CHEMISTRY LETTERS, pp. 153-156, 1987.

Novel Syntheses of Bis(trialkylsilyl)amines by Reductive Trialkylsilylation of Azo Compounds[#,1)]

Mitsuo KIRA, Satoshi NAGAI, Mitsushi NISHIMURA, and Hideki SAKURAI
Department of Chemistry, Faculty of Science, Tohoku University, Sendai 980

Reduction of azo compounds with a system of a trialkylchlorosilane and lithium has been found to afford bis(trialkylsilyl)amines in the presence of a transition metal halide as a catalyst in THF. The reaction course was significantly modified by using t-butyldimethylchlorosilane as a trialkylchlorosilane.

As one of the practical synthetic routes to primary alkyl- and aryl-amines, reduction of azo compounds with fission of the N=N double bond has been widely utilized.[2)] We wish here to report the novel reduction of azo compounds to give directly bis(trialkylsilyl)amines, which may be synthetically useful as protected primary amines.[3)]

The reduction was achieved by using a system of a trialkylchlorosilane, lithium, and a catalytic amount of a transition metal halide in THF at room temperature (Eq. 1). The results are summarized in Table 1.

$$\text{R-N=N-R} \xrightarrow[\text{THF}]{\text{R}'_3\text{SiCl/Li/Catalyst}} 2\ \text{RN(SiR}'_3)_2 \qquad (1)$$

In a typical run, a mixture of azobenzene (**1**, 10 mmol), finely cut Li wire (80 mmol), trimethylchlorosilane (60 mmol), and ferric chloride (2 mmol) in THF (20 ml) was stirred for 7 h under argon at room temperature. The solvent was replaced by diethyl ether, and then the mixture was filtered. N,N-Bis(trimethylsilyl)aniline (**2**) was obtained in 77% yield by simple distillation; bp 82 °C (5 mmHg). Bis(trimethylsilyl)amines were obtained usually in high yields from aromatic azo compounds, but in fairly low yields from azoalkanes. Immoderately large excess amounts of Me_3SiCl and Li should not be used since the undesired side reactions, e.g. trimethylsilylation at the nuclear positions of the product occurred. Optimum yields of disilylanilines were achieved when the following molar ratio of the starting materials was used; azobenzene:Me_3SiCl:Li:$FeCl_3$= 1:6:8:0.2. Whereas $TiCl_4$, $CoCl_2$, $ZrCl_4$, $PdCl_2$, and Cp_2TiCl_2 were equally effective as a catalyst, the presence of a transition metal catalyst was indispensable to the reaction. The reduction of azobenzene with the Me_3SiCl/Li/THF system in the absence of a catalyst

---

[#] Dedicated to Professor Teruaki Mukaiyama on the occasion of his 60th birthday.

Table 1. Reaction of Azo Compounds with Trialkylchlorosilane/Li/THF in the Presence of a Catalyst at Room Temperature[a]

Entry	R-N=N-R/R'$_3$SiCl	Reaction time/h	Catalyst	Products	Yield/%[b]
1	Ph-N=N-Ph(**1**)/Me_3SiCl(**2**)	7	$FeCl_3$	$PhN(SiMe_3)_2$ (**3**)	77
2	**1**/**2**	3	$TiCl_4$	**3**	84
3	**1**/**2**	3	$CoCl_2$	**3**	70
4	**1**/**2**	3	$ZrCl_4$	**3**	68
5	**1**/**2**	3	$PdCl_2$	**3**	75
6	**1**/**2**	3	$(C_5H_5)_2TiCl_2$	**3**	73
7	p-$CH_3C_6H_4N$=$NC_6H_4CH_3$-p(**4**)/**2**	5	$FeCl_3$	p-$CH_3C_6H_4N(SiMe_3)_2$ (**5**)	77
8	p-$CH_3OC_6H_4N$=$NC_6H_4OCH_3$-p(**6**)/**2**	5	$FeCl_3$	p-$CH_3OC_6H_4N(SiMe_3)_2$ (**7**)	74
9[c]	Ph-N=N-$SiMe_3$ (**8**)/**2**	5	$FeCl_3$	**3** $(Me_3Si)_3N$ (**9**)	37 25
10	n-BuN=NBu-n (**10**)/**2**	3	$FeCl_3$	n-$BuN(SiMe_3)_2$ (**11**)	19[d]
11	i-PrN=NPr-i (**12**)/**2**	3	$FeCl_3$	i-$PrN(SiMe_3)_2$ (**13**)	29[d]
12[e]	**12**/**2**	18	$TiCl_4$	**13**	42
13	**1**/i-$PrMe_2SiCl$(**14**)	3	$FeCl_3$	$PhN(SiMe_2Pr\text{-}i)_2$(**15**)	87
14	**1**/i-$Pr_2MeSiCl$(**16**)	7	$FeCl_3$	$PhN(SiMePr\text{-}i_2)_2$(**17**)	94
15[f]	**1**/t-$BuMe_2SiCl$(**18**)	10	$FeCl_3$	$PhNHSiMe_2Bu$-t (**19**)	84
16[g]	**1**/**18**	30	$FeCl_3$	$PhN(SiMe_2Bu\text{-}t)_2$(**20**) **19**[h]	31 --

