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Electrophilic ipso substitution of trimethylsilyl groups in fluorobenzenes

Paul L. Coe^{a,*}, Alison M. Stuart^a, David J. Moody^b

^a School of Chemistry, The University of Birmingham, Edgbaston, Birmingham B15 2TT, UK ^b Zeneca LifeScience Materials, Grangemouth Works, Grangemouth, Stirlingshire FK3 8XG, UK

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Abstract

Using variants of literature methods 2,4- and 2,6- difluorophenyltrimethylsilanes have been bromodesilylated to the corresponding bromodifluorobenzenes in moderate to good yields, 3-bromo-2,6-difluorophenyltrimethylsilane afforded 1,3-dibromo-2,4-difluorobenzene whilst 1,3-difluoro-2,4-bis(trimethylsilyl)benzene yielded 3-bromo-2,6-difluorophenyltrimethylsilane. Application of either the Eaborn or Chvalovsky methods of nitrodesilylation to 4-fluorophenyltrimethylsilane, 2,4-difluorophenyltrimethylsilane and 2,6-difluorophenyltrimethylsilane afforded largely the corresponding desilylated products together with products associated with initial protodesilylation, followed by nitration of the resulting fluorobenzenes. The results obtained show that *ipso* desilylation in the fluoroaromatic series does follow the expected pattern previously obtained in the hydrocarbon analogues. They also show that in some cases the formation of unusually substituted fluoroarenes can be achieved more readily than by the methods previously used. © 1998 Elsevier Science S.A. All rights reserved.

1. Introduction

The cleavage of aryl silicon bonds by electrophiles has been known since the turn of the century [1] but it was not until much later that the reaction was fully studied as a potential method of regioselective preparation of functionalised arenes [2-5]. More recently, the area has been the subject of a wide ranging review [6]. However, apart from some work described by Bennetau [7], there have been few reports of desilylation reactions involving fluoroarenes. As part of our study on the reactions of elemental fluorine with fluoroarenes and fluoroaryltrimethylsilanes [8], we wished to make a comparison between these reactions and known electrophilic desilylation reactions to see what, if any, were the similarities and differences between them. Hopefully this would enable us to draw mechanistic conclusions about the fluorination studies. In particular, we decided to study bromdesilylation and nitrodesilylation reactions of the range of fluoroaryltrimethylsilanes which we also wished to fluorinate. Intrinsically, these reactions were of synthetic interest in their own right, since they could provide routes to bromoand nitro-fluoroarenes which could be potentially important compounds for the preparation of intermediates for the synthesis of analogues of known drug molecules. Most of the products we obtained are known but the routes by which they are obtained are often multistep processes in low overall yield e.g 1,3-dibromo-2,4-difluorobenzene and our reactions which are unoptimised present an alternative short route albeit not necessarily, and especially in the case of silyldenitration reactions, in high yield, but nevertheless in yields which may be acceptable when compared with the alternatives.

2. Experimental details

The ¹H and ¹³C NMR spectra were recorded at 300 MHz on a Bruker AC30NMR spectrometer and the ¹⁹F spectra were recorded using a Jeol FX90Q NMR spectrometer at 84.26 MHz. All spectra were recorded using CDCl₃ as the solvent. Tetramethylsilane was used as internal reference for proton spectra and the shifts are quoted downfield from the reference in ppm. CFCl₃ was used as the reference for fluorine spectra and the shifts are measured in ppm. Most of the bromo and nitrofluoroarenes produced in these reactions are commercially available and samples for spectroscopic comparison were obtained either from Sigma-Aldrich or from Fluorochem Ltd. The syntheses of most of the aryltrimethylsilanes used were described in an earlier paper [8].

^{*}Corresponding author. Fax: +44-1214144403.

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2.1. Bromodesilylation of 2,4difluorophenyltrimethylsilane

Liquid bromine (6.3 g, 0.04 mol) was added dropwise over 20 min to 2,4-difluorophenyltrimethylsilane (7.3 g, 0.04 mol) with stirring at 0°C. The mixture was heated at 80°C for 3 h, cooled, poured into dichloromethane (25 cm³) and the organic layer washed with 5% sodium metabisulphite solution (2×75 cm³), 5% sodium bicarbonate solution (2×75 cm³) and water (3×75 cm³). The organic layer was dried (MgSO₄), the solvent removed and the resulting oil distilled to yield 1-bromo-2,4-difluorobenzene [15] (2.84 g, 38%) identical to an authentic sample.

