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The synthesis of bromo and iodo trifunctionalised tribenzosilatranes

Rubén Alvarez and Georg H. Mehl*

Department of Chemistry, University of Hull, Hull HU6 7RX, UK

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Abstract—In this report we present a direct synthesis of bromo **8** and iodo **9** trisubstituted tribenzosilatranes. Commercially available *o*-anisidine **1** was transformed into the triarylamine **3** in a two-step sequence, which was halogenated to furnish the tribromo **4** or the triiodo **5** substituted triamines, respectively. Subsequent deprotection of the methyl ethers furnished the novel tripod ligands **6** and **7**. A transilylation reaction in the last step led to the synthesis of the desired *para*-halogenated tribenzosilatranes **8** and **9**.

The effect of hypervalency of organic compounds containing elements of group 14 has been known and studied for more than three decades. Silatranes, which are of interest due to their biological and physicochemical properties, are a good example of such hypercoordination of silicon. Five substituents are bonded to the silicon atom in a quasi trigonal bipyramidal geometry. Tribenzosilatranes, where three benzene rings are fused together have received much attention in fundamental research and in the context of materials science.[1–3]

In the main, research has focused on functionalisation of the apex position of the silicon atom or substitution of the three equatorial oxygen atoms for other heteroatoms (such as N, S, C, etc).[3,4] Tribenzosilatrane molecules where the aromatic systems substituted with aliphatic chains were used, yield materials, which display liquid crystal properties.[5,6] Arguably the design of a route to trifunctionalised tribenzosilatranes, where the silatrane group can be functionalised further would enhance access to this class of materials.

A very efficient manner to build up extended aromatic ring systems, attractive in materials science (i.e., fluorescence, light emission properties) is the use of cross-coupling reactions. Many of these require halogenated, preferably brominated groups. Moreover iodinated materials are also important due their biological activity.[7] This requires reactions with high regioselectivity, which takes into account that reactivity in large aromatic systems is difficult to predict.

Different approaches were attempted towards the synthesis of bromo **8** and iodo **9** substituted tribenzosilatranes. The best results were obtained when the triarylamine **3** was halogenated leading to new materials **4** and **5**. Deprotection of the trimethoxyamines **4** and **5** led to **6** and **7**, which could be used as tripod ligands for elements of groups 13, 14 and 15 or by substituting the halogen atoms for other molecules with more diverse functionalities.

The synthetic route to halogenated tribenzosilatranes **8** and **9** was achieved in four steps beginning with commercially available *o*-anisidine as shown in Scheme 1. Diazotisation and subsequent iodination of *o*-anisidine **1** led to the formation of *o*-iodoanisole **2** in a moderate yield. The combination of **1** and **2** in a copper catalysed reaction furnished the triarylamine **3**,[8] which was brominated selectively at the *para*-positions at room temperature to give **4**, which bears three bromine atoms in its structure. The synthesis of the triiodobenzeneamine **5** was achieved successfully by iodination of **3** with silver(I) trifluoroacetate and molecular iodine in chloroform.

Bromination of the arylamine **3** proceeded successfully under mild conditions.[9] A solution of bromine in chloroform was added dropwise at −78 °C giving as the major product the *para*-substituted tribromo derivative **4** with minor by-products, which could be removed readily by column chromatography. For the insertion of iodine groups a different approach had to be used. A range of reagents and conditions such as I_2/chloroform,

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* Corresponding author. E-mail: g.h.mehl@hull.ac.uk