a) Unless otherwise noted, following molar ratio of the starting materials was used: an azo compound:Me_3SiCl:Li:a catalyst= 1:6:8:0.2.

b) Isolated yields based on an azo compound which should give 2 mol of the corresponding amines.

c) The relatively low yields of the corresponding amines might partly be due to the poor purity of **8** which was prepared by a reported method.[4]

d) The yields of alkylamines might be lowered by the undesirable side reactions. The reactivity was also severely influenced by the steric hindrance due to the alkyl groups; 2,2'-azoisobutane gave only trace amount of t-$BuN(SiMe_3)_2$ under the similar conditions.

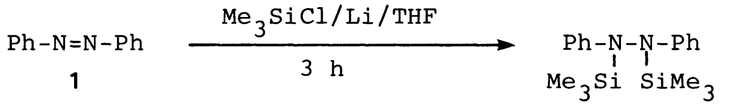
e) The starting molar ratio of **12**:Me_3SiCl:Li:$TiCl_4$ was 1:8:10:0.2.

f) The starting molar ratio of **18**:t-$BuMe_2SiCl$:Li:$FeCl_3$ was 1:3:8:0:2.

g) The reaction was carried out at 66 °C.

h) Not isolated. The yield of **19** was analyzed by glc to be comparable with that of **20**.

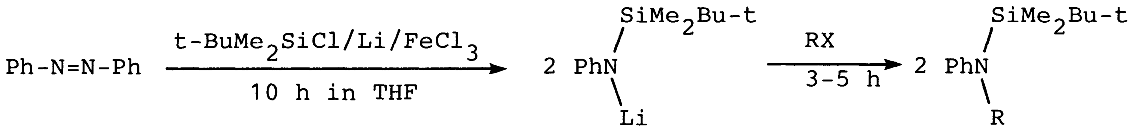
afforded only N,N'-bis(trimethylsilyl)-N,N'-diphenylhydrazine (**21**) in 76% yield as a single isolated product (Eq. 2),[5] whereas N-trimethylsilylaniline and **3** was produced in relatively low yields (9 and 22% yields, respectively) after stirring for 8 h at room temperature; **21**, mp 108-109 °C (lit.[6] 111.5-112.5 °C). Although the N-N single bond of **21** can be cleaved with the $Me_3SiCl/Li/THF$ system in the presence of $FeCl_3$ affording **3** in 64% yield (Eq. 3), the long reaction time required suggests that the reduction of **1** to **3** may not involve **21** as a discrete intermediate product. However under similar conditions in the absence of a catalyst, **21** was recovered in 77% yield without formation of **3**.



$$\underset{\mathbf{1}}{\text{Ph-N=N-Ph}} \xrightarrow[\text{3 h}]{\text{Me}_3\text{SiCl/Li/THF}} \underset{\mathbf{21},\ 76\%}{\underset{\text{Me}_3\text{Si}\ \ \text{SiMe}_3}{\text{Ph-N-N-Ph}}} \qquad (2)$$

$$\mathbf{21} \xrightarrow[\text{20 h}]{\text{Me}_3\text{SiCl/Li/FeCl}_3\text{/THF}} \underset{\mathbf{3},\ 64\%}{2\ \text{PhN(SiMe}_3)_2} \qquad (3)$$

