Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

REARRANGEMENTS OF p-$LiC_6H_4SMR_3$ TO p-$R_3MC_6H_4SLi$ COMPOUNDS ($M=Ge$ OR Si). A NOVEL SYNTHESIS OF ORGANOGERMYL- AND -SILYLBENZENE THIOLS

A. R. BASSINDALE AND D. R. M. WALTON
School of Molecular Sciences, University of Sussex, Brighton BN1 9QJ, Sussex (Great Britain)

(Received July 1st, 1970)

SUMMARY

Organolithium reagents prepared from $BrC_6H_4SMR_3$ compounds ($R_3M=Me_3Si$, Et_3Si, $PhMe_2Si$, Me_3Ge) and butyllithium rearrange rapidly in ether solution to $R_3MC_6H_4SLi$ species, which upon treatment with water yield benzene thiols $R_3MC_6H_4SH$. Under Wurtz–Fittig "*in situ*" conditions the organosodium intermediate $NaC_6H_4SSiMe_3$ does not rearrange but couples normally with Et_3SiBr to give $Et_3SiC_6H_4SSiMe_3$, which on methanolysis gives $Et_3SiC_6H_4SH$. These reactions provide useful new routes to silyl- and germyl-substituted benzene thiols.

INTRODUCTION

The trimethylsilyl group finds considerable use as a protecting agent for aromatic amines[1] and for phenols[2] in Grignard, organolithium and Wurtz–Fittig syntheses. The success of the method depends essentially upon the resistance of N–Si and O–Si bonds to attack by the organometallic intermediates in such reactions, whereas these bonds are readily broken under the acid or neutral hydrolytic conditions associated with subsequent working up procedures. In attempting to extend this protective technique to thiol groups, we have discovered a useful synthesis of germyl- and silyl-substituted benzene thiols which involves migration of the germyl and silyl groups to a carbanion centre.

RESULTS AND DISCUSSION

p-Bromo-and chlorobenzene thiol, selected as model compounds, were readily converted to their respective S-trimethylsilyl derivatives by established procedures[3], either by treatment with phenyllithium followed by chlorotrimethylsilane, or by boiling under reflux with chlorotrimethylsilane and triethylamine or with excess of hexamethyldisilazane. All three methods gave the required products in excellent yield, but the silazane method, which avoids a troublesome filtration and exposure of ether solutions to atmospheric moisture, was found to be superior as it gave products free from unsilylated thiol. This preparative method was adopted for other S-germyl and -silyl derivatives discussed below.

Initially, p-bromo-S-(trimethylsilyl)benzene thiol was treated with butyllithium followed by chlorotrimethylsilane. Work up of the reaction mixture under anhydrous conditions gave a product which analysed correctly for *p*-trimethylsilyl-*S*-(trimethylsilyl)benzene thiol and which upon boiling under reflux with methanol gave *p*-(trimethylsilyl)benzene thiol in virtually quantitative yield. This reaction sequence does not necessarily imply successful protection of the thiol group however, since although it demonstrates that the bromo compound undergoes halogen-metal exchange with butyllithium, the intermediate (I) so formed could have rearranged by an inter- or intramolecular process to give (II)

$$p\text{-LiC}_6\text{H}_4\text{SSiMe}_3\ (\text{I}) \rightarrow p\text{-Me}_3\text{SiC}_6\text{H}_4\text{SLi}\ (\text{II})$$

and reaction of either (I) or (II) with chlorotrimethylsilane would give *p*-trimethylsilyl-*S*-(trimethylsilyl)benzene thiol. In order to distinguish between these alternatives, the intermediate from the halogen-metal exchange [*i.e.* (I) or (II)] was coupled with bromotriethylsilane, and the product (III) was submitted to methanolysis. *p*-(Trimethylsilyl)benzene thiol was again obtained together with triethylmethoxysilane and no *p*-(triethylsilyl)benzene thiol could be detected among the reaction products. This result demonstrates unequivocally that rearrangement (I)→(II) had indeed occurred and that the intermediate (III) was *p*-trimethylsilyl-*S*-(triethylsilyl)benzene thiol. Confirmation of a rearrangement was provided by treating the organolithium intermediate with water; as expected, *p*-(trimethylsilyl)benzene thiol was the sole reaction product.

