Reaction of Group IV Organometallic Compounds. XXXII[1] Modified Synthesis of Imidazolidines with *N,N'*-Bis(trimethylsilyl)-1,2-diamines

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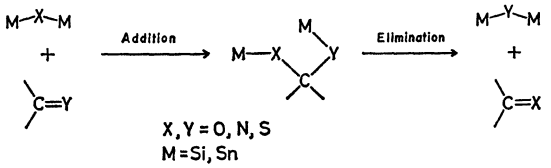
(Received February 28, 1975)

N,N'-Bis(trimethylsilyl)-1,2-diamines gave imidazolidine derivatives accompanied with the elimination of hexamethyldisiloxane in excellent yields by condensation reactions with carbonyl compounds under mild conditions. These reactions are regarded as the typical addition-elimination reaction of group IV organometallics.

Imidazolidine derivatives have been synthesized by a dehydration condensation reaction between diamine and carbonyl compounds. This preparative reaction, however, is reversible, and removal of generated water is required to complete the reaction. This operation takes generally long time and is inadequate to prepare water-sensitive homologues.

In this paper we describe a modified preparation of imidazolidine skeleton by means of *N,N'*-bis(trimethylsilyl)ethylene- and -*o*-phenylenediamines. Elimination of unreactive hexamethyldisiloxane should favor an irreversible generation of imidazolidine under mild reaction conditions. In addition, the present manipulation is easy to carry out simple separation of hexamethyldisiloxane *in vacuo*. These condensation reactions constitute an extension of addition-elimination reactions of main group organometallics from the standpoint of organometallic chemistry.



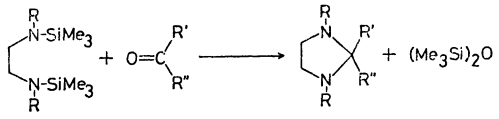
(1)

The most important driving force in either β-addition-β-elimination of heptamethyldimetallazane (M=Me_3Si,[2,3] Me_3Ge,[4] and Me_3Sn[2,5] X=NMe), or β-addition-ω-elimination (M=$^nBu_3Sn$; Y=$O(CH_2)_nO$,[6] $NR(CH_2)_2O$,[7] $NR(CH_2)_2NR$[7]) was the organometallic affinity differences between product (with stable M–Y bonds) and starting materials (with labile M–X bonds).[8]

This work is devoted to examine the possibility of utilization of the strong silicon-oxygen bond formation (a hard-hard interaction) in the imidazolidine cyclizations, because we previously elucidated that an inverse soft-soft interaction of tin-sulfur bond formation had substantial synthetic potential in iminocarbonylation or cyclization to thione-carbonate and spiro-orthoesters.

Results and Discussion

Reactions of electronically and sterically different various *N,N'*-bis(trimethylsilyl)-1,2,-diamines with aldehyde or ketones gave corresponding imidazolidine derivatives in excellent yields.



(2)

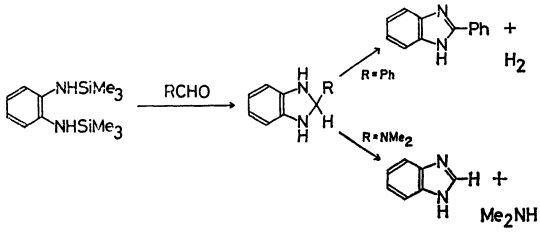
Hexamethyldisiloxane generated as a sole by-product could be removed completely by evaporation *in vacuo* at room temperature. When dimethylformamide was used as a reactant with *N,N'*-bis(trimethylsilyl)ethylenediamine and -*o*-phenylenediamine, subsequent elimination of dimethylamine induced the generation of 2-imidazoline and 2-benzimidazole, respectively. Preparative results are summarized in Table 1. Analytical and spectroscopic results are shown in Table 2.

