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Alkaline-earth-metal arenesulfonates as precursors to organic derivatives of Group 2 metals[†]

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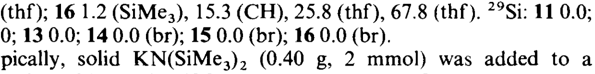
Treatment of the readily accessible alkaline-earth-metal arenesulfonates $M(OSO_2R)_2$ (from $MCO_3 + 2RSO_3H$) with one of a range of Li, Na or K organic compounds in tetrahydrofuran (thf) afforded the corresponding alkaline-earth-metal organic compound ln high yield, including the novel compounds $LiM(OSO_2R)_2[CH(SiMe_3)_2](thf)$ and $KM[CH(SiMe_3)_2]_3(thf)_3$ (M = Ca, Sr or Ba; R = C_6H_4Me-4, $C_6H_2Me_3$-2,4,6 or $C_6H_4Bu^t$-4.

There is much current interest in lipophilic organic compounds $MX_2(L)_n$ of the heavier alkaline-earth metals M.[1] Appropriate ligands X^- are bulky, have a multiplicity of methyl groups and are free from β-hydrogen; examples include the amides $N(SiMe_3)_2$,[2–4] 2,6-di-*tert*-butylphenoxides (*e.g.* $OC_6H_2Bu^t_2$-2,6-Me-4),[2,4] alkyls $CH(SiMe_3)_2$ and cyclopentadienyls [*e.g.* η^5-C_5Me_5 or η-$C_5H_3(SiMe_3)_2$-1,3].[5]

We have previously described the synthesis of some of these lipophilic compounds from the anhydrous metal trifluoromethanesulfonates $M(O_3SCF_3)_2$ and the appropriate sodium or potassium organic compound;[6] a feature of this procedure was the ease of preparation and handling characteristics of $M(O_3SCF_3)_2$. We now report (*i*) an improved synthesis of these $MX_2(L)_n$ compounds (Scheme 1) and its application to a wider range of such compounds, using as precursor the alkaline-earth-metal arenesulfonates $M(OR)_2$ (R = $SO_2C_6H_4Me$-4, M = Ca **1**, Sr **2** or Ba **3**; R = $SO_2C_6H_2Me_3$-2,4,6, M = Ca **4**, Sr **5** or Ba **6**; R = $SO_2C_6H_4Bu^t$-4, M = Ca **7**, Sr **8** or Ba **9**) (hydration of **5** gave the nonahydrate **10**); (*ii*) the characterisation of the new compounds **1**–**9** by IR[‡] and NMR[§] spectroscopy; and (*iii*) the spectroscopic characterisation of the novel alkylmetalate complexes $LiM(OSO_2C_6H_4Me$-$4)_2[CH(SiMe_3)_2](thf)$ (thf = OC_4H_8, M = Ca **11**, Sr **12** or Ba **13**) and $KM[CH(SiMe_3)_2]_3(thf)_3$ (M = Ca **14**, Sr **15** or Ba **16**)[§].

Compounds **1**–**9** were prepared in high yield from the appropriate sulfonic acid and MCO_3, Scheme 1.[¶] Treatment of compounds **1**–**9** with one of a range of alkali-metal organic compounds M′X under ambient conditions in thf gave the corresponding $MX_2(thf)_n$ compound in high yield [X = $N(SiMe_3)_2$, $OC_6H_2Bu^t_2$-2,6-Me-4, η^5-C_5Me_5 or η^5-$C_5H_3(SiMe_3)_2$-1,3], Scheme 2.[¶] A significant improvement over our earlier $M(O_3SCF_3)_2$-based syntheses[6] is that the barium amide $Ba[N(SiMe_3)_2]_2(thf)_2$ was readily obtained, whereas reaction between $NaN(SiMe_3)_2$ and $Ba(O_3SCF_3)_2$ under similar conditions gave $Ba[N(SiMe_3)_2][\mu$-$N(SiMe_3)_2]_2$-$Na(thf)_2$.[6] Furthermore, when the solvent was changed from thf to diethyl ether, $KN(SiMe_3)_2$ with $M(OR)_2$ **1**–**9** gave the homoleptic amide $[M\{N(SiMe_3)_2\}\{\mu$-$N(SiMe_3)_2\}]_2$.

