Synthesis and Structure of Azobenzenes Bearing Silyl, Germyl, and Stannyl Groups at 2-Position

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Azobenzenes, 2-$R^1{}_2R^2MC_6H_4N{=}NPh$ (M = Si (**1a–c**), Ge (**7**), and Sn (**8**)), were synthesized by reactions of 2-lithioazobenzene (**6**) with the corresponding chloro compounds, $R^1{}_2R^2MCl$, respectively, in good to moderate yields. The crystal structure of **1c** was established by the X-ray crystallographic analysis.

The chemistry of azobenzenes is well studied because of their easiness of *cis-trans* photoisomerization[1] and their application to the liquid crystals.[2] The properties of the azobenzene such as absorption maxima in the UV/vis spectra are effected by the electron-withdrawing and electron-donating groups at 2-position of an azobenzene as well as those at 4-position.[3] These results prompted us to investigate on azobenzenes with heavier group 14 element substituents at 2-position, which can act only inductively. On the other hand, a 2-(phenylazo)phenyl group is expected to be useful in stabilization of pentacoordinate organosilicon compounds judging from the structural resemblance with the van Koten ligand[4] and many examples of transition metal complexes which are intramolecularly coordinated by an azo group.[5] Although few 2-silylazobenzenes were previously reported, the conventional synthetic methods for them have been restricted to azo-coupling reaction of diazonium salt with [3-(dimethylamino)phenyl]silanes.[6] This method is not effective for the synthesis of 2-silylazobenzenes without electron-donating substituents. Neither useful synthetic methods for the naked 2-silyl-azobenzenes, nor the crystal structure of the 2-silylazobenzenes has been reported yet. We report here an effective synthetic method for 2-silylazobenzenes and the synthesis of germyl and stannyl derivatives. We have also established the molecular structure of one of 2-silylazobenezenes by X-ray crystallographic analysis.

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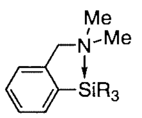
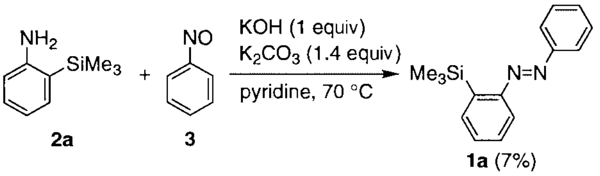


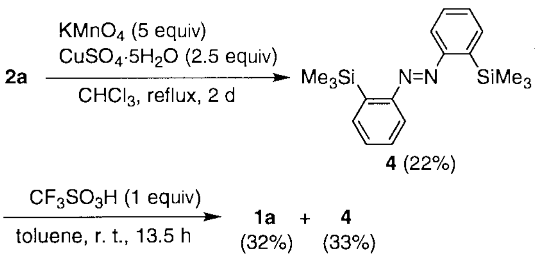
silanes bearing van Koten ligand

First trial for the synthesis of **1a** by dehydrative coupling reaction of 2-anilinotrimethylsilane **2a**[7] and nitrosobenzene **3** in acetic acid, which was used for the synthesis of unsymmetrically substituted azobenzenes,[8] was failed because of instability of both **1a** and **2a** under acidic conditions. We used basic conditions for the coupling reaction of **2a** (83 mg, 0.5 mmol) and **3** (2 equiv) with KOH (1 equiv) and K_2CO_3 (1.4 equiv), in pyridine (5 mL) at 70 °C (Scheme 1). Although **1a** was obtained in 7% yield after stirring for 2 days and usual work up, **2a** was mainly recovered.[9] Furthermore, use of anilines with bulkier silyl groups, 2-anilino(dimethyl)phenylsilane **2b**, instead of **2a** in the above coupling reaction was unsuccessful probably due to the steric hindrance.



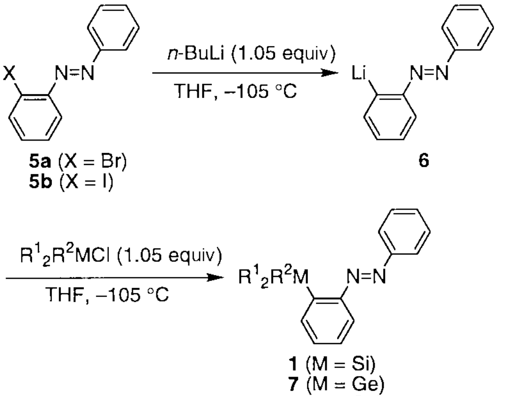
Scheme 1.

We next tried mono-desilylation of 2,2'-bis(trimethylsilyl)-azobenzene (**4**) (22%) prepared from **2a** with trifluoromethanesulfonic acid as shown in Scheme 2.[10] Compound **1a** was obtained in 32% yield with recovery of **4** (33%) after chromatographic separation.



Scheme 2.