Reaction of N,N'-*Bis(trimethylsilyl)ethylenediamine (**1**).* *N,N'*-Bis(trimethylsilyl)ethylenediamine (**1**) reacted with diethyl ketone and cyclohexanone to give the expected imidazolidines (**4b**) and (**4a**), which were readily purified by distillation. Analytical and spectral informations are in consistent with the depicted structures.

Dimethylformamide reacted with **1** at 120 °C to give imidazoline (**4c**) by way of further elimination of dimethylamine. Although 2-substituted imidazolines have been prepared by dehydration condensation under highly drastic conditions (200—220 °C), parent skeleton of 2-imidazoline has not been obtained. This method is extremely useful to prepare simplest 2-imidazoline (**4c**). The mechanism of this reaction was discussed later. Benzaldehyde did not give expected imidazolidine by ω-elimination of hexamethyldisiloxane but afforded *N,N'*-dibenzylideneethylenediamine (**4d**), which was definitely identified by analysis, IR ($\nu_{C=N}$ 1640 cm^{-1}), and NMR [τ_{CH} 1.80 (2H, s), τ_{CH_2} 6.16 (4H, s)].

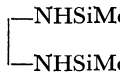
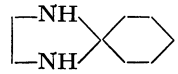
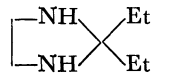
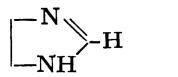
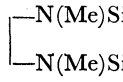
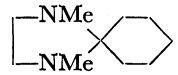
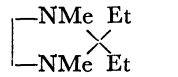
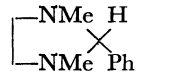
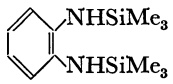
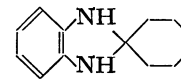
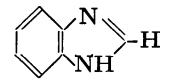
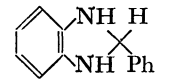
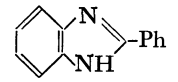
Reaction of N,N'-*Bis(trimethylsilyl)*-N,N'-*dimethylethylenediamine (**2**).* Introduction of methyl groups on each nitrogen atom of **2** increased both electron density and steric hindrance around the nitrogen atom. The reaction of **2** with diethyl ketone, cyclohexanone, and even benzaldehyde, however, gave quantitatively the corresponding imidazolidines, **5b**, **5a**, and **5c**, which were unambiguously identified by analytical and spectral informations. Dimethylformamide did not react with **2** even at 120 °C for 6 hr indicative of the participation of steric effect to some extent.

Reaction of N,N'-*Bis(trimethylsilyl)*-o-*phenylenediamine (**3**).* Benzimidazoline derivatives (**6b** and **6a**) were obtained successfully by the reaction of **3** with benzaldehyde or cyclohexanone in excellent yields,



(3)

Table 1. Cyclization reaction of bis(trimethylsilyl)diamines with carbonyl compounds

Bis(TMS)-diamine	Carbonyl compound	Method[a]	Reaction conditions	Product	Bp (°C/mmHg) [mp] (°)	Yield[b] (%)
 (**1**)		**A**	20 °C/2 min	 (**4a**)	41/0.2	59 (98)
(**1**)	$Et_2C=O$	**B**	120 °C/1 hr	 (**4b**)	31/2	59 (98)
(**1**)	Me_2NCHO	**B**	120 °C/1 hr	 (**4c**)	50/1	87
(**1**)	PhCHO	**A**	20 °C/2 min	$(PhCH{=}N{-}CH_2)_2$ (**4d**)	152/0.8	98
 (**2**)		**A**	20 °C/2 min	 (**5a**)	72/50	56 (100)
(**2**)	$Et_2C=O$	**B**	180 °C/24 hr	 (**5b**)	40/7	33 (100)
(**2**)	Me_2NCHO	**B**	120 °C/6 hr	No reaction		
(**2**)	PhCHO	**A**	20 °C/2 min	 (**5c**)	63/1	93 (100)
 (**3**)		**A**	20 °C/2 min	 (**6a**)	[131—133]	66 (100)
(**3**)	$Et_2C=O$	**B**	180 °C/24 hr	No reaction		
(**3**)	Me_2NCHO	**B**	120 °C/12 hr	 (**6d**)	[173—175]	97
(**3**)	PhCHO	**B**	50 °C/3 hr	 (**6b**)	[63—65]	91 (100)
(**3**)	PhCHO	**B**	120 °C/12 hr	 (**6c**)	[298—300]	29

a) See experimental section. b) Yield is isolated yield and that in parentheses is determined by NMR.

whereas diethyl ketone did not react with **3** even at 180 °C.

