

REACTIONS OF GROUP IV ORGANOMETALLIC COMPOUNDS  $x^1$   
 A NOVEL SYNTHESIS OF SUBSTITUTED CHLOROFORMAMIDINES  
 OR GUANIDINE BY THE REACTION OF ORGANOSILYLAMINES  
 AND ISOCYANIDEDICHLORIDE

KENJI ITOH, AKIRA NOZAWA, AND YOSHIO ISHII

Department of Synthetic Chemistry, Faculty of Engineering,  
 Nagoya University. Furo-cho, Chikusa-ku, Nagoya, Japan

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Several addition reactions of organosilylamines to unsaturated compounds<sup>2</sup> or cyclic compounds<sup>3-5</sup> were extensively studied during these few years.

In this publication, reactions between trimethylsilylamines and phenylisocyanidedichloride(I) are reported, which occur at 85° for 24 hours and afford chloroformamidines(II) in excellent yield through expulsion of trimethylchlorosilane.

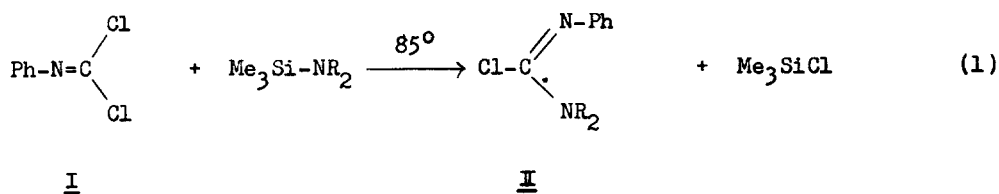


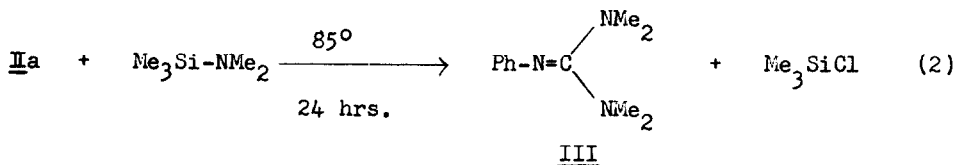
TABLE I included reaction conditions, yield of products, and physical properties of chloroformamidines, which were identified by elementary analysis, infra-red, and nmr spectra. This reaction would offer a convenient method for the preparation of substituted chloroformamidines.

TABLE I

Chloroformamidines(I) by the Reaction of I with Trimethylsilyldialkylamines

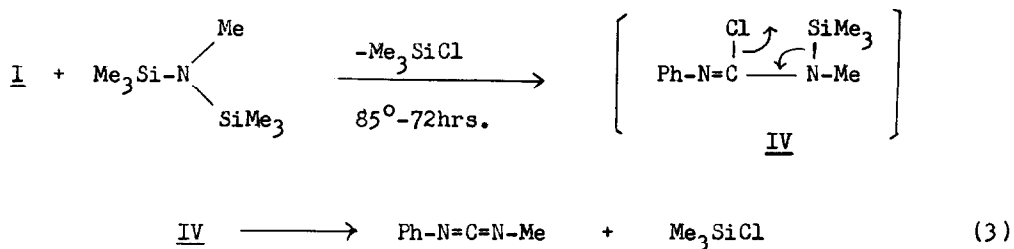
R	Reaction conditions (°C- hrs.)	Yield (%)		B. p. of <u>II</u> (°C/mmHg)	$\nu_{C=N}$ ( $\text{cm}^{-1}$ )
		$\text{Me}_3\text{SiCl}$	<u>II</u>		
a $\text{CH}_3$	85-24	44	54	70/0.05	1660
b $\text{C}_2\text{H}_5$	85-24	89	83	88/0.07	1660
c $n\text{-C}_3\text{H}_7$	75-16	93	84	105/0.3	1660

When I was treated with further one mole of trimethylsilylamine, N-phenyl-N',N',N'',N'''-tetramethylguanidine (III) was obtained in 98.5% in the case of  $\text{R}=\text{CH}_3$  together with 69% of trimethylchlorosilane. Guanidine III could be prepared from the reaction between 2:1 mole ratio of  $\text{Me}_3\text{SiNMe}_2$  and I similarly. N-Phenyl-N',N',N'',N'''-tetramethylguanidine (III) was identified as picrate (m.p.  $157^\circ$ , Calcd. for  $\text{C}_{17}\text{H}_{20}\text{N}_6\text{O}_7$ ; C, 48.57, H, 4.80. Found; C, 48.36, H, 4.32).

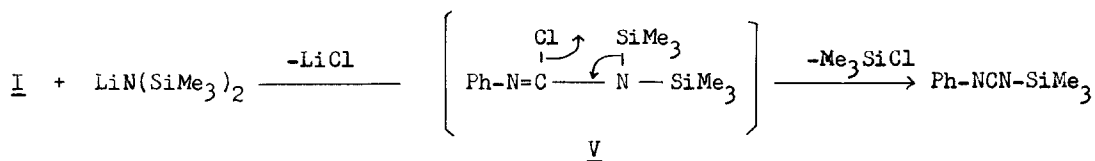


However, similar reaction did not proceed in the case of trimethylsilyl-diethyl- or di-n-propylamine, probably because of steric hindrance of dialkylamino group.

In the reaction of N-methylhexamethyldisilazane with I, the anticipated chloroformamidine(IV) could never be isolated and the products obtained were methylphenylcarbodiimide (72%) and trimethylchlorosilane (43%) which suggested subsequent  $\beta$ -elimination of IV as eq. 3.



Similar  $\beta$ -elimination of trimethylchlorosilane was also observed in the reaction of I with lithium bis(trimethylsilyl)amide. Treatment of I with equimolar amounts of  $\text{LiN}(\text{SiMe}_3)_2$  at  $100^\circ$  for 24 hrs. afforded trimethylchlorosilane, lithium chloride, and trimethylsilylphenylcarbodiimide (65% based on converted I): b. p.<sub>0.1</sub>  $49^\circ$ ;  $\tau_{\text{CH}_3-\text{Si}}$  9.72(9H),  $\tau_{\text{C}_6\text{H}_5}$  2.95-3.05(5H) in  $\text{CCl}_4$ ;  $\nu_{\text{N}=\text{C}=\text{N}}$   $2170 \text{ cm}^{-1}$ , as well as recovered I (60%).



Extensive study to utilize the above reactions as synthetic method of various chloroformamidines, guanidines, and carbodiimides, is now in progress.

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