); 1494 m (Ar); 1347 s (NO_2); 1114 m (C–O–C) cm^{-1}. ^1H NMR δ: 8.24 (2H, H–Ar, m, $J=9$ Hz); 7.04 (2H, H–Ar, m, $J=9$ Hz); 4.57 (2H, CH_2, t, $^3J(HF)=12.5$ Hz) ppm. ^{13}C NMR δ: 162, 143, 126, 115 (C–Ar); 105–120 (nCF_2+CF_3, m); 65 (CH_2, t, $^2J(CF)=27.5$ Hz) ppm.

3. Results and discussion

Various methods have been developed to synthesize fluoroalkyl aryl ethers. 2,2,2-Trifluoroethyl iodide reacts with sodium phenoxides in *N,N*-dimethylformamide (DMF) to give the wanted ether, but in low yields [9], because fluorine substituents in the alkyl iodides strongly decrease S_N2 reactivity on the β-carbon atom and lead to β-eliminations [10]. The reaction of 2,2,2,-trifluorodiazoethane and phenol [11] is limited to this special case. A further method not generally applicable is the replacement of iodine in aromatics carrying electron-releasing groups by the 2,2,2-trifluoroethoxy group in the presence of copper(I) iodide as catalyst [12]. Longer-chain alkoxides lead to the formation of complex product mixtures or fail completely.

We used different routes for the synthesis of fluoroalkyl p-nitrophenyl ethers, demonstrated in Scheme 1.

Only the 1H,1H-perfluoroethyl p-nitrophenyl ether was known. Idoux, Gupton and coworkers [5–7] prepared this compound using direct aromatic nucleophilic fluoroalkoxylation. This reaction takes place with activated aryl and also heteroaryl halides. The nitro group is such an activating substituent in aromatics. Thus, the sodium trifluoroethoxide formed from the fluoroalcohol and sodium hydride in hexamethyl-phosphoric triamide (HMPA) reacted with p-chloronitrobenzene at 150 °C in a high yield (88%). However, a side reaction of HMPA with the activated aryl chloride occurs at temperatures around 150 °C. To avoid the side reaction we used DMF as solvent at 130 °C and obtained the trifluoroethyl p-nitrophenyl ether **5a** in a slightly better yield of 92%.

However, the direct aromatic fluoroalkoxylation seems to be limited by increasing chain length in the alkoxide nucleophile [5]. We obtained the new compound **5b** with a pentafluoropropyl group only in 55% yield using similar conditions, and another route to the fluoroalkyl p-nitrophenyl ethers (**5c–5g**) was preferred.

The fluoroalkylation of p-nitrophenol was the first method applied to prepare trifluoroethyl p-nitrophenyl ether [4]. While the reaction of 2,2,2-trifluoroethyl iodide with sodium phenoxide in DMF was not successful, due to β-elimination, Camps et al. [4] used 2,2,2-trifluoroethyl methanesulphonate.

Generally, several types of sulphonic acid esters are known as alkylating agents and we studied three of them.

p-Toluenesulphonic acid esters (tosylates) are commonly used. The 2,2,2-trifluoroethyl tosylate was prepared by addition of a mixture of trifluoroethanol with triethylamine to the solution of tosyl chloride in diethylether at 0 °C in 76% yield

[8]. We improved the method by using chloroform as solvent and room temperature and obtained the same product **2a** in very high yield (98%). The reactivity of the trifluoroethyl tosylate is important for its reaction with sodium p-nitrophenoxide. But, according the study of Bordwell and Brannen [13] on the reactivity of potassium iodide in S_N2 reactions, the trifluoroethyl tosylate had a deactivating effect. We confirmed this effect in the reaction with the nucleophile sodium p-nitrophenoxide. The trifluoroethyl p-nitrophenyl ether **5a** was obtained in only 70% yield using the corresponding tosylate **2a**, but in 98% if the mesylate **3a** was used. Our further investigation had to include other sulphonic acid esters like mesylates and triflates.

Methanesulphonic acid esters (mesylates) of some fluoroalcohols are already known. Crossland and Servis [14] synthesized the trifluoroethyl ester by the use of triethylamine as base and methylene chloride as solvent at a temperature below 0 °C. We prepared the mesylates **3a–3c**, **3f** and **3g** in high yields in a similar manner, but with chloroform as solvent and at room temperature. Mesylates have two advantages compared with tosylates, a greater stability against hydrolysis and less steric hindrance at a nucleophilic attack. Thus, the fluoroalkoxylation of p-nitrophenol with 2,2,2-trifluoroethyl mesylate **3a** delivered 98% product **5a**. Surprisingly the reaction with 1H,1H-perfluoropropyl mesylate **3b** yielded only in 23% of the corresponding product **5b**. The conversion of p-nitrophenol with mesylates of longer 1H,1H-perfluoroalcohols failed totally. That is the reason why for further syntheses the triflates of the corresponding 1H,1H-perfluoroalcohols had to be used.

2,2,2-Trifluoroethyl trifluoromethanesulphonate (triflate) **4a** was prepared by Burdon and McLoughlin [15] from trifluoroethanol in different manner. Firstly, the reaction product from sodium hydride and trifluoroethanol reacted with trifluoromethanesulphonyl fluoride at 120 °C. But, bis(2,2,2-trifluoroethyl)ether was found as a by-product, obtained by alkylation of the trifluoroethylate by the trifluoroethyl triflate just formed. Secondly, trifluoromethanesulphonyl fluoride, pyridine and trifluoroethanol were kept in a sealed tube at room temperature for 48 h and then at 110 °C for 2.5 h. Besides **4a**, bis(2,2,2-trifluoroethyl)ether was found here too. Thirdly, the best method was the reaction of trifluoromethanesulphonic anhydride with trifluoroethanol under reflux for 30 min. But, this method has the disadvantage that the anhydride is not so easily available as the acid fluoride and is unstable in the presence of organic impurities [16].

Hansen [17] reported on a variation of the second method of Burdon and McLoughlin, replacing pyridine by triethylamine and using methylene chloride as solvent at temperatures below 0 °C. He did not find any by-product in the preparation of **4a–4c**. We used trifluoromethanesulphonyl chloride to react with fluoroalcohols **1c–1g** at the presence of triethylamine in methylene chloride at room temperature and obtained the series of triflates **4c–4g** in moderate to high yield. These triflates were converted into the 1H,1H-perfluoroalkyl p-nitrophenylethers **5c–5g** by reaction with p-nitrophenol and sodium hydride in HMPA at 110 °C in high yield (80–98%).

Fluoroalkyl trifluoromethanesulphonates are highly powerful fluoroalkylating agents, around 10^4 times more reactive than the corresponding tosylates [17]. We found, the conversion to p-nitrophenyl ethers was nearly complete in 15 min. No side reactions were observed with triflates (in contrast to Refs. [15,18]). Their reactivity does not decrease with the fluoroalkyl chain length. It seems that the use of triflates is generally suitable for the fluoroalkylation of phenolates, not only the p-nitro-substituted ones.

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