2.2. Bromodesilylation of 2,6difluorophenyltrimethylsilane

Using the same method as the above, the reaction of 2,6difluorophenyltrimethylsilane (7.0 g) and bromine (7.4 g)afforded 1-bromo-2,6-difluorobenzene [16] (3,7 g, 50%)identical to an authentic sample.

2.3. Bromodesilylation of 3-bromo-2,6difluorophenyltrimethylsilane

As above, the reaction of 3-bromo-2,6-difluorophenyltrimethylsilane (7.0 g) and bromine (7.3 g) afforded 1,3-dibromo-2,4-difluorobenzene [16] (3.85 g, 54%) bp 88°/10 mm Hg. $\delta_{\rm H}$ =6.9 (1H, td ${}^{3}J_{\rm HF}$ = ${}^{3}J_{\rm HH}$ =8.8 Hz, ${}^{5}J_{\rm HF}$ =2 Hz), 7.5 (1 H, ddd, ${}^{3}J_{\rm HH}$ =8.5 Hz, ${}^{4}J_{\rm HF}$ =7.5 Hz, ${}^{4}J_{\rm HF}$ =5,5 Hz); $\delta_{\rm F}$ =-95.9(1 Fm, 2-F), -105.7 (1 F,m,4-F) m/z (El) 270/272/274 (M)⁺, 191/193 (M-Br)⁺, 112 (M-2Br)⁺

2.4. Bromodesilylation of 1,3-difluoro-2,4bis(trimethylsilyl)-benzene

Bromine (1 M in acetic acid, 18 cm³, 0.018 mol) was added dropwise to a stirred solution of 1,3-difluoro-2.4bis(trimethylsilyl)benzene (4.6 g, 0.018 mol) in acetic acid (20 cm³). The mixture was then heated at 75°C for 21 h poured into water (200 cm³) and the resulting solution neutralised with sodium bicarbonate. The lower organic layer was extracted with ether and combined with the ether extracts (2×25 cm³) of the aqueous layer, the combined ether layers were washed with water, dried (MgSO₄) and the ether evaporated to leave a yellow oil (1.48 g). Column chromatography on silica (hexane as eluant) afforded 3bromo -2,6-difluorophenyltrimethylsilane (1.02 g, 21%) identical to an authentic sample and to a sample prepared as shown below.

2.5. Nitrodesilylation of 4-fluorophenyltrimethylsilane

2.5.1. (a) By Chvalovsky's method

Nitric acid (70%, 1.4 g, 0.016 mol) was added dropwise (CARE) over 30 min to a stirred solution of 4-fluorophe-

nyltrimethylsilane in acetic anhydride (1.8 g) and the mixture was heated at 60°C for 3 h. After cooling, the mixture was poured into 10% sodium hydroxide solution (10 cm³) and extracted with ether (5×15 cm³). The combined organic layers were washed with water, dried (MgSO₄) and the ether removed to yield a yellow oil (1.69 g). Distillation using a Kugelrohr apparatus afforded 4-fluoronitrobenzene [17] (0.82 g, 58%) with identical spectra to an authentic sample and a trace (0.04 g) of a compound thought to be a fluoronitrophenyltrimethylsilane; [MS (EI) m/z 213 (M)⁺, 198 (M–Me)⁺]. Chemical shift data would indicate that the nitro group is in the 3-position, i.e next to the trimethylsilyl group but we cannot make a positive assignment of the structure on current data.

