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A CONVENIENT SYNTHESIS OF ARYLBIS(ETHYLTRIFLUOROSILICONATE)S

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Abstract: The syntheses of new arylbis(ethyltrifluorosiliconate)s with potassium:18-crown-6, NBu4, NEt4 and NMe4 counterions are reported. These were prepared by reacting the corresponding arylbis(ethyldifluorosilane)s with the appropriate source of fluoride. Alternatively, the NBu4 and potassium:18-crown-6 salts were prepared in nearly quantitative yield in a novel one pot reaction between arylbis(ethyldiethoxysilane)s and a tetrabutylammonium fluoride /HF or KF/18-crown-6/HF mixture.

Pentacoordinate silicon compounds have been intensively studied over the past thirty years from a structural investigation point of view and also as possible reactive intermediates in nucleophilic displacement reactions at silicon.¹ In particular, fluorosilicates have received much attention from several groups and many structural determinations have been carried out.² One example is the potassium:18-crown-6 salt of difluorotriphenylsiliconate (1) prepared by Damrauer and Danahey.^{2a}



The recently developed Hiyama coupling reaction between arylfluorosilanes and aryliodides or aryl triflates to give biaryls is mediated by a palladium catalyst and tetrabutylammonium fluoride (TBAF) as a 'transmetallation accelarator' (Scheme 1).^{3,4}



The authors implicate the pentacoordinate siliconate species 2 as an intermediate. They speculate that formation of a third strong Si-F bond (541 kJ/mol) weakens the aryl-Si bond and facilitates transfer of the aryl group to palladium in the transmetallation step of the catalytic cycle. Evidence for the involvement of pentacoordinated

silicon was provided by the direct reaction of 1 with 4-iodoacetophenone in the presence of Pd but with no added fluoride to give the resultant biaryl in 96% yield (Scheme 2).⁵ Scheme 2

We were interested in investigating the potential of the Hiyama reaction for aryl-aryl and aryl-acetylene coupling in the synthesis of poly(*para*-phenylene)s (PPP's) and poly(*para*-phenylene-acetylene)s (PPPA's). Arylbis(ethyltrifluorosiliconate)s were targetted as monomers. Here the syntheses of some pure, crystalline arylbis(ethyltrifluorosiliconate)s via a novel one pot reaction of arylbis(ethyldiethoxysilane)s with TBAF/HF or KF/18-crown-6/HF are described.

Arylbis(ethyldiethoxysilane)s 3, 4 and 5 were synthesized from the corresponding dibromides in a Barbier-Grignard type reaction with Mg and triethoxyethylsilane (TEES) (Scheme 3).⁶ They were isolated by distillation as clear, colourless liquids in good (65-75%) yields.



Attempts to prepare the arylbis(ethyldifluorosilane)s by reaction of 3-5 with excess HF led to low yields of impure products (in contrast to the production of aroyloxymethyltrifluorosilanes by this method⁷). However, reaction with excess BF₃.OEt₂ provided 6-8 as clear, somewhat unstable oils in 50 - 60% yield(Scheme 4).⁸ Scheme 4



Reaction of the substituted bis(difluorosilane)s 7 and 8 with two equivalents of TBAF, tetraethylammonium fluoride (TEAF) or tetramethylammonium fluoride (TMAF) resulted in the formation of the corresponding bissiliconates as oils or semi-solids. Suitable recrystallization solvents could not be found. Reaction of 6 with two equivalents of 18-crown-6/KF in THF gave in high yield the non-hygroscopic bistrifluorosiliconate 9 (Scheme 5).⁹

9 could be purified by recrystallization from ether/acetone. It was noticed that THF solutions of 9 became gradually hazy with time eventually precipitating an unidentified, insoluble white solid, a process which was accelarated by warming. In a strongly coordinating solvent like THF there is likely to be competition between the solvent molecules and the crown ether for complexation with the potassium cation; it is speculated that if the

crown ether were to become dislodged the resulting potassium arylethyltrifluorosilicate (or dipotassium arylbis(ethyltrifluorosiliconate)) might irreversibly precipitate.