The alkaline-earth-metal trifluoromethanesulfonates $M(O_3SCF_3)_2$ also proved to be unreactive towards bis(trimethylsilyl)methyl-potassium or -lithium, but by contrast $M(OSO_2C_6H_4Me$-$4)_2$ and $LiCH(SiMe_3)_2$ or $KCH(SiMe_3)_2$ in thf gave the metalates **11**–**16**, Scheme 2 (the other alkaline-earth-metal sulfonates **4**–**9** gave similar products).[¶] Although X-ray quality crystals of **11**–**16** {or the other arenesulfonate analogues of $LiM(OSO_2C_6H_4Me$-$4)_2[CH(SiMe_3)_2](thf)$} have



$$MCO_3 \xrightarrow{(i)} M(OSO_2R)_2(H_2O)_n \xrightarrow{(ii)} \underset{\textbf{1–9}}{M(OSO_2R)_2}$$

Scheme 1 Synthesis (99%) of the alkaline-earth-metal arenesulfonates **1**–**9**. R = C_6H_4Me-4, M = Ca **1**, Sr **2** or Ba **3**; R = $C_6H_2Me_3$-2,4,6, M = Ca **4**, Sr **5** or Ba **6**; R = $C_6H_4Bu^t$-4, M = Ca **7**, Sr **8** or Ba **9**. (*i*) 5% excess of metal carbonate, $2HOSO_2R$, H_2O, 25 °C; stirred for 4 h, followed by filtration and removal of water *in vacuo*; (*ii*) 200 °C at 10^{-5} Torr (≈0.001 33 Pa), 12 h

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[†] No reprints available.

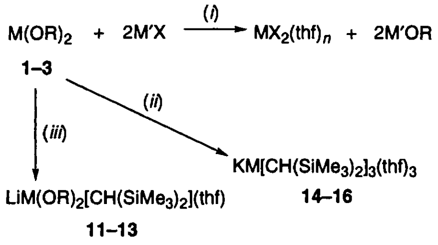
[‡] IR spectroscopic data (cm^{-1}): $\nu_{asym}(SO_3)$ **1**–**9** hidden by aromatic absorptions; $\nu_{sym}(SO_3)$ **1** 1145, **2** 1150, **3** 1134, **4** 1197, **5** 1193, **6** 1193, **7** 1148, **8** 1145, **9** 1142; $\delta_{sym}(SO_3)$ **1** 698, **2** 682, **3** 693, **4** 687, **5** 683, **6** 685, **7** 662, **8** 662, **9** 660; $\delta_{asym}(SO_3)$ **1** 596, 586, 566, 551; **2** 585, 564; **3** 586, 577, 564, 550; **4** 582, 551; **5** 581, 553; **6** 583, 553; **7** 585, 560; **8** 582, 560; **9** 580, 559.