This rearrangement provides a novel, simple route to silyl-substituted benzene thiols, and provides an attractive alternative to the method used hitherto, namely reaction of silyl-substituted aryl Grignard reagents with sulphur[5]. The generality of the method was demonstrated by treating *p*-bromobenzene thiol with (diethylamino)-triethylsilane or dimethyl(ethylamino)phenylsilane. The *S*-silylated products thus obtained when treated with butyllithium followed by water gave excellent yields of the thiols $p\text{-Et}_3\text{SiC}_6\text{H}_4\text{SH}$ and $p\text{-(PhMe}_2\text{Si)C}_6\text{H}_4\text{SH}$, respectively. The reaction sequence was successfully extended to the synthesis of the compound $p\text{-Me}_3\text{Ge-C}_6\text{H}_4\text{SH}$, the first example of a germanium substituted benzene thiol.

In situ techniques often allow reactive intermediates to be trapped and have been successfully employed in the synthesis of organosilicon compounds in recent years[4]. In this context a Wurtz–Fittig reaction between *p*-chloro-*S*-(trimethylsilyl)-benzene thiol and bromotriethylsilane gave a single product (IV) which upon methanolysis afforded *p*-(triethylsilyl)benzene thiol and methoxytrimethylsilane. Clearly the organosodium intermediate $p\text{-NaC}_6\text{H}_4\text{SSiMe}_3$ is trapped by coupling with the bromosilane before a rearrangement similar to the transformation (I)→(II) can take place, so that in this instance the trimethylsilyl group does act in a protective capacity.

EXPERIMENTAL

p-Chloro-S-(trimethylsilyl)benzene thiol

A filtered solution of phenyllithium, prepared from bromobenzene (52.3 g, 0.33 mole) and lithium (6.9 g, 1.0 g-atom) in ether (250 ml), was added at 0° to a stirred solution of *p*-chlorobenzene thiol (65 g, 0.30 mole) in ether (100 ml). The mixture was boiled under reflux for 10 min to complete the metallation, then chlorotrimethylsilane (34.7 g, 0.32 mole) was added and the mixture was boiled under reflux for a further

2 h. Precipitated salts were filtered off under a blanket of dry nitrogen and the filtrate was distilled to give a forerun of *p*-chlorobenzene thiol (1.5 g) followed by *p*-chloro-*S*-(trimethylsilyl)benzene thiol (nc) (63.8 g, 92%) b.p. 95°/3.3 mm, n_D^{25} 1.5460. (Found: C, 49.7; H, 6.2; Cl, 16.3. $C_9H_{13}ClSSi$ calcd.: C, 49.9; H, 6.1; Cl, 16.4%.)

p-Bromo-S-(trimethylsilyl)benzene thiol

Method 1. Chlorotrimethylsilane (56.3 g, 0.52 mole) was added during 1 h to a solution of *p*-bromobenzene thiol (90 g, 0.5 mole) in anhydrous triethylamine (52.5 g, 0.52 mole) and ether (250 ml). The mixture was subsequently boiled under reflux for 1 h then cooled and filtered. The precipitated salts were washed with ether (100 ml) and the combined filtrates were distilled to give a forerun of *p*-bromobenzene thiol (5.3 g) b.p. 74–76°/1.5 mm which crystallised in the receiver followed by *p*-bromo-*S*-(trimethylsilyl)benzene thiol (nc) (112 g, 86%) b.p. 98°/2.0 mm, n_D^{25} 1.5642. (Found: C, 41.4; H, 5.0; Br, 30.7. $C_9H_{13}BrSSi$ calcd.: C, 41.4; H, 5.0; Br, 30.6%.)

