

Formation of *N,N'*-Disubstituted Methanediimine Derivatives from Hexamethyldisilazane and Aldehydes via Stepwise Reactions

Kozaburo NISHIYAMA,* Masaki SAITO, and Makoto OBA

Department of Chemistry, Tokyo Metropolitan University, 2-1-1, Fukasawa, Setagaya, Tokyo 158

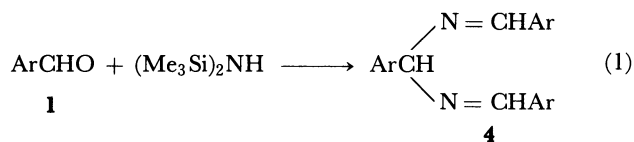
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Synopsis. The ZnCl_2 -catalyzed reaction of aldehydes with hexamethyldisilazane (HMDS) resulted in the formation of *N,N'*-disubstituted methanediimines, which were found to be formed stepwisely via 1:1- and 1:2-adducts of HMDS and aldehydes.

Although alkali metal salts of hexamethyldisilazane (HMDS) are well-known to be hindered bases for organic synthesis, only a few reports concerning the synthetic utility of disilazane itself can be found in the literature. Recently, two groups¹⁾ reported the introduction of an amino moiety into organic molecules by using HMDS; the conversion of acyl halides into amides. On the other hand, we have been interested in the reactivity of a variety of Si–N bond of organosilicon compounds, e.g. silyl azide,²⁾ silyl isocyanate,³⁾ and silyl isothiocyanate.⁴⁾ As a continuation of our work in this area, the ZnCl_2 -catalyzed reaction of aldehydes (**1**) with hexamethyldisilazane (HMDS), having two reactive Si–N bonds in a molecule, was investigated and we now report our results in this paper.

Results and Discussion

Treatment of benzaldehyde (**1a**) with 2 equiv of HMDS and a catalytic amount of ZnCl_2 in dichloromethane at room temperature for 24 h resulted in the formation of colorless needles (hexane), mp 100–101 °C, which were identified as *N,N'*-dibenzylidenephénylmethanediimine (**4a**). Without zinc chloride or in hexane, the reaction between benzaldehyde and HMDS did not proceed at all and starting materials were quantitatively recovered. When the reaction was interrupted in 1 h, the sole product was **4a** in a low yield (16%). Analogously, four *N,N'*-bis-(arylmethylene)arylmethanediimines (**4b–e**) were obtained from the corresponding aromatic aldehydes (Eq. 1 and Table 1). On the other hand, Duffaut and



a, Ar=Ph, b, Ar=*p*-MeOC₆H₄, c, Ar=*p*-MeC₆H₄,
d, Ar=*p*-CNC₆H₅, e, Ar=*p*-NO₂C₆H₄

Dupin reported that the treatment of ketones and benzaldehyde with silazanes $[(\text{Me}_3\text{Si})_2\text{NR}]$; R=H and Me] and silyl amines (Me_3SiNHPH and Ph_3SiNH_2) in the presence of Zn/Cd at 165 °C for 40 h gave the corresponding imines ($>\text{C}=\text{NR}$; R=H, Me, and Ph) in yields of 30–95%.⁵⁾

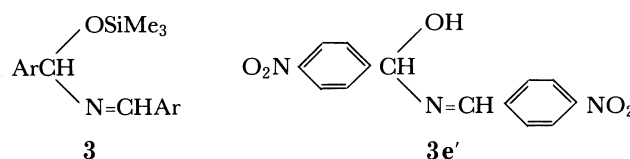
With *p*-cyanobenzaldehyde (**1d**), a trace amount of *N*-(*p*-cyanobenzylidene)-1-(*p*-cyanophenyl)-1-(trimethylsiloxy)methanamine (**3d**) with **4d** (46%) was isolated