[§] NMR chemical shifts (δ) [at 298 K in CD_3OD (**1**–**9**) or NC_5D_5 (**11**–**16**) for ^1H and NC_5D_5–MeOH (**1**–**3**), CD_3OD–MeOH (**4**–**9**) for ^{13}C or NC_5D_5–NC_5H_5 (**11**–**16**) for ^{13}C and ^{29}Si. ^1H at 360.14 MHz, ^{13}C at 62.90 MHz and ^{29}Si at 49.70 MHz]. ^1H: **1**–**3** 2.20 (s, 6 H), 7.16 and 7.18 (4 H, ^3J = 8.2), 7.48 and 7.50 (4 H, ^3J = 8.2); **4**–**6** 2.23 (s, 6 H), 2.60 (s, 12 H), 6.87 (s, 4 H); **7**–**9** 1.22 (s, 18 H), 7.35 and 7.39 (4 H, ^3J = 8.6), 7.63 and 7.66 (4 H, ^3J = 8.6); **11** −0.33 (CH), 0.06 ($SiMe_3$), 1.59 (thf), 2.12 (Me), 3.63 (thf), 7.04 and 7.07 (^3J = 7.8), 8.26 and 8.29 (^3J = 8.0); **12** −0.33 (CH), 0.03 ($SiMe_3$), 1.59 (thf), 2.12 (Me), 3.63 (thf), 7.03 and 7.06 (^3J = 7.8), 8.21 and 8.24 (^3J = 7.9); **13** −0.34 (CH), 0.03 ($SiMe_3$), 1.59 (thf), 2.11 (Me), 3.63 (thf), 7.04 and 7.07 (^3J = 7.3), 8.22 and 8.25 (^3J = 7.8 Hz); **14** −0.31 (CH), 0.04 ($SiMe_3$), 1.60 (thf), 3.65 (thf); **15** −0.33 (CH), 0.03 ($SiMe_3$), 1.59 (thf), 3.63 (thf); **16** −0.38 (CH), 0.05 ($SiMe_3$), 1.40 (thf), 3.57 (thf). ^{13}C: **1**–**3** 143.6 ± 0.4 ($COSO_2$), 127.3 (*o*-C), 130.1 (*m*-C), 142.1 ± 0.2 (*C*Me); **4**–**6** 20.7 (*p*-C*Me*), 23.1 (*o*-C*Me*), 140.5 ($COSO_2$), 131.7 (*o*-*C*Me), 138.2 (*m*-C), 140.1 (*p*-*C*Me); **7**–**9** 31.5 (qt), 35.6 (s), 155.1 ($COSO_2$), 126.2 (*o*-C), 126.8 (*m*-C), 142.6 ± 0.2 (*p*-*C*Bu^t); **11** 1.4 ($SiMe_3$), 21.0 (Me), 25.8 (thf), 67.8 (thf), 126.8, 128.9, 139.6, 144.8 (aromatic); **12** 1.4 ($SiMe_3$), 21.0 (Me), 25.8 (thf), 67.8 (thf), 126.5, 128.8, 139.8, 144.2 (aromatic); **13** 1.4 ($SiMe_3$), 21.0 (Me), 25.8 (thf), 67.8 (thf), 126.8, 128.8, 139.5, 145.1 (aromatic); **14** 1.0 ($SiMe_3$), 15.3 (CH), 25.8 (thf), 67.8 (thf); **15** 1.2 ($SiMe_3$), 15.4 (CH), 25.8 (thf), 67.8 (thf); **16** 1.2 ($SiMe_3$), 15.3 (CH), 25.8 (thf), 67.8 (thf). ^{29}Si: **11** 0.0; **12** 0.0; **13** 0.0; **14** 0.0 (br); **15** 0.0 (br); **16** 0.0 (br).

[¶] Typically, solid $KN(SiMe_3)_2$ (0.40 g, 2 mmol) was added to a suspension of 1 mmol $M(OSO_2C_6H_4Me$-$4)_2$ (M = Ca 0.38 g, Sr 0.43 g or Ba 0.48 g) in thf (100 cm^3) and the mixture was stirred at ambient temperature for 4 h. The mixture was filtered into a weighed Schlenk tube and the solvent was removed from the filtrate *in vacuo* giving $M[N(SiMe_3)_2]_2(thf)_2$ (M = Ca 0.43 g, 86%; Sr 0.45 g, 82%; or Ba 0.46 g, 77%). Reacting the toluene-*p*-sulfonates and the potassium amide under similar conditions, using diethyl ether rather than thf, gave the base-free amides $[M\{N(SiMe_3)_2\}\{\mu$-$N(SiMe_3)_2\}]_2$ (M = Ca 0.55 g, 80%; Sr 0.57 g, 78%; or Ba 0.55 g, 71%).