Method 2. Hexamethyldisilazane (43.5 g, 0.27 mole) was added to a stirred solution of *p*-bromobenzene thiol (90 g, 0.5 mole) in ether (200 ml) and a white solid precipitated immediately from solution. The mixture was boiled under reflux for 2 h, whereupon the solid dissolved and ammonia was evolved. Fractionation of the resulting clear solution gave *p*-bromo-*S*-(trimethylsilyl)benzene thiol (128 g, 98%) b.p. 80°/0.6 mm, n_D^{25} 1.5642.

p-Bromo-S-(triethylsilyl)benzene thiol

(Diethylamino)triethylsilane (23.4 g, 0.13 mole) was added to *p*-bromobenzene thiol (20.8 g, 0.11 mole) in ether (100 ml) and the mixture was boiled under reflux for 2 h. A white precipitate initially formed which did not completely dissolve during this time, so ether was fractionated from the reaction mixture and the temperature of the still pot raised to give a steady evolution of diethylamine, and under these conditions the precipitate dissolved. After 1 h the residue was distilled under reduced pressure to give *p*-bromo-*S*-(triethylsilyl)benzene thiol (nc) (30 g, 90%) b.p. 104°/0.10 mm, n_D^{25} 1.5600. (Found: C, 47.7; H, 6.4; Br, 26.2. $C_{12}H_{19}BrSSi$ calcd.: C, 47.5; H, 6.3; Br, 26.3%.)

p-Bromo-S-(dimethylphenylsilyl)benzene thiol

p-Bromobenzene thiol (5.0 g, 0.026 mole) and dimethyl(ethylamino)phenylsilane (8.0 g, 0.04 mole) were heated together to 90° and ethylamine was slowly distilled from the reaction mixture. When the ethylamine evolution had ceased (4 h) the mixture was distilled to give excess of dimethyl(ethylamino)phenylsilane followed by *p*-bromo-*S*-(dimethylphenylsilyl)benzene thiol (nc) (7.5 g, 96%) b.p. 94°/0.1 mm. (Found: C, 57.0; H, 4.7. $C_{14}H_{15}BrSSi$ calcd.: C, 57.0; H, 4.9%.)

p-Bromo-S-(trimethylgermyl)benzene thiol

p-Bromobenzene thiol (5.0 g, 0.026 mole), (dimethylamino)trimethylgermane (5.0 g, 0.031 mole) and ammonium sulphate (0.2 g) were heated together at 80° until evolution of dimethylamine had ceased (8 h). The mixture was then distilled to give excess of (dimethylamino)trimethylgermane followed by *p*-bromo-*S*-(trimethylgermyl)benzene thiol (nc) (5.0 g, 70%) b.p. 62°/0.1 mm, n_D^{25} 1.5887. (Found: C, 35.7; H, 4.4. $C_9H_{13}BrGeS$ calcd.: C, 35.5; H, 4.3%.)

p-Trimethylsilyl-S-(trimethylsilyl)benzene thiol

n-Butyllithium (16 ml of 1.5 *M* solution in hexane) was added during 30 min to *p*-bromo-*S*-(trimethylsilyl)benzene thiol (5.2 g, 0.020 mole) in ether (50 ml). The mixture was boiled under reflux for 10 min, then cooled. Chlorotrimethylsilane (2.7 g, 0.025 mole) was added and heating was continued for a further 2 h. Precipitated salts were filtered off under nitrogen and the filtrate was distilled to give *p*-trimethylsilyl-*S*-(trimethylsilyl)benzene thiol (nc) (4.1 g, 80%) b.p. 92°/1.0 mm, n_D^{25} 1.5208. (Found: C, 56.5; H, 8.6. $C_{12}H_{22}SSi_2$ calcd.: C, 56.6; H, 8.7%.)