2.5.2. (b) By Eaborn's method

Nitric acid (70%, 2.7 g, 0.03 mol) was added dropwise to acetic anhydride (8.4 g, 0.08 mol) cooled in an ice bath. This solution was then added dropwise to a stirred solution of 4-fluorophenyltrimethylsilane (2.5 g, 0.015 mol) in acetic acid (9.6 g, 0.016 mol) at room temperature. The reaction mixture was heated at 60°C for 22 h with the evolution of copious amounts of nitrogen dioxide. The mixture was cooled and poured into a cold solution of 10% sodium hydroxide solution. The aqueous layer was extracted with ether $(6 \times 25 \text{ cm}^3)$, the combined extracts were washed with water, dried (MgSO₄) and the ether removed to leave a yellow oil (1.99 g). Purification by column chromatography (hexane, then hexane/ether 10/1 on silica) gave unreacted starting material (0.56 g, 22.2%), 4-fluoronitrobenzene (0.41 g, 19.6%), identical to an authentic sample, and a trace of a fluoronitrotrimethylsilane; $[MS (EI) m/z 213 (M)^{+} 198 (M-Me)^{+}, 182 (M-MeO)^{+}]^{19}F$ NMR $\delta_{\rm F} = -118.6$ (m).

2.5.3. (c) Eaborn's method with double the amount of nitrating agent

Nitric acid (2.7 g, 0.03 mol) was added dropwise with cooling to acetic anhydride (8.4 g, 0.08 mol) and this nitrating mixture was added dropwise to a cooled, stirred solution of 4-fluorophenyltrimethylsilane (2.5 g, 0.015 mol). The mixture was then heated at 50°C for 23 h, when a further portion of the nitrating agent was added. The mixture was heated for a further 4 h when tlc indicated the total disappearance of starting material. Work up as above afforded an orange oil (2.12 g). Purification by column chromatography afforded 4-nitrofluorobenzene (0.7 g, 35.9%) identical with an authentic sample, 2,4-dinitrofluorobenzene [17] (0.09 g, 3.3%) identical with an authentic sample, and the same nitrofluorotrimethylsilane as above (0.03 g, 0.9%).

2.6. Nitrodesilylation of 2,4-difluorophenyltrimethylsilane

2.6.1. (a) By Chvalovsky's method

Nitric acid (70%, 1.43 g, 0.016 mol) was added dropwise over 20 min to a stirred solution of 2,4 -difluorophenyltri-

methylsilane (1.86 g, 0.01 mol.) in acetic anhydride (1,8 g, 0.018 mol) at room temperature. The mixture was then heated at 45°C for 5 h and the progress of the reaction was monitored by TLC. Since starting material was still present more nitric acid (1.43 g) was added and heating was continued for further 17 h. Work up as above afforded an oil (1.62 g). Purification by column chromatography (hexane/ ether [5:1] on silica) gave 2,4-difluoronitrobenzene (0.52 g, 32.7%), 1,3-difluorobenzene (0.03 g, 2.3%) both identical to authentic samples and 3-fluoro-4,6- dinitrophenol (0.14 g, 6.8%) mp 82–83°C $\delta_{\rm H}$ =7.10 (d, 1H, ${}^{3}J_{\rm HF}$ =11.2 Hz, Hz, 2-H), 9.06 (d, 1H, ${}^{4}J_{\rm HF}$ =7.8 Hz, 5-H) and 11.10 (s, 1H, OH); [MS (EI) *m*/*z* 202(M)⁺, 186 (M–O)⁺, 172 (M–NO)⁺].