More effective synthetic methods are desirable for the introduction of various silyl groups at 2-position of azobenzene because yields by these two methods were quite low. We finally attempted the lithium–halogen transmetallation of 2-haloazobenzene followed by the reaction with a variety of electrophiles. 2-Bromoazobenzene (**5a**)[8] (0.36 g, 1.4 mmol) was treated with *n*-BuLi (1.05 equiv) and chlorotrimethylsilane (1.05 equiv) successively in THF (8 mL) at –105 °C to give **1a** in 25% yield (Scheme 3, Table 1).[11] Lithiation of 2-iodoazobenzene (**5b**) instead of **5a** afforded 2-lithioazobenzene (**6**)



Scheme 3.

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Table 1. Synthesis and electronic spectra of azobenzenes

X	$R^1{}_2R^2MCl$	Product	Yield/%	λ_{max}/nm (log ε)		
Br	Me_3SiCl	**1a**	25	233 (4.0)	325 (4.2)	450 (2.7)
I	Me_3SiCl	**1a**	80	—	—	—
I	$Me_2PhSiCl$	**1b**	92	233 (4.2)	325 (4.4)	453 (2.9)
I	Ph_2HSiCl	**1c**	79	232 (4.3)	327 (4.3)	451 (2.8)
I	Me_3GeCl	**7**	98	233 (4.0)	325 (4.1)	446 (2.7)
I	*n*-Bu_3SnCl	**8**	65	233 (4.1)	327 (4.2)	446 (2.8)

efficiently, and successive treatment of chlorotrimethylsilane afforded **1a** in satisfactory yield (80%). This method is effective for the synthesis of other silyl derivatives such as dimethylphenyl derivative **1b** (92%), and hydrodiphenylsilyl derivative **1c** (79%). Furthermore, treatment of **6** with the chlorotrimethylgermane and tri-*n*-butylchlorostannane afforded the corresponding germanium and tin derivatives **7** (98%) and **8** (65%), respectively. In electronic spectra, the absorption maxima of these 2-silyl, germyl, and stannyl substituted azobenzenes in CH_2Cl_2 are red shifted compared with those of unsubstituted azobenzene (232, 318, 441 nm) (Table 1). These red-shifts are explained by strong electropositiveness of silyl, germyl, and stannyl groups.

The crystal structure of 2-silylazobenzene **1c** was determined by X-ray structural analysis (Figure 1).[12] Trans conformation was confirmed for 2-silylazobenzene **1c** where azobenzene unit is almost coplanar judging from the dihedral angle between two phenyl groups attached to the azo group (8.37°). The N1–N2 bond length (1.255(2) Å) exhibited little structural difference compared to the average dimensions (1.25 Å) of previously reported *trans*-azobenzenes.[13] Silyl groups and N2 atom are arranged in a trans fashion with regard to the C1–N1 axis unlike the many transition metal complexes bearing an azobenzene unit where the nitrogen atom coordinates to the central metal atom.[5] These results apparently indicate the absence of Si1–N2 intramolecular interaction. A steric repulsion overcomes the attractive electrostatic interaction which provides the intramolecular coordination. The distance between Si1 and N1 [3.010(5) Å] is necessarily in the range of sum of the van der Waals radii of silicon and nitrogen, 3.65 Å, although it is much longer than the sum of the covalent bond radii, 1.92 Å.[14] Any conformational change from tetrahedral structure, however, was not observed for the silicon atom, indicating the lack of intramolecular coordination of N1 to Si1.[15] This is the first example of X-ray crystallographic analysis of a 2-silylazobenzene. The chemical shift of ^{29}Si NMR (δ_{Si} –19.90 ppm in $CDCl_3$) also supports the tetracoordinate structure of the Si1 atom in solution state. Other 2-silylazobenzenes **1a** and **1b** showed the chemical shifts at –3.98 and –7.53 ppm, respectively, suggesting their tetracoordinate structures similar to **1c** in solution state.

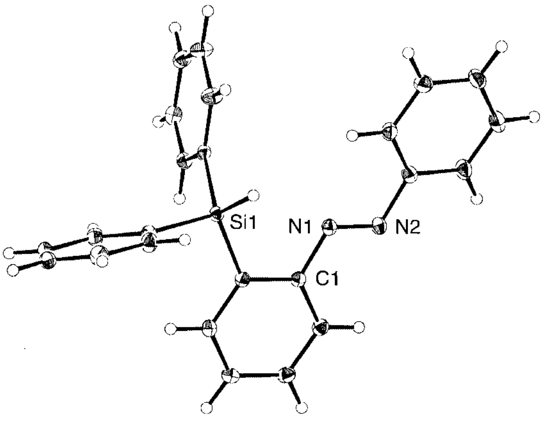

Figure 1. ORTEP drawing of **1c** (30% probability).

In summary, we have developed a novel synthetic method for 2-silylazobenzenes whose absorption maxima are red shifted. The first X-ray crystallographic analysis of 2-silylazobenzene **1c** revealed tetrahedral structure of the silicon atom. 2-Lithioazobenzene was found to be a useful synthetic intermediate for group 14 element derivatives and its reaction would be versatile for the synthesis of other main group element derivatives.

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