p-(Trimethylsilyl)benzene thiol

p-Trimethylsilyl-*S*-(trimethylsilyl)benzene thiol (3.8 g, 0.015 mole) was added to methanol (30 ml). The mixture was refluxed for 30 min then fractionally distilled to give methoxytrimethylsilane and excess of methanol followed by *p*-(trimethylsilyl)-benzene thiol (2.5 g, 90%) b.p. 68°/1.3 mm, n_D^{25} 1.5418 (lit.[5] b.p. 115–117°/20 mm). An NMR spectrum (10% solution in $CDCl_3$ with TMS as internal standard) showed τ values as follows: Me_3Si 9.78 (s), SH 6.63 (s), C_6H_4 2.5–2.7 (d).

p-Trimethylsilyl-S-(trimethylsilyl)benzene thiol

To *p*-bromo-*S*-(trimethylsilyl)benzene thiol (5.2 g, 0.020 mole) in ether (50 ml) was added n-butyllithium (16 ml of 1.5 *M* hexane solution). The mixture was boiled under reflux for 10 min then bromotriethylsilane (4.4 g, 0.022 mole) was added and refluxing was continued for a further 2 h. The mixture was then filtered and the filtrate distilled to give *p*-trimethyl-*S*-(triethylsilyl)benzene thiol (nc) (4.0 g, 75%) b.p. 104°/0.2 mm, n_D^{25} 1.5246. (Found: C, 60.8; H, 9.4. $C_{15}H_{28}SSi_2$ calcd.: C, 60.7; H, 9.5%.) The product (3.6 g) was refluxed with excess of methanol for 30 min and distilled directly to give methoxytriethylsilane (1.6 g) b.p. 59°/50 mm, n_D^{25} 1.4100 (lit.[6] b.p. 141.5°, n_D^{20} 1.4129), followed by *p*-(trimethylsilyl)benzene thiol (90%) b.p. 67°/1.2 mm, n_D^{25} 1.5416.

Rearrangement products from reactions of $p\text{-}BrC_6H_4SMR_3$ compounds ($MR_3 = SiEt_3$ $SiPhMe_3$ or $GeMe_3$) with n-butyllithium

p-(Trimethylsilyl)benzene thiol. n-Butyllithium (60 ml of 1.5 *M* hexane solution) was added to *p*-bromo-*S*-(trimethylsilyl)benzene thiol (20.9 g, 0.08 mole) in ether (100 ml) maintained at 0°. The mixture was boiled under reflux for 10 min then poured into ice water and dilute HCl (0.1 *M*) was added until the aqueous layer was just acid to litmus. The organic layer was separated, dried (Na_2SO_4) and distilled to give *p*-(trimethylsilyl)benzene thiol (12.6 g, 86%) b.p. 65°/1.1 mm, n_D^{25} 1.5419.

p-(Triethylsilyl)benzene thiol. n-Butyllithium (50 ml of 1.5 *M* hexane solution) was added to *p*-bromo-*S*-(triethylsilyl)benzene thiol (2.24 g, 0.065 mole). The mixture was boiled under reflux for 15 min, then poured onto crushed ice and worked up as described above. Fractional distillation gave *p*-(triethylsilyl)benzene thiol (1.49 g, 88%) b.p. 82°/0.6 mm, n_D^{25} 1.5473.

p-(Dimethylphenylsilyl)benzene thiol. To *p*-bromo-*S*-(dimethylphenylsilyl)-benzene thiol (4.5 g, 0.015 mole) in ether maintained at 0° was added an ether solution of n-butyllithium (0.020 mole). Following the addition the mixture was boiled under reflux for 30 min, then poured onto crushed ice. Following acidification, the ether layer was separated, dried (Na_2SO_4) and distilled to give *p*-(dimethylphenylsilyl)-

benzene thiol (nc) (3.1 g, 85%) b.p. 70°/0.1 mm. (Found: C, 69.2; H, 6.4. $C_{14}H_{16}SSi$ calcd.: C, 68.9; H, 6.6%.) An NMR spectrum had the correct integration and τ value as follows: Me_2Si 9.23 (s), SH 6.60 (s) and C_6H_5, C_6H_4 multiplet centred at 2.55.