2.6.2. (b) By Eaborn's method

Nitric acid (70%, 2.7 g, 0.03 mol) was added dropwise over 5 min. to acetic anhydride (8.4 g, 0.082 mol) with stirring in a conical flask cooled in an ice bath (CARE). This mixture was then added dropwise with stirring over 15 min to 2,4-difluorophenyltrimethylsilane (2.8 g)0.015 mol) in acetic acid (9.6 g, 0.16 mol) at room temperature. The reaction mixture was heated and stirred at 50° C for 4 h, when a second identical portion of the nitrating mixture was added and the mixture was then heated at 50°C for a further 17 h. Finally, a third portion of the nitrating mixture was added and the whole mixture heated for a further 48 h. After this time the mixture was worked up as for the Eaborn method above to yield an oil (3.88 g). Purification by column chromatography (hexane and then hexane/ether 10:1 on silica) gave unreacted starting material (0.53 g, 19%), 2,4-difluoronitrobenzene (0.39 g, 16.2%), 1,3-difluoro-4,6-dinitrobenzene (0.01 g, 0.03%), 3-fluoro-4,6-dinitrophenol (0.02 g, 0.7%) identical with authentic 2,4-difluoro-5-nitrophenyltrimethylsilane samples and (0.12 g, 3.4%) $\delta_{\rm H}$ =0.37 (d 9H, ⁵ $J_{\rm HF}$ =1 Hz, SiMe₃), 6.95 (dd, 1H, ${}^{3}JHF=11$ Hz, ${}^{3}J_{HF}=7.8$ Hz, 3-H), 8.13 (dd, 1H, ${}^{4}J_{\rm HF}$ =9 Hz, ${}^{4}J_{\rm HF}$ =5.5 Hz, 6-H), $\delta_{\rm F}$ =-86.4 (m, 1F, 2-F), -111.7 (ddd, 1F ${}^{4}J_{FF}=16.3$ Hz, ${}^{3}J_{HF}=10.6$ Hz, ${}^{4}J_{HF}=9$ Hz, 4-F), the ¹³C NMR spectrum was consistent with the structure.

2.7. Nitrodesilylation of 2,6-difluorophenyltrimethylsilane by Chvalovsky's method

Nitric acid (70%, 1.46 g, 0.016 mol) was added dropwise over 30 min to a solution of 2,6-difluorophenyltrimethylsilane (1.86 g, 0.01 mol) in acetic anhydride at room temperature. The reaction mixture was heated at 65°C for 5 h, when a second identical portion of nitric acid was added over 15 min. The mixture was further heated at 65° for 24 h. The mixture was worked up as above to yield an oil (0.66 g), which on purification by column chromatography (hexane/ ether 20:1 on silica) afforded 1,3-difluorobenzene (0.15 g, 13.4%), 2,4-difluoronitrobenzene (0.04 g, 2.6%), a trace of 2,6-difluoronitrobenzene, all identical with authentic samples and 2,6-difluoro-3-nitrophenyltrimethylsilane (0.27 g, 11.7%); $\delta_{\rm H}$ =0.42 (t, 9H, ${}^{5}J_{\rm HF}$ =1.5 Hz, SiMe₃), 6.95 (ddd,1H, ${}^{3}J_{\rm HF}$ =9 Hz, ${}^{3}J_{\rm HH}$ =7 Hz, ${}^{5}J_{\rm HF}$ =1.5 Hz, 5-H), 8.08 (td, 1H, ${}^{4}J_{\rm HF}$ =9 Hz, ${}^{3}J_{\rm HH}$ =6 Hz, 4-H), $\delta_{\rm F}$ =-85.8 (m, 1F, 6-F), -100.2 (m, 1F, 2-F) MS (EI) *m/z* 231 (M)⁺, 216 (M–Me)⁺, 171 (M–MeNO)⁺. The 13 C NMR spectrum was consistent with the proposed structure.

2.8. Preparation of 3-bromo-2,6difluorophenyltrimethylsilane

A solution of 1-bromo-2,4-difluorobenzene (10 g, 0.052 mol) in dry THF (30 cm³) was added dropwise to a solution of LDA (0.052 mol in THF (25 cm³) at -78° C. The mixture was stirred for 1 h and chlorotrimethylsilane (10 g 0.092 mol) was added over 30 min. The mixture was stirred overnight as it was gradually warmed to room temperature. The lithium chloride which formed was filtered off and the filtrate was washed successively with 5% NaHCO3 and water. The aqueous washings were extracted with ether and the combined organic layers were dried (MgSO₄) and the solvent evaporated to leave an oil (11.3 g) which on distillation in vacuo afforded 3-bromo-2,6-difluorophenyltrimethylsilane (6.3 g, 46%) bp 80–85°C @ 5.5 mm Hg. MS m/z 266/264 [M]⁺, 251/249 [M–Me]⁺, δ H 0.38 (t, 9H ${}^{5}J_{\rm HF}$ =1.5 Hz), 6.73 (m,1H) 7.47 (m,1H) δF –91 (m,1F), -98.9 (m,1F). Accurate mass: requires 263.999814, Found: 263.998009.