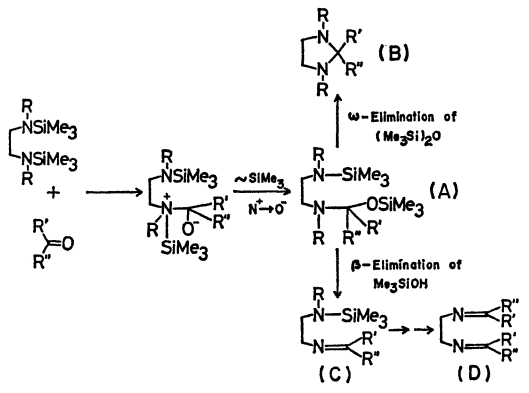
When **3** was reacted with benzaldehyde and with dimethylformamide at elevated temperature (120 °C), 2-phenylbenzimidazole (29%) and benzimidazole (97%) were generated respectively by way of the successive β-elimination of hydrogen and dimethylamine. In fact, 2-phenylbenzimidazoline (**6b**), prepared from **3** and benzaldehyde at room temperature, caused smooth elimination reaction of hydrogen to aromatize to benzimidazole at 120 °C.

Mechanism. Above-mentioned preparative reactions are reasonably explained by a β-addition-ω-elimination reaction controlled by the affinity difference between labile Si–N and stable Si–O bonds. The primary step is the nucleophilic attack of either nitrogen atom in *N,N'*-bis(trimethylsilyl)-1,2-diamines to the carbonyl carbon atom, followed by the rapid migration of trimethylsilyl group to oxy anion to give intermediate insertion product [A]. Formation of extremely stable hexamethyldisiloxane is the driving force of the ω-elimination reaction to give imidazolidine [B] as cyclization product. The reaction between **1** and benzaldehyde belongs to an exceptional case and facile β-elimination of trimethylsilanol is induced to give [C] which captures the second benzaldehyde at

Table 2. Analytical and spectroscopic results of products

	Analysis (Found)		^{1}H NMR (τ)	IR (cm^{-1})
4a	C	68.91(68.54)	7.18(4H, s)[a]	3250 (ν_{NH})[a]
	H	11.71(11.50)	8.55(10H, m)	
	N	19.38(19.98)	8.82(2H, s)	
4b	C	65.30(65.59)	7.20(4H, s)[a]	3260 (ν_{NH})[a]
	H	12.41(12.58)	8.40—9.34 (12H, overlapping of NH, CH_2, and CH_3)	
	N	22.29(21.85)		
4c	C	52.05(51.41)	3.01(1H, m)[b]	3420 (ν_{NH})[c]
	H	9.05(8.62)	5.89(1H, m)	
	N	38.89(39.96)	6.49(4H, m)	
4d	C	81.54(81.34)	1.80(2H, s)[a]	1640 ($\nu_{C=N}$)[a]
	H	7.06(6.83)	2.55(10H, m)	
	N	11.40(11.85)	6.16(4H, s)	
5a	C	72.04(71.36)	7.35(4H, s)[a]	2770 (ν_{N-CH_3})[a]
	H	11.98(11.91)	7.89(6H, s)	
	N	16.05(16.64)	8.60(10H, m)	
5b	C	69.47(69.16)	7.27(4H, s)[a]	2770 (ν_{N-CH_3})[a]
	H	13.10(12.90)	7.75(6H, s)	
	N	17.43(17.92)	8.79(4H, q, J=7Hz)	
			9.33(6H, t, J=7Hz	
5c	C	75.27(74.96)	2.75(5H, m)[a]	2760 (ν_{N-CH_3})[a]
	H	9.30(9.15)	6.89(1H, s)	
	N	15.43(15.89)	7.20(4H, AA'BB')	
			7.97(6H, s)	
6a	C	76.94(76.53)	3.55(4H, m)[a]	3320, 3230 (ν_{NH})[d]
	H	8.57(8.57)	6.54(2H, s)	
	N	14.48(14.88)	8.38(10H, m)	
6b	C	79.31(79.56)	1.60(1H, s)[a]	3470, 3370 (ν_{NH})[d]
	H	5.89(6.16)	2.42(5H, m)	
	N	14.00(14.27)	3.27(4H, m)	
			6.00(2H, s)	
6c	C	80.25(80.39)		mass m/e 194 (M^+)
	H	5.08(5.19)	sparingly soluble	
	N	14.31(14.42)		
6d	C	70.60(71.19)	1.85(1H, s)[e]	mass m/e 118 (M^+)
	H	5.28(5.12)	2.63(4H, m)	
	N	23.92(23.72)		

