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PROTECTION OF SUBSTITUTED ANILINES WITH 1,1,4,4-TETRAMETHYL-1,4-BIS(N,N-DIMETHYLAMINO)DISILETHYLENE

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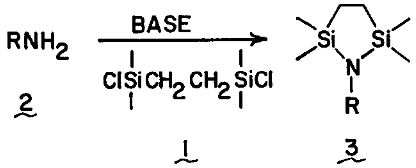
Summary: A simple high yield method has been developed for the protection of substituted anilines with 1,1,4,4-tetramethyl-1,4-bis(N,N-dimethylamino)disilethylene.

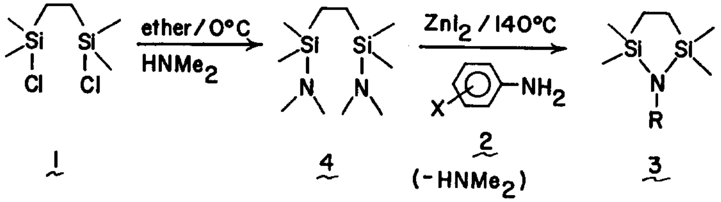
Magnus, Djuric and Venit[1] have described the use of 1,1,4,4-tetramethyl-1,4-dichlorodisilethylene (1) for the protection of primary amines (eq.1). Triethylamine was used as the base with 1 for protecting primary amines with pKa's in the range 10-11. For primary amines with lower pKa's (e.g. toluidines and bromoanilines) *n*-butyllithium was required as the base. Although 3a (R= *m*-BrC_6H_4) could be prepared this way, an easier procedure for preparing larger amounts was desired.



(1)

To this end, reaction of 1 (Petrarch Systems, Inc.) with 5 equiv of dimethylamine (Kodak Laboratory Chemicals) in ether at 0°C for 5h gave 1,1,4,4-tetramethyl-1,4-bis(N,N-dimethylamino)disilethylene (4) in 90% distilled yield as a moisture-sensitive liquid. Heating equimolar amounts of 4 and *m*-bromoaniline (2a) at 200°C under a slow stream of nitrogen for 8h gave 3a quantitatively. However, reaction of 2b (R= *m*-$CH_3C_6H_4$) with 4 at 200°C for 48h gave a mixture of products. Proton NMR analysis of the reaction mixture indicated that one half of the dimethylamine had evolved.[2] It was discovered that addition of a small amount of zinc iodide to the reaction mixture after 8h of heating at 180°C caused complete evolution of dimethylamine and quantitative formation of 3b within 10 min.

Optimal conditions for the protection of substituted anilines 2a-2f (see Table) were heating a mixture of equimolar amounts of 4 and 2, and zinc iodide (0.5 mole %) under a slow stream of nitrogen at 140°C for 5h (eq.2).[3,4] The products were purified by vacuum distillation from the reaction vessel.[5] The protecting group was best removed in ether in the presence of 2.05 equiv of methanol and a small amount of *p*-toluenesulfonic acid monohydrate (0.2 mole %) to give the corresponding primary amine quantitatively.



(2)

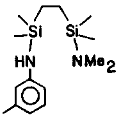
Table. Yields and Boiling Points of Compounds 4 and 3a-3f

Compound	Distilled Yield	Boiling Point (°C)
4	90%	101-103 (13 mm)
3a (R= *m*-BrC$_6$H$_4$)[a]	94%	117-120 (0.35 mm)
3b (R= *m*-CH$_3$C$_6$H$_4$)	92%	72-74 (0.29 mm)
3c (R= *p*-CH$_3$C$_6$H$_4$)	94%	92-93 (1.3 mm)
3d (R= *o*-BrC$_6$H$_4$)	88%	109-110 (0.89 mm)
3e (R= *p*-BrC$_6$H$_4$)	93%	118-120 (0.45 mm)
3f (R=-C$_6$H$_5$)	90%	72-73 (1.0 mm)

a) Synthesis of 3a has been accomplished on a 200g scale with no difficulty.

References

1. Djuric S.; Venit, J.; Magnus, P. *Tetrahedron Lett.* **1981**, *22*, 1787.
2. Analysis of the reaction mixture by field ionization mass spectrometry indicated the presence of starting materials, some of the desired product, and compounds 5 and 6. Compounds 5 and 6 were not fully characterized.



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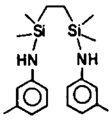

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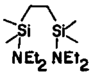
3. Foaming of the reaction mixture occurred for 2b (*m*-CH$_3$), 2c (*p*-CH$_3$), and 2f (*p*-H) at approximately 70°C. After 1h at 70°C the foaming subsided and the reaction temperature was raised to 140°C.
4. Reaction of 1 with excess diethylamine in diethyl ether at 0°C gave 7 in 51% distilled yield [bp 76-79°C (0.15 mm)]. Reaction of 1 with one equiv of methylamine and 2.1 equiv of triethylamine in toluene at 0°C gave 8 in 60% distilled yield (bp 145-149°C).



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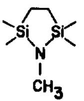

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Reaction of 2b or 2a with 7 or 8 as described with 4 gave crude 3a or 3b quantitatively within 8h.

5. Satisfactory elemental analyses and/or exact mass molecular weights were obtained for compounds 3a-3f, 4, 7 and 8. In all cases the spectral data (IR, NMR, etc.) were consistent with the assigned structures.

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