3. Results and discussion

The preparation of the desired trimethylsilanes has been described previously using the reaction of the corresponding fluoroaryllithium or magnesium reagents [8]. Bromodesilylations have been carried out in a variety of ways but most work has been done either with elemental bromine in acetic acid [3-5] or by using elemental bromine alone.[9] We initially chose to study the reactions in acetic acid, as used by Eaborn et al., and the reactions were monitored by GC. In each of the cases studied, the reactions appeared to proceed in good yields, by GC analysis, but there were considerable losses in workup by the literature method, which involved washing away the acetic acid with large volumes of water. This problem was partially overcome by pouring the product into water followed by a standard ether extraction/ sodium bicarbonate washing procedure. In this way, moderate yields of the desired bromofluoro-compounds were obtained. Thus, 2,4-difluorophenyltrimethylsilane afforded bromo-2,4-difluorobenzene in 18% yield, 2,6-difluorophenyltrimethylsilane gave bromo-2,6-difluorobenzene in 25% yield and interestingly 3-bromo-2,6-difluorophenytrimethylsilane was also obtained in 21% yield from 1,3difluoro-2,4-bis (trimethylsilyl)benzene. This latter reaction showed that it is possible to remove trimethylsilyl groups in this series selectively, confirming related observations by Bennetau [7].



i Br₂/HAc/50°/16.5hr ii Br₂/80°/3hr iii Br₂/HAc/50° 40hr iv Br₂/65° 7hr v Br₂/HAc/60°/96hr vi Br₂/55°/21hr vii Br₂/HAc/75°/21hr

Fig. 1.

Clearly the yields obtained in these reactions could be improved and in the light of Bennetau's work with iodine chloride [7] and Whitmore's early report [9], we decided to investigate the use of elemental bromine alone in an attempt to obtain better yields. The reactions were carried out without the use of solvent at 50-80°C using a solid CO₂ condenser to keep the bromine in the system. In this way a considerable improvement in yields were obtained, typically in the range 38-54% isolated yield. Importantly the reaction time was cut from between 16 and 90 h to 3-7 h for reactive silanes and to 21 h for unreactive compounds. The rates of reaction of the silanes varied considerably depending on the relative positions of the silvl groups and the fluorine atoms (see below). In all these bromodesilylations we found no evidence for competing protodesilylations from any HBr which may have been present in the reaction mixture. These reactions are summarised in Fig. 1.

In contrast to the relatively clean bromodesilylation reactions, we expected to find a more complex system when we turned our attention to nitrodesilylations. These reactions were first discussed in detail by Chvalovsky [10] then by Benkeser in [11] and more mechanistically by Eaborn [12]. All these authors concluded that the rates of nitrodesilylation and nitrodeprotonation were comparable and that mixtures of products were obtained. Furthermore the mode of nitration was and to an extent still is in dispute. Eaborn originally suggested that dinitrogen pentoxide was the active nitrating agent and then later proposed that the reaction took place via nitrosation followed by oxidation. A comparison of the various methodologies for the reaction showed that Chvalovsky's procedure consistently gave better isolated yields of the desired nitrodesilyation product and so this procedure was used first. Reaction of 4-fluorophenyltrimethylsilane with nitric acid in acetic anhydride at 60°C for 3 h afforded 4-nitrofluorobenzene in 58% yield and fluorobenzene in 6% yield, showing that nitrodesilylation appeared to be the major reaction in this case. In a control experiment under the same reaction conditions fluorobenzene did not nitrate significantly to the 4-nitro derivative. When the reaction with 2,4-difluorophenyltrimethylsilane was carried out, the process was found to be much slower and required further nitric acid to be added after 5 h of heating and then a further heating period of 17 h before all the starting material was consumed. The products were separated by column chromatography on silica (hexane/ether 5:1 as eluant). Analysis by ¹H and ¹⁹F NMR spectroscopy confirmed that the products were 2,4-difluoronitrobenzene (33% yield) (the nitrodesilylation product), 1,3-difluorobenzene (2.3% yield) (the protodesilylation product) and somewhat surprisingly 3-fluoro-4,6-dinitrophenol (7% yield). This later product arises from nucleophilic attack of water displacing one of the highly activated fluorine atoms in some 1,3-difluoro-2,6- dinitrobenzene formed in the original reaction. We have observed similar reactions in dinitrotetrafluorobenzenes and dinitrotrifluoropyridines [13]. In a similar, but even slower reaction, 2,6difluorophenytrimethylsilane required a total of 46 h heating at 60°C to remove all of the starting material. Only trace amounts of the desired nitrodesilylation product were found and the major products were 2,6-difluoro-3-nitro-phenyltrimethylsilane (12%), 1,3-difluorobenzene (13.4%) and 2,4difluoronitrobenzene (2.6%). The remainder of the product was thought to be unreacted starting material but because of its very high volatility we were unable to isolate it using the