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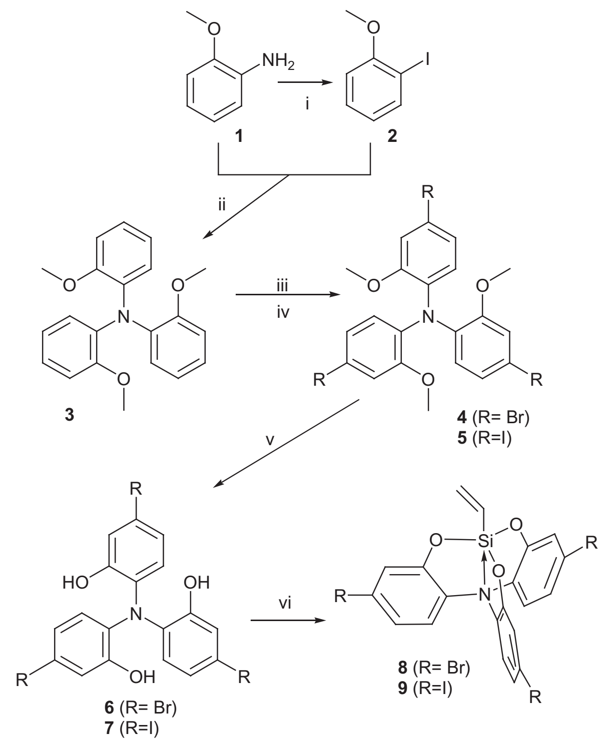

Scheme 1. Reagents and conditions: (i) H_2SO_4, $NaNO_2$, KI; (ii) K_2CO_3, Cu powder, 18-crown-6 ether, (1,2)-dichlorobenzene; (iii) Br_2, dichloromethane; (iv) I_2, silver(I) trifluoroacetate, $CHCl_3$, (v) BBr_3, −78 °C, CH_2Cl_2; (vi) vinyltrichlorosilane, dry di-*n*-butyl ether.

I_2/AcOH,[10] I_2/AcOH/CrO_3,[11] and I_2/HIO_3/AcOH,[12] were investigated but gave unsatisfactory yields. Attempts using I_2/HgO,[13] gave selective *para*-iodination but the results were not always reproducible and the yields tended to be poor. The best results for *para*-substitution were achieved using I_2/silver(I) trifluoroacetate,[14] leading to the desired triiodoarylamine in reproducible yields of 15%.

The removal of the three methyl ethers with BBr_3 at −78 °C was achieved in one step for both iodo **5** and bromo **4** triarylamines leading to the corresponding trihydroxy derivatives **6** and **7**, respectively, which were refluxed in the presence of trichlorovinylsilane and dry di-*n*-butyl ether to give the desired trihalosubstituted tribenzosilatranes **8** and **9** as white solids.[15,16]

A reliable synthetic route towards the selective derivatisation of tribenzosilatranes at the 6′,6″ and 6‴ positions with bromo or iodo groups has been developed. As these groups can be reacted further, this extends the chemistry associated with tribenzosilatranes.

Supplementary data

Experimental details and analytical data are available. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2004.11.034.

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15. Spectroscopic data for **8**: mp = 183 °C, TLC (SiO_2, CH_2Cl_2): $R_f = 0.74$, ^1H NMR ($CDCl_3$) δ: 6.18 (3H, m), 7.09 (3H, dd, $J = 8.4, 2.2$), 7.23 (3H, d, $J = 2.2$), 7.51 (3H, d, $J = 8.4$). ^{13}C NMR ($CDCl_3$) δ: 121.67, 122.51, 125.62, 127.19, 130.64, 134.83, 135.84, 153.81. ^{29}Si NMR DEPT ($CDCl_3$) δ: −71.25. Anal. Calcd for $C_{20}H_{12}Br_3NO_3Si$ (582.12): C, 41.27; H, 2.08; N, 2.41. Found: C, 41.29; H, 2.28; N, 2.42. MS (MALDI-TOF) = 583.94 $[M]^+$, 582.95 $[M]^+$.
16. Spectroscopic data for **9**: mp = 245 °C, TLC [SiO_2, CH_2Cl_2/hexane (1:1)]: $R_f = 0.51$, ^1H NMR ($CDCl_3$) δ: 6.06 (3H, m), 7.19 (3H, dd, $J = 8.2, 1.8$), 7.27 (3H, d, $J = 8.2$), 7.32(3H, d, $J = 1.8$). ^{13}C NMR ($CDCl_3$) δ: 93.77, 127.48, 127.51, 130.67, 131.63, 135.49, 135.80, 153.64. ^{29}Si NMR DEPT ($CDCl_3$) δ: −71.75. Anal. Calcd for $C_{20}H_{12}I_3NO_3$ (723.11): C, 33.22; H, 1.67; N, 1.94. Found: C, 33.48; H, 1.32; N, 1.92.