The reaction of 6 with TMAF, TEAF or TBAF provided 10 and 11 as highly crystalline (THF insoluble) salts and 12 as a clear viscous oil, all in quantitative yields (Scheme 6).¹⁰

Scheme 6
6
$$\underline{\text{TMAF, TEAF or TBAF}}_{F_3 \text{Et}\tilde{\text{Si}}} = \underbrace{\begin{array}{c} 10 \\ \tilde{\text{Si}} \text{Et}F_3 \end{array}}_{Si \text{Et}F_3} 2 \text{NR}_4^+ \begin{array}{c} 11 \\ 11 \\ R = \text{Et} \end{array}$$

In order to prepare a crystalline TBA derivative compound 13 was prepared.¹¹ It was discovered that dropwise addition of a THF solution of 13 to a THF solution containing two equivalents of TBAF and four equivalents of HF gave (after solvent removal) a quantitative yield of 14 as a white solid, pure by NMR (Scheme7).¹² Recrystallization from THF/ether produced fine needles. Compounds 9 and 12 could be prepared analagously in high yield. This one pot procedure avoids the necessity of preparing the bis(difluorosilane) intermediates and should prove useful for the preparation of a wide range of fluorosiliconate derivatives.¹³ The use of these novel arylbis(ethyltrifluorosiliconate)s in the preparation of PPP's is currently under investigation.



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6. Shea, K. J.; Loy, D. A.; Webster, O. J. Am. Chem. Soc. **1992**, 114, 6700. A typical procedure is given for the preparation of 3. 1,4-dibromobenzene (39.2 g, 0.166 mol) in THF (100 ml) was added dropwise to Mg turnings (11.9 g, 1.5 eq.) suspended in THF (100 ml) and TEES (250 ml, freshly distilled from CaH₂) at reflux temperature. After complete addition reflux was continued for two hours. The cooled solution was filtered and solvents and excess TEES removed by rotary evaporation. Distillation of the residue gave pure 3 (43.7 g, 71%). ¹H NMR (CDCl₃) δ 7.62 (s, 4, ArH), 3.79 (q, 8, OCH₂), 1.20 (t, 12, OCH₂CH₃), 0.96 (t, 6, SiCH₂CH₃), 0.82 (q, 4, SiCH₂). ¹³C{¹H} NMR (CDCl₃) δ 135.5, 133.3, 58.2, 18.1, 6.1, 4.5. Data for 4: ¹H NMR (CDCl₃) δ 7.12 (s, 2, ArH), 3.95 (q, 8, OCH₂), 3.78 (s, 6, OCH₃), 1.35 (t, 6, OCH₂CH₃), 1.01 overlapping (SiCH₂CH₃). ¹³C{¹H} NMR (CDCl₃) δ 158.0, 125.0, 117.2, 58.0, 55.1, 17.9, 5.9, 5.0. Data for **5**: ¹H NMR (CDCl₃) δ 7.12 (s, 2, ArH), 3.97 (t, 4, ArOCH₂), 3.85 (q, 8, SiOCH₂), 1.79 (m, 4, CH₂), 1.50 (m, 4, CH₂), 1.34 (m, 8, CH₂), 1.24 (t, 12, SiOCH₂CH₃), 0.95 (t, 6, CH₃), 0.95 overlapping (SiCH₂CH₃). ¹³C{¹H} NMR (CDCl₃) δ 157.5, 124.9, 118.0, 67.9, 58.1, 31.5, 29.4, 25.6, 22.4, 18.1, 13.6, 6.1, 5.3.

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8. Even after repeated distillation the arylbis(ethyldifluorosilane)s could not be completely purified; the impurity (5%) did not affect their subsequent reactions, however. Data for 6: ¹H NMR (CDCl₃) δ 7.76 (s, 4, ArH), 1.10 overlapping (SiCH₂CH₃). ¹³C{¹H} NMR (CDCl₃) δ 133.0, 132.8(t), 4.8, 3.9(t). Data for 7: ¹H NMR (CDCl₃) δ 7.09 (s, 2, ArH), 3.82 (s, 6, OCH₃), 1.04 overlapping (SiCH₂CH₃). ¹³C{¹H} NMR (CDCl₃) δ 158.8, 123.0(t), 116.4, 155.8, 4.5(t), 4.4. Data for 8: ¹H NMR (CDCl₃) δ 7.05 (s, 2, ArH), 3.96 (t, 4, ArOCH₂), 1.77 (m, 4, CH₂), 1.49 (m, 4, CH₂), 1.35 (m, 8, CH₂), 0.92 (t, 6, CH₃), 0.92 overlapping (SiCH₂CH₃). ¹³C{¹H} NMR (CDCl₃) δ 159.0, 123.8(t), 69.5, 32.0, 29.8, 26.3, 23.0, 14.2, 5.9(t), 5.7.