(i) $HNO_3/60^{\circ}$ /3hr. (ii) $HNO_3/Ac_2O/60^{\circ}/22hr.$ (iii) $HNO_3/Ac_2O/50^{\circ}$ 23hr and 4hr (second aliquot) (iv) $HNO_3/60^{\circ}/4hr$. then 17hr.(second aliquot) (v) (HNO_3/Ac_2O)x3 50°/72hr (vi) $HNO_3x3/60^{\circ}/46hr$

Fig. 2.

work up procedure necessary to remove all the acids. When we repeated the reactions using Eaborn's method (i.e. the addition of a solution of the silane in acetic acid to a premixed mixture of nitric acid in acetic anhydride) the situation was worse in terms of protodesilylation vis-a-vis nitrodesilylation, and the two sets of results are compared in Fig. 2. Thus, it can be concluded that as a preparative method, except as a method for substituted nitrofluorobenzenes of unusual orientation, nitrodesilylation has few advantages over other methods. This is in contrast to bromodesilylation which clearly has significant value as a synthetic method. Some of the minor products in both bromo- and nitrodesilylations were isolated in such small amounts that they were not totally characterised. From the evidence we obtained from spectroscopic data and from mass spectrometric data we are confident that the structural assignments are correct even though we could not obtain elemental analyses.

However, from a mechanistic point of view, even allowing for the problems of competing protodesilylation outlined above, a pattern of reactivity clearly arises. Reactions of compounds which contain the trimethylsilyl group with a fluorine atom in the *para* position are much more reactive than those compounds which do not have this orientation, as shown in Figs. 1 and 2. These results may be readily explained by considering the effects of both the charge

density at the carbon atom bearing the trimethylsilyl group and the stability of the Wheland intermediate formed by the ipso attack at this carbon atom. The intermediates involved are shown in Fig. 3. It is well established [14] that intermediates of type A are relatively more stable than those of type **B** for electrophilic substitution of halobenzenes. Thus, fluorobenzene with the large -I effect which deactivates the ortho position and the large +M effect which stabilises an α -positive charge, shows a very high *p*:*o* ratio, whilst bromobenzene shows a much smaller p:o ratio. Translating these effects to the trimethylsilanes in question, the intermediates of type C would be expected both to form faster having a higher electron density on the carbon bearing the silyl group available for electrophilic attack, and lead to a more stable Wheland intermediate after the initial attack of the electrophile, when compared with the formation and



stability of intermediates of type **D**. These predictions are in good agreement with the experimental observations we have made in the present study.

We have therefore, demonstrated in the fluoroarene series that halodesilylation is a preparatively viable reaction and indeed leads to some very useful compounds for further synthesis. On the other hand, nitrodesilyation as in the hydrocarbon series, is not of very good general use because of the competing protodesilvlation, but may be of value in certain cases. We believe, that in agreement with the relatively few reactions of Bennetau on monofluoroarene derivatives, that nonprotic electrophilic substitutions e.g. Friedel-Crafts type reactions would also be of value in this series. Furthermore, we have shown a pattern of reactivity, particularly in the bromodesilyation reactions, which should allow us to make a meaningful comparison with the results obtained from the elemental fluorination studies to see if they follow the same trends as known electrophilic reactions and hence can reasonably be classed as electrophilic fluorodesilylations. The results of these studies have been published elsewhere [8].

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