# A New Synthesis of Organosilicon Azo Compounds

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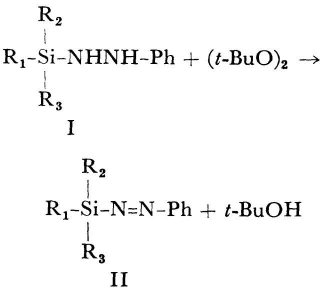
Although numerous methods have been proposed for synthesizing azo compounds, there are only a few reports on the formation of organometallic azo compounds with one or two silicon atoms substituted on nitrogen atoms. Mixed aryl azo organosilanes have been prepared in low yields by Krüger and Wannagat.[1] However, their method is circuitous and troublesome[2] and purity of the products was at best 90%.

We wish to report a new synthetic method for the preparation of organosilyl azo compounds in good yields by the reaction of organosilylhydrazines with radical generating agents such as di-*t*-butyl peroxide or azobisisobutyronitrile.



$$R_1\text{-}\overset{R_2}{\underset{R_3}{\text{Si}}}\text{-NHNH-Ph} + (t\text{-BuO})_2 \rightarrow$$

I

$$R_1\text{-}\overset{R_2}{\underset{R_3}{\text{Si}}}\text{-N=N-Ph} + t\text{-BuOH}$$

II

a) $R_1=\text{Ph}$, $R_2=R_3=\text{Me}$
b) $R_1=R_2=R_3=\text{Et}$

A mixture of Ia[3] (3.63 g, 15 mmol) and di-*t*-butyl peroxide (3.30 g, 22.5 mmol) was refluxed on a metal bath (210—230°C) for 3 hr under nitrogen and heated further at 180—200°C (metal bath temp.) for 1—1.5 hr, during which a mixture of low boiling materials (3.25 g; mainly *t*-butyl alcohol and the unreacted peroxide) was distilled off. Distillation of the resulting mixture gave 2.02 g (56%) of IIa, a deep blue liquid, bp 162—165°C/11 mmHg. Similarly, the reaction was effected employing Ib[4] and the peroxide to give a deep blue liquid of IIb. The analytical results are summarized in Table 1.

Compounds IIa and IIb are shown to be distillable, stable under nitrogen and considerably stable in dry air, and the solution in cyclohexane remains unchanged for a few months.

The present method is especially suitable for the preparation of such organometallic compounds sensitive to moisture or water in the reaction system. The results show that the isolation of the product from the reaction mixture is carried out with great ease due to the simplicity of the reaction system.

It is of interest to apply this method to the synthesis of other types of azo compounds. The usefulness is shown by the following example: hydrazobenzene (1.84 g, 10 mmol) was treated with the peroxide (2.02 g, 15 mmol) and worked up as described above to yield a dark-brown molten mass which was solidified on cooling. Purification of the solid by alumina column chromatography with benzene as an eluent afforded, after recrystallization from ethanol, 1.40 g, (77%) of orange-red fine crystals of azobenzene, mp 66.5—68.0°C.

TABLE 1. ANALYTICAL RESULTS OF DEEP BLUE PRODUCTS

| Compound | Yield % | Elemental anaysis | | Bp °C/mmHg | NMR spectrum[a] $\delta$, ppm | IR spectrum N=N[b]; Si-C cm$^{-1}$ | $\lambda_{\max}$[c](m$\mu$); $\varepsilon$, $n\rightarrow\pi^*$ |
|---|---|---|---|---|---|---|---|
| | | Found % | Calcd % | | | | |
| IIa | 56 | Si 11.85<br>C 70.16<br>H 6.94 | 11.68<br>69.95<br>6.71 | 162—165/11 | 7.85—7.17 (m)[d]<br>0.59 (s)[e] | 1450; 1250<br>923 | 581; 39 |
| IIb | 59 | Si 12.49<br>C 66.11<br>H 9.63 | 12.74<br>65.40<br>9.15 | 125—130/10 | 7.85—7.17 (m)[f]<br>0.99 (m)[g] | 1447; 1240<br>925 | 592; 25 |

a) $\text{CCl}_4$ solution; TMS internal standard, b) see Ref. 1, c) cyclohexane solution, d) and f) phenyl protons, e) methyl protons, g) ethyl protons

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[1] C. Krüger and U. Wannagat, *Z. Anorg. Allg. Chem.*, **326**, 288, 296, 304 (1964).

[2] Wiberg and his co-workers have prepared bis-(trimethylsilyl)diimine by another method; see *Angew. Chem.*, **80**, 661 (1968).

[3] Bp 185—187°C/10 mmHg; $n_D^{20}$ 1.5736; Analysis, Found: C, 69.12; H, 7.62%. Calcd for $C_{14}H_{18}N_2Si$: C, 69.37; H, 7.48%.

[4] U. Wannagat and W. Liehr, *Z. Anorg. Allg. Chem.*, **299**, 341 (1959).