9. The structure was confirmed by NMR. ¹H NMR (DMSO) δ 7.75 (s, 4, ArH), 3.59 (s, 48, crown ether), 1.00 (t, 6, SiCH₂CH₃), 0.71 (q, 4, SiCH₂). ¹³C{¹H} NMR (DMSO) δ 136.0, 133.9, 69.3 (crown ether), 8.8, 7.9. At 30°C no fluorine/carbon coupling was seen.

10. A general procedure involved stirring **6** with the reagents in THF solution at room temperature for about twenty minutes followed by solvent removal. Data for **10**: ¹H NMR (DMSO) δ 7.51 (s, 4, ArH), 3.01 (s, 24, NCH₃), 0.88 (t, 6, SiCH₂CH₃), 0.51 (q, 4, SiCH₂). ¹³C{¹H} NMR (DMSO) δ 145.5, 134.6, 54.2, 12.5, 9.8. Data for **11**: ¹H NMR (DMSO) δ 7.62 (s, 4, ArH), 3.18 (q, 16, NCH₂), 1.04 (t, 24, NCH₂CH₃). Other signals masked by resonance at 1.04 ppm. ¹³C{¹H} NMR (DMSO) δ 141.8, 134.1, 51.8, 9.4, 8.3, 7.1. Data for **12**: ¹H NMR (DMSO) δ 7.71 (s, 4, ArH), 3.32 (t, 16, NCH₂), 1.71 (m, 16, NCH₂CH₂), 1.37 (m, 16, NCH₂CH₂CH₂CH₂), 0.94 (t, 24, NCH₂CH₂CH₂CH₃). Other signals masked by resonance at 0.94 ppm. ¹³C{¹H} NMR (DMSO) δ 142.2, 134.6, 59.0, 24.2, 20.1, 13.7, 8.6, 7.7.

11. Compound 13 was prepared from 4,4'-dibromobiphenyl. ¹H NMR (CDCl₃) δ 7.76 (d, 4, ArH), 7.66 (d, 4, ArH), 3.90 (q, 8, SiOCH₂), 1.30 (t, 12, SiOCH₂CH₃), 1.05 (t, 6, SiCH₂CH₃), 0.92 (q, 6, SiCH₂). ¹³C{¹H} NMR (CDCl₃) δ 142.9, 137.8, 130.2, 127.0, 59.3, 14.4, 9.1, 8.7.

12. CAUTION: HF is highly toxic. Suitable protective clothing should be worn. Data for 14: ¹H NMR (DMSO) δ 7.98 (d, 4, ArH), 7.45 (d, 4, ArH), 3.37 (t, 16, NCH₂), 1.68 (m, 16, NCH₂CH₂), 1.36 (m, 16, NCH₂CH₂CH₂), 1.04 (t, 6, SiCH₂CH₃), 0.95 (t, 24, NCH₂CH₂CH₂CH₃), 0.69 (q, 4, SiCH₂). ¹³C{¹H} NMR (DMSO) δ 147.8, 140.7, 138.5, 125.0, 58.9, 24.3, 20.1, 13.8, 13.4, 10.3.

13. For example, the potassium:18-crown-6 salt of tetrafluoro-(2-methoxy-5-methyl)phenylsiliconate was prepared by the dropwise addition of triethoxy(2-methoxy-5-methyl)phenylsilane to a THF solution of KF/18-crown-6/HF. ¹H NMR (DMSO) δ 7.21 (d, 1, ArH), 6.85 (dd, 1, ArH), 6.63 (d, 1, ArH), 3.68 (s, 3, ArOCH3), 3.61 (s, 24, crown ether), 2.18 (s, 3, ArCH3). ¹³C{¹H} NMR (DMSO) δ 162.4, 134.6, 128.0, 111.3, 70.7 (crown ether), 56.4, 20.8. As others have found^{2a} the resonance of the aryl carbon bonded to silicon was not seen at 30°C.

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