Table 1. ZnCl_2 -Induced Reaction of Carbonyl Compound with HMDS

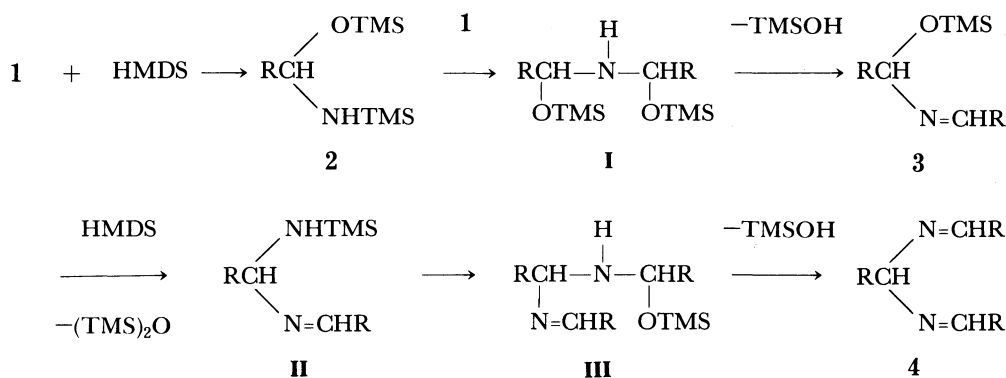
Carbonyl compd	Product (Yield/%)	Mp θ_m (bp θ_b)/°C
1a	(0) ^{a)}	
1a	4a (16) ^{b)}	100–101
1a	4a (79)	
1b	4b (66)	128–129
1c	4c (73)	93–94
1d ^{c)}	3d (23)	117
	4d (32)	122–124
1d	4d (46)	
1e	4e (30)	140 (decomp)
<i>t</i> -BuCHO (1f)	4f (42)	(173/2 mmHg)
<i>cyclo</i> -C ₆ H ₁₀ O (1g)	4g (53)	(163/2 mmHg)
Cl ₃ CCHO (1h)	2h (70)	(80–82/4 mmHg)

a) Without ZnCl_2 . b) Stirred for 1 h. c) Stirred for 10 h.

by fractional recrystallization from benzene and hexane. Since compound **3d** could be a precursor of **4d**, the reaction of **1d** with HMDS was again carried out for 10 h at room temperature. Consequently, compounds **3d** and **4d** were obtained in 23 and 32% yields, respectively. Similarly, the treatment of **1e** with HMDS for 24 h afforded a mixture of **3e**, which was too unstable to be fully characterized, and **4e** (30%). An attempt to separate the mixture by column chromatography on alumina (eluent; CHCl_3) gave *p*-nitrobenzylideneamino-*p*-nitrophenylmethanol (**3e'**).

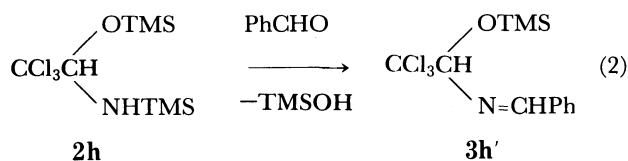


From these findings, it is clear that the formation of **4** involves stepwise reactions which must proceed via **3** and that an electron-withdrawing group of the aldehyde would retard either step(s) of the successive reactions. More remarkably, in cases of aliphatic aldehydes, the product was dependent upon an electronic rather than a steric effect of the alkyl group. With 2,2-dimethylpropanal (**1f**) and cyclohexanone (**1g**), *N,N'*-bis(2,2-dimethylpropylidene)-2,2-dimethyl-1,1-propanediimine (**4f**) and *N,N'*-dicyclohexylidene-1,1-cyclohexanediimine (**4g**) were produced in 42% and 53% yields,⁶⁾ respectively, as a sole product, whereas only a 1:1-adduct of trichloroethanal (**1h**) and HMDS, *N*-trimethylsilyl-1-trimethylsiloxy-2,2,2-trichloroethanamine (**2h**), was obtained in a 70% yield. The treatment of **2h** with benzaldehyde under similar conditions gave *N*-benzylidene-1-trimethylsiloxy-2,2,2-trichloroethanamine (**3h'**) in a 53% yield. As to this



Scheme

reaction course, it was postulated that the addition of the remaining Si-N bond in **2h** to benzaldehyde followed by the elimination of trimethylsilanol occurred to give **3h'** (Eq. 2).



On the basis of the above results, we suggest the reaction pathway shown in the Scheme to account for the formation of the *N,N'*-bis(arylmethylene)arylmethanediamines **4** from aldehyde with HMDS. The first and second steps are ZnCl_2 -induced addition reactions of Si-N bonds to the carbonyl group of the aldehyde, giving the 1:1-adduct **2** and 1:2-adduct **I**, respectively. Furthermore, the latter undergoes the elimination of trimethylsilanol to produce *N*-benzylidenephnylmethane derivative **3**. Condensation of **3** with HMDS gives hexamethyldisiloxane and the di-amino intermediate **II**; **II** adds to another aldehyde to give the adduct **III**, which would be subjected to the further elimination of trimethylsilanol, giving the final product **4**. The conversion step of **3** into **II** finds analogy in another study of ours; in which *gem*-diazides were found to be isolated via α -siloxy azides from the similar reaction of aldehydes²⁾ and ketones⁷⁾ with silyl azide. For these reactions, an electron-withdrawing group of aldehydes retards the addition process and compounds **4** having an electron-donating group were obtained in higher yields under the conditions employed.