p-(Trimethylgermyl)benzene thiol. n-Butyllithium (0.015 mole) in ether (20 ml) was added to *p*-bromo-*S*-(trimethylgermyl)benzene thiol (4.2 g, 0.014 mole) in ether (20 ml) at 0°. The mixture was subsequently boiled under reflux for 15 min, then poured onto ice and worked up as described above. Fractional distillation gave *p*-(trimethylgermyl)benzene thiol (nc) (1.6 g, 50%) b.p. 60°/0.075 mm, n_D^{25} 1.5500. (Found: C, 47.9; H, 6.8. $C_9H_{14}GeS$ calcd.: C, 47.5; H, 6.65%.) An NMR spectrum showed the following τ values: Me_3Ge 9.65 (s), SH 6.60 (s) and C_6H_4 2.68 (s).

Wurtz–Fittig synthesis without rearrangement

p-Triethylsilyl-S-(trimethylsilyl)benzene thiol. A toluene solution of *p*-chloro-*S*-(trimethylsilyl)benzene thiol (21.6 g, 0.1 mole) and bromotriethylsilane (21.6 g, 0.12 mole) was added dropwise to a rapidly stirred suspension of sodium (5.1 g, 0.22 g-atom) in refluxing toluene (80 ml). The mixture was subsequently boiled under reflux for 45 min and the purple colour characteristic of Wurtz–Fittig syntheses gradually developed. Precipitated salts were then filtered off and the filtrate was distilled to give *p*-triethylsilyl-*S*-(trimethylsilyl)benzene thiol (nc) (21.4 g, 72%), b.p. 106°/0.2 mm, n_D^{25} 1.5240. (Found: C, 60.6; H, 9.3. $C_{15}H_{28}SSi_2$ calcd.: C, 60.7; H, 9.5%.)

p-(Triethylsilyl)benzene thiol. *p*-Triethylsilyl-*S*-(trimethylsilyl)benzene thiol (15.0 g, 0.05 mole) obtained in the Wurtz–Fittig reaction was boiled under reflux with methanol (100 ml) for 30 min and the mixture was distilled directly to give methoxytrimethylsilane and excess of methanol followed by *p*-(triethylsilyl)benzene thiol (nc) (10.6 g, 0.047 mole) b.p. 80°/0.5 mm, n_D^{25} 1.5470. (Found: C, 64.2; H, 8.9. $C_{12}H_{20}SSi$ calcd.: C, 64.2; H, 9.0%) The NMR spectrum showed τ values as follows: Et_3Si 9.75–9.78 (d), SH 6.62 (s) and C_6H_4 2.58 (s).

ACKNOWLEDGEMENTS

We thank the Nobel Division of Imperial Chemical Industries Ltd. for the award of a Research Studentship (to A.R.B.).

REFERENCES

1 W. Broser and W. Harrer, *Angew. Chem. Int. Ed.*, 4 (1965) 1081; D. R. M. Walton, *J. Chem. Soc. C*, (1966) 1707.
2 J. L. Speier, *J. Amer. Chem. Soc.*, 74 (1952) 1003; K. C. Frisch and P. D. Shroff, *J. Amer. Chem. Soc.*, 75 (1953) 1049; R. G. Neville, *J. Org. Chem.*, 25 (1960) 1063 and 26 (1961) 3031.
3 E. W. Abel and D. A. Armitage, *Adv. Organomet. Chem.*, 5 (1967) 1.
4 R. L. Merker and M. J. Scott, *J. Amer. Chem. Soc.*, 85 (1963) 3343; C. Eaborn, K. L. Jaura and D. R. M. Walton, *J. Chem. Soc.*, (1964) 1198.
5 Y. Sakata and T. Hashimoto, *J. Pharm. Soc. Japan*, 79 (1959) 872; *Chem. Abstr.*, 54 (1960) 357.
6 B. N. Dolgov, N. P. Kharitonov and M. G. Voronkov, *Zh. Obshch. Khim.*, 24 (1954) 1178.