Although similar results were obtained when isopropyldimethylchlorosilane and diisopropylmethylchlorosilane were used as a chlorosilane (Table 1, Entries 13, 14), sterically bulky t-butyldimethylchlorosilane modified the reaction significantly. Thus, the monosilylation was the main reaction course under the similar conditions as above: bis(t-butyldimethylsilyl)aniline was obtained but in fairly low yield at higher temperature and longer reaction time (Table 1, Entries 15, 16). As expected, addition of alkyl halides to the reaction mixture of the mono-t-butyldimethylsilylation gave the corresponding N-alkyl-N-t-butyldimethylsilylanilines (Eq. 4). This reaction sequence constitutes a new synthetic method of silylalkylanilines from azobenzene in one-pot operation. The results are shown in Table 2.



$$\text{Ph-N=N-Ph} \xrightarrow[\text{10 h in THF}]{\text{t-BuMe}_2\text{SiCl/Li/FeCl}_3} 2\ \text{PhN}\begin{matrix}\text{SiMe}_2\text{Bu-t}\\ \text{Li}\end{matrix} \xrightarrow[\text{3-5 h}]{\text{RX}} 2\ \text{PhN}\begin{matrix}\text{SiMe}_2\text{Bu-t}\\ \text{R}\end{matrix} \qquad (4)$$

Whereas the role of transition metal catalysts is still unclear, it may be important to note that on the mechanistic points, the present reaction may be closely related to the nitrogen fixation reported by Shiina[7] as well as to the Calas' reaction[8] with similar reagent systems.

Related works are now in progress.

Table 2. Reductive Cleavage of Azobenzene with t-BuMe$_2$SiCl/Li/FeCl$_3$ in THF Followed by Alkylation[a)]

Alkyl(or silyl) halide (RX)	Molar ratio of RX/1	Product yields/%	
		PhNR(SiMe$_2$Bu-t)	PhNH(SiMe$_2$Bu-t)
MeI	6	72	--
EtI	8	73	--
n-BuI	8	40[b)]	50[b)]
n-BuBr	8	40[b)]	16[b)]
Me$_3$SiCl	4	85	--

a) The following molar ratio of the starting materials was used for the first step of the reactions in Eq. 4: 1:t-BuMe$_2$SiCl:Li:FeCl$_3$= 1:3:8:0.2. After 10 h of the first-step reaction time, excess amounts of an alkyl halide were added and then the reaction mixture was sitrred for 3-5 h additionally. Unless otherwise noted, isolated yields are shown based on the amounts of azobenzene.

b) Yield determined by ^{1}H NMR analysis.

References

1) Chemistry of Organosilicon Compounds 229.
2) B. T. Newbold, "The Chemistry of the Hydrazo, Azo, and Azoxy Groups," ed by S. Patai, John Wily, London (1975), Part 2, Chap. 15; R. Ohme and A. Zubek, "Preparative Organic Chemistry," ed by G. Hilgetag and A. Martini, John Wiley, New York (1972), Chap. 7.
3) W. Broser and W. Harrer, Angew. Chem., Int. Ed. Engl., 4, 1081 (1965); J. R. Pratt, W. D. Massey, F. H. Pinkerton, and S. F. Thames, J. Org. Chem., 40, 1090 (1975).
4) H. Watanabe, K. Inoue, and Y. Nagai, Bull. Chem. Soc., Jpn., 43, 2660 (1970).
5) The disilylation of azobenzene may proceed via the initial formation of N,N'-dilithio-N,N'-diphenylhydrazine as reported by Gilman et al.: D. Wittenberg, M. V. George, T. U. Wu, D. H. Miles, and H. Gilman, J. Am. Chem. Soc., 80, 4532 (1958); M. V. George, D. Wittenberg, and H. Gilman, *ibid.*, 81, 361, (1959).
6) M. V. George, W. P. Neumann, and H. P. Becker, J. Organomet. Chem., 5, 397, (1966).
7) K. Shiina, J. Am. Chem. Soc., 94, 9266 (1972).
8) R. Calas and J. Dunoguès, J. Organomet. Chem. Library, 2, 277 (1976), and references cited therein.

(Received October 9, 1986)