Compound **4** is important as an intermediate for trisubstituted imidazole derivatives; the dehydrogenation of *N,N'*-dibenzylidenephnylmethanediamine gives 2,4,5-triphenyl-1*H*-imidazole.⁸⁾

Experimental

Melting points are uncorrected. Infrared spectra were measured on a Hitachi 260-10 infrared spectrometer. ¹H NMR spectra were determined with a Hitachi R-600 using tetramethylsilane as an internal standard. Mass spectra (MS) were obtained using a JEOL DX-300 spectrometer.

Hexamethyldisilazane (HMDS) and aldehydes were commercial products and were purified by distillation or recrystallization if necessary.

ZnCl₂-Induced Reaction between Aldehyde (1a–1f) and HMDS. General Procedure. A suspension of aldehyde (30 mmol), HMDS (60 mmol), and ZnCl_2 (6 mmol) in CH_2Cl_2 (30 cm³) was stirred for 24 h at room temperature. The reaction mixture was poured into water (30 cm³) and dichloromethane (30 cm³). Extraction with three 30 cm³ portions of dichloromethane followed by washing with water completed the work-up. The extract was dried over anhydrous MgSO_4 and concentrated in vacuo. The resulting mixture was triturated with hexane (for **4a–4d**) or benzene (for **4e**) and the precipitated solid was collected by filtration. The solid was recrystallized from an appropriate solvent (hexane, a mixture of hexane and benzene, or acetonitrile). When the product was liquid (**4f** and **4g**), it was directly distilled under reduced pressure. The yields of products are listed in Table 1. Spectral and physical data are as follows.

4a: colorless needles (hexane); mp 100–101 °C (lit.⁹ 100 °C). IR (KBr) ν 1625 (C=N) cm⁻¹. MS m/z 194 (M^+ – N=CHPh). ¹H NMR (CDCl_3) δ =5.93 (s, 1H), 7.20–7.89 (m, 15H), and 8.51 (s, 2H). **4b:** colorless needles (hexane); mp 128–129 °C IR (KBr) ν 1620 (C=N) cm⁻¹. MS m/z 254 (M^+ – N=CHC₆H₄OCH₃-*p*). ¹H NMR (CDCl_3) δ =3.75 (s, 3H), 3.81 (s, 6H), 5.80 (s, 1H), 6.84, 7.38 (ABq, 4H), 6.86, 7.74 (ABq, 8H), and 8.40 (s, 2H). Found: C, 74.15; H, 6.30; N, 7.20%. Calcd for C₂₄H₂₄N₂O₃: C, 74.21; H, 6.23; N, 7.21%. **4c:** colorless powder (hexane); mp 93–94 °C. IR (KBr) ν 1620 (C=N) cm⁻¹. MS m/z 222 (M^+ – N=CHC₆H₄CH₃-*p*). ¹H NMR (CDCl_3) δ =2.32 (s, 3H), 2.40 (s, 6H), 5.87 (s, 1H), 7.13, 7.35 (ABq, 4H), 7.16, 7.68 (ABq, 8H), and 8.45 (s, 2H). Found: C, 84.96; H, 7.43; N, 8.01%. Calcd for C₂₄H₂₄N₂: C, 84.67; H, 7.11; N, 8.23%. **4d:** pale yellow powder (1:1 mixture of benzene and hexane), mp 122–124 °C. IR (KBr) ν 2210 (C=N) and 1625 (C=N) cm⁻¹. MS m/z 244 (M^+ – N=CHC₆H₄CN-*p*). ¹H NMR (CDCl_3) δ =6.06 (s, 1H), 7.62 (s, 8H), 7.67, 7.92 (ABq, 4H), and 8.53 (s, 2H). Found: C, 77.43; H, 4.24; N, 18.96%. Calcd for C₂₄H₁₅N₅: C, 77.20; H, 4.05; N, 18.75%. The mother liquor of **4d** was concentrated in vacuo and the residual solid was recrystallized from hexane, giving colorless needles, **3d**, mp 116–117 °C. IR (KBr) ν 2200 (C=N), 1630 (C=N), and 1060 (Si-O-C) cm⁻¹. MS m/z 204 (M^+ – N=CHC₆H₄CN-*p*). ¹H NMR (CDCl_3) δ =0.20 (s, 9H), 6.30 (s, 1H), 7.57 (s, 4H), 7.66, 7.83 (ABq, 4H), and 8.50 (s, 1H). Found: C, 68.50; H, 5.85; N, 12.53%. Calcd for C₁₉H₁₉N₃OSi: C, 68.44; H, 5.74; N, 12.60%. **4e:** pale yellow plates (acetonitrile), mp 140 °C (decomp). IR (KBr) ν 1625 (C=N) and 1505, 1340 (NO₂) cm⁻¹. MS m/z 283 (M^+ – N=CHC₆H₄NO₂-*p*). Found: C, 58.23; H, 3.44; N, 15.98%. Calcd for C₂₁H₁₅N₅O₆: C, 58.20; H, 3.49; N, 16.16%. The ¹H NMR spectrum of **4e** could not be determined because the isolated **4e** did not dissolve in CDCl_3 and CD_3CN and decomposed in DMSO-*d*₆. **3e'**: pale yellow powder (CHCl_3), mp 203–204 °C. IR (KBr) ν 3275 (OH), 1635 (C=N), and 1500,