Solid $LiCH(SiMe_3)_2$ (0.34 g, 2 mmol) was added to a suspension of 1 mmol $M(OSO_2C_6H_4Me$-$4)_2$ (M = Ca 0.38 g, Sr 0.43 g or Ba 0.48 g) in thf (100 cm^3) and the mixture was stirred at ambient temperature for 12 h. The mixture was filtered into a weighed Schlenk tube and the solvent was removed from the filtrate *in vacuo* giving $LiM(OSO_2$-C_6H_4Me-$4)_2[CH(SiMe_3)_2](thf)$ (M = Ca, Sr or Ba).

Similarly from solid $KCH(SiMe_3)_2$ (0.40 g, 2 mmol) and 1 mmol $M(OSO_2C_6H_4Me$-$4)_2$ (M = Ca 0.38 g, Sr 0.43 g or Ba 0.48 g) in thf (100 cm^3), there was obtained $KM[CH(SiMe_3)_2]_3(thf)_3$ (M = Ca, Sr or Ba) in *ca.* 80% yield.



Scheme 2 Synthesis of alkaline-earth-metal complexes from the metal toluene-*p*-sulfonates. R = $SO_2C_6H_4Me$-4, M = Ca **11** or **14**, Sr **12** or **15**, or Ba **13** or **16**; M′X = KN((SiMe$_3$)$_2$, KOC$_6$H$_2$Bu$^t{}_2$-2,6-Me-4, Na(η^5-C$_5$Me$_5$) or Li[η^5-C$_5$H$_3$(SiMe$_3$)$_2$-1,3]. (*i*) thf, 25 °C, 4 h; (*ii*) 2KCH(SiMe$_3$)$_2$, thf, 25 °C, 12 h; (*iii*) 2LiCH(SiMe$_3$)$_2$, thf, 25 °C, 12 h; followed in each of (*i*)–(*iii*) by filtration and removal of the solvent from the filtrate *in vacuo*

not yet been obtained, their formulations are based on satisfactory microanalyses and NMR spectra and comparison of the latter with corresponding data for M[CH(SiMe$_3$)$_2$]$_2$(thf)$_3$ (M = Ca or Sr)[4] and K[CH(SiMe$_3$)$_2$](thf)$_n$.[7] The reaction between M(OSO$_2$C$_6$H$_4$Me-4)$_2$ and LiCH(SiMe$_3$)$_2$ yielding LiM(OSO$_3$C$_6$H$_4$Me-4)$_2$[CH(SiMe$_3$)$_2$](thf) **11**–**13** is reminiscent of that between Ba(η^5-C$_5$Me$_5$)$_2$(thf)$_2$ and LiCH(SiMe$_3$)$_2$ which gave LiBa(η^5-C$_5$Me$_5$)$_2$[CH(SiMe$_3$)$_2$](thf) **17**.[8] Compounds **11**–**17** may well all be structurally related and are either M'^+–M^- solvated ion pairs (M′ = an alkali metal) containing alkaline-earth-metalate anions M′(MX$_2$X′) or bridged bimetallic compounds MX′(μ-X)$_2$M′, related to the X-ray characterised ytterbium compound [Yb{N(SiMe$_3$)$_2$}{μ-N(SiMe$_3$)$_2$}$_2$Na].[9]

The syntheses described above for various alkaline-earth-metal organic compounds, using as precursor the alkaline-earth-metal toluene-*p*-sulfonate **1**–**3** (or its obvious equivalent **4**–**9**, each readily available from the metal carbonate), are capable of extension to other metals and a wider range of ligands. While toluene-*p*-sulfonate has long been a valuable leaving group in organic chemistry, it has not hitherto been employed in the inorganic sphere; although in the context of Group 2 metal chemistry it is evidently superior to trifluoromethanesulfonate.

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