a) in CCl_4, b) in $CDCl_3$, c) in $CHCl_3$, d) in KBr, e) in $(CD_3)_2CO$



the another end to generate *N,N'*-dibenzylideneethylenediamine [D].

Experimental

IR spectra were recorded with a Japan Spectroscopic Co., Ltd. IR-S instrument. ^{1}H NMR spectra were measured with a Japan Electron Optics Lab. Co., Ltd. C-60 HL instrument. *N,N'*-Bis(trimethylsilyl)diamines were prepared according to Birkofer, Kühlthau, and Ritter.[9] Carbonyl compounds were freshly distilled before use.

Synthesis of Imidazolidines. To the *N,N'*-bis(trimethylsilyl)diamine (3.5—13.5 mmol) were added dropwise equimolar amounts of carbonyl compounds under an atmosphere of nitrogen at 0 °C.

In *Method* **A** the reaction mixture was warmed to room temperature. In *Method* **B** the mixture was heated in a sealed tube. In both methods formed hexamethyldisiloxane was removed from the reaction mixture to leave imidazolidine under reduced pressure (*ca.* 30 mmHg). For the purpose of elemental analysis, imidazolidines were distilled under reduced pressure. The elemental analyses, ^{1}H NMR spectra, IR spectra and other properties provided an adequate support for the structure assigned.

Reaction of N,N'-*Bis(trimethylsilyl)ethylenediamine with Benzaldehyde. Synthesis of* N,N'-*Dibenzylideneethylenediamine (**4d**).* To *N,N'*-bis(trimethylsilyl)ethylenediamine (2.75 g, 13.5 mmol) was added benzaldehyde (1.36 g, 12.8 mmol) dropwise under nitrogen at −78 °C. When the reaction mixture was warmed gradually to room temperature, exothermic reaction occurred to give transparent liquid separated into two layers. The reaction mixture was then distilled under reduced pressure (152 °C/0.8 mmHg) to yield colorless needles (1.48 g, 98% yield based on benzaldehyde used). Mp 52.0—54.0 °C. Found: C, 81.54; H, 7.06; N, 11.40%. Calcd for $C_{16}H_{16}N_2$: C, 81.34; H, 6.83; N, 11.85%. IR (in KBr) 1640 cm^{-1} ($\nu_{C=N}$). ^{1}H NMR (in CCl_4) τ 6.16 (4H, s), 2.25 (10H), and 1.80 (2H, s).

*Conversion of 2-Phenylbenzimidazoline (**6b**) to 2-Phenylbenzimidazole (**6c**).* By the heating of the benzene solution of 2-phenylbenzimidazoline (1.00 g, 5.11 mmol) in sealed tube at 120 °C for 12 hr, colorless precipitates sparingly soluble in benzene separated out. Upon recrystallization from acetone 2-phenylbenzimidazole precipitated as colorless prisms (0.291 g) in a 29% yield. The mp and spectroscopic data of the product were in good agreement with those of authentic sample.

References

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