1340 (NO_2) cm^{-1} . MS m/z 301 (M^+). Found: C, 55.40; H, 3.62; N, 14.00%. Calcd for $\text{C}_{14}\text{H}_{11}\text{N}_3\text{O}_5$: C, 55.82%; H, 3.68; N, 13.95%. **4f**: colorless liquid, bp 173 °C/2 mmHg (1 mmHg=133.322 Pa.). IR (neat) ν 1660 ($\text{C}=\text{N}$) cm^{-1} . MS m/z 154 ($\text{M}^+ - \text{N}=\text{CHBu}-t$). ^1H NMR (CDCl_3) δ =0.89 (s, 9H), 1.09 (s, 18H), 3.83 (s, 1H), and 7.49 (s, 2H). **4g**: colorless liquid, bp 155–163 °C/2 mmHg. IR (neat) ν 1660 ($\text{C}=\text{N}$) cm^{-1} . MS m/z 274 (M^+). ^1H NMR (CDCl_3) δ =1.00–2.40 (m).

Reaction of Trichloroethanal (1h) with HMDS. A mixture of **1h** (4.42 g, 30 mmol), HMDS (9.69 g, 60 mmol), and ZnCl_2 (0.82 g, 6 mmol) in CH_2Cl_2 (30 cm^3) was stirred for 75 h at room temperature. Direct distillation of the reaction mixture gave a colorless oil, which boiled at 80–82 °C/4 mmHg and was assigned to **2h**, yield, 6.48 g (70%). IR (neat) ν 3380 (NH) and 1250 ($\text{C}-\text{SiMe}_3$) cm^{-1} . MS m/z 190 ($\text{M}^+ - \text{CCl}_3$). ^1H NMR (CDCl_3) δ =0.20 (s, 9H), 0.25 (s, 9H), 4.63 (s, 1H), and 4.85 (s, 1H). Found: C, 30.81; H, 6.59; N, 4.55%. Calcd for $\text{C}_8\text{H}_{20}\text{Cl}_3\text{OSi}_2$: C, 31.12; H, 6.53; N, 4.54%.

When the reaction between **1h** (11.08 g, 75 mmol) and HMDS (12.13 g, 75 mmol) in the presence of ZnCl_2 (2.05 g, 15 mmol) in CH_2Cl_2 (75 cm^3) was carried out for 24 h at room temperature, repeated distillation afforded a detrimethylsilylated compound **2h'** (1-trimethylsiloxy-2,2,2-trichloroethanamine) instead of **2h**, yield 6.12 g (35%). Bp 49–50 °C/4 mmHg. IR (neat) ν 3400 and 3300 (NH_2) and 1250 ($\text{C}-\text{SiMe}_3$) cm^{-1} . MS m/z 118 ($\text{M}^+ - \text{CCl}_3$). ^1H NMR (CDCl_3) δ =0.18 (s, 9H), 2.00 (s, 2H), and 4.60 (s, 1H). Found: C, 25.55; H, 5.15; N, 6.08%. Calcd for $\text{C}_5\text{H}_{12}\text{Cl}_3\text{NOSi}$: C, 25.38; H, 5.11; N, 5.92%.

Reaction of 2h with Benzaldehyde. A mixture of **2h** (5.26 g, 17 mmol), benzaldehyde (**1a**, 1.81 g, 17 mmol), and ZnCl_2 (0.46 g, 3.4 mmol) in CH_2Cl_2 (17 cm^3) was stirred for 24 h at

room temperature. After usual work-up, direct distillation (bp 108 °C/2 mmHg) of the dried mixture gave a pale yellow liquid which was characterized to *N*-benzylidene-1-trimethylsiloxy-2,2,2-trichloroethanamine (**3h'**), yield 2.1 g (38%). IR (neat) ν 1635 ($\text{C}=\text{N}$) and 1250 ($\text{C}-\text{SiMe}_3$) cm^{-1} . MS m/z 206 ($\text{M}^+ - \text{CCl}_3$). ^1H NMR (CDCl_3) δ =0.35 (s, 9H), 5.61 (s, 1H), 7.40–7.96 (m, 5H), and 8.53 (s, 1H). Found: C, 44.49; H, 5.26; N, 4.35%. Calcd for $\text{C}_{12}\text{H}_{16}\text{Cl}_3\text{NOSi}$: C, 44.39; H, 4.97; N, 4.31%.

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