

SYNTHESES AND ULTRAVIOLET SPECTRA OF N-ORGANOSILYL KETIMINES*

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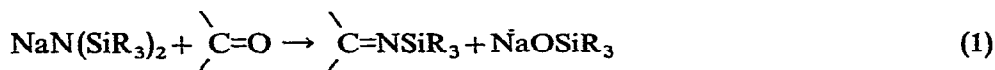
INTRODUCTION

In 1963, Krüger *et al.* synthesized the first N-organosilyl ketimines¹. These compounds were found to be intensely yellow in color and to have a low-intensity, long-wavelength absorption in the ultraviolet region. This absorption corresponds to the $n \rightarrow \pi^*$ transition, which involves the excitation of an electron in the nonbonding orbital of nitrogen to the antibonding π^* orbital of the C=N bond. Since the nitrogen lone pair and the π system of the C=N bond in silyl ketimines may be involved in $d_\pi-p_\pi$ interaction with the vacant d orbital of silicon, we hoped to study this interaction in C=N-Si systems through the investigation of the $n \rightarrow \pi^*$ absorption. This paper reports the preparation and ultraviolet spectral study of twenty-eight new N-organosilyl ketimines and several germanium and tin analogs.

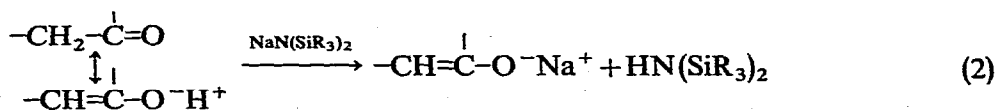
RESULTS AND DISCUSSION

Synthesis

Two general synthetic methods were employed to obtain the compounds under study. Sodium bis(triorganosilyl)amide reacts with non-enolizable ketones in refluxing benzene to form N-triorganosilyl ketimine¹:



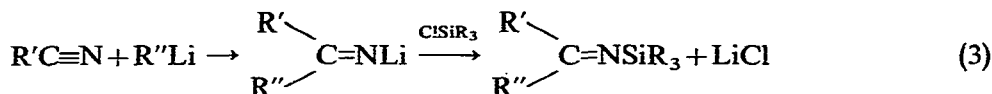
The reaction mechanism, as proposed by Krüger *et al.*, involves the addition of the ionic sodium reagent to the carbonyl double bond, followed by the elimination of a sodium triorganosilanolate molecule. This cannot be applied to enolizable ketones because the hydroxy proton in the enol form is readily exchanged with the sodium ion of the silyl amide, and consequently sodium enolate and disilylamine are formed:



* Taken from the thesis submitted by Lui-Heung Chan in partial fulfillment of the requirements for the Ph.D. degree from Harvard University, 1966.

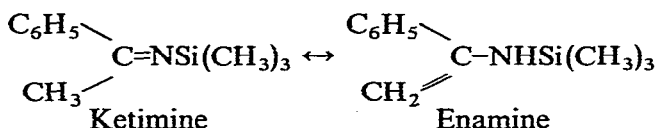
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We have found an alternative and novel method for synthesizing this class of compounds which involves the action of the lithium derivative of a ketimine, $>\text{C}=\text{NLi}$, on organohalosilanes. Lithium derivatives of ketimines can be obtained by the addition of an organolithium reagent to the $\text{C}\equiv\text{N}$ group in nitriles:



This method can also be applied to synthesize ketimines containing other Group IV elements. $\text{M}-\text{Cl}$ bonds ($\text{M} = \text{Ge}, \text{Sn}$ and Pb) react readily with the ketimine-lithium reagent. The carbon-chlorine bond in corresponding organic compounds is not polar enough to undergo such reaction, with the exception of that in triphenylchloromethane.

Reaction (3) proceeds smoothly in good yields when both R' and R'' are aryl groups. With aliphatic substituents, the hydrogen in the α -position in ketimines enters into enamine tautomerism². Consequently an equilibrium mixture of ketimine and enamine is obtained. This phenomenon is encountered, for instance, in the preparation of *N*-(trimethylsilyl)acetophenone imine:

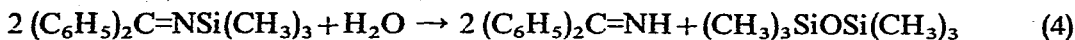


Such tautomerism is clearly indicated in the proton magnetic spectrum of the compound, which shows olefinic proton signals for the ene-amine (4.07 ppm downfield from tetramethylsilane) as well as C -methyl proton signals of the ketimine form (2.33 ppm), in addition to the signals due to phenyl and silyl methyl protons. An infrared spectral band at 3400 cm^{-1} indicates the presence of the $\text{N}-\text{H}$ bond.

Owing to the difficulties arising from enolization and enamination, pure silyl derivatives of aliphatic ketimines containing α -hydrogen were not obtained. The compounds prepared were mostly metal substituted benzophenone imines. In Table 2 the compounds are listed and grouped into six categories according to the effects studied in their ultraviolet spectra: (I) *N*-(trialkylsilyl)benzophenone imines, (II) *N*-silylbenzophenone imines with π -electron donors on silicon, such as phenyl, vinyl, alkoxy and amino groups, (III) *N*-(trimethylsilyl)benzophenone imines with substituents on the phenyl rings, (IV) benzophenone imine derivatives of various Group IV elements, $(\text{C}_6\text{H}_5)_2\text{C}=\text{NMR}_3$, ($\text{R} = \text{CH}_3$ or C_6H_5), (V) compounds containing more than one ketimine group, $[(\text{C}_6\text{H}_5)_2\text{C}=\text{N}]_x\text{SiR}_{4-x}$ and (VI) silyl ketimines of other ketones, *e.g.* acetophenone, anthraquinone, fluorenone and hexafluoroacetone.

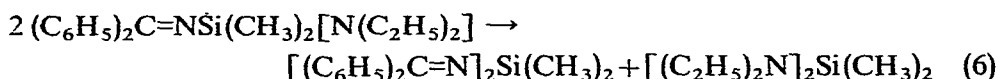
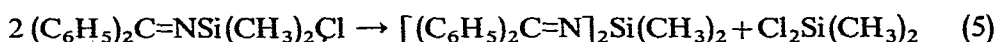
Properties

Metal-substituted ketimines of silicon, germanium, tin and lead are hygroscopic yellow oils or yellow crystalline solids, miscible with most organic solvents. When allowed to react with water, a silyl ketimine in ether solution is decolorized readily, giving the parent organic ketimine and siloxane. The hydrolysis reaction of *N*-(trimethylsilyl)benzophenone imine is written as an example:



Cleavage of the silicon–nitrogen bond to initiate hydrolysis and alcoholysis seems to be hindered by bulky substituents on silicon such as phenyl groups. N-(triphenylsilyl)benzophenone imine, a yellow crystalline solid, appears to be quite stable toward atmospheric moisture. In the series of $[(C_6H_5)_2C=N]_xSiR_{4-x}$ compounds, liability to hydrolysis increases with the number of ketimine groups attached to a silicon atom.

Compounds containing amino, chlorine and alkoxy groups on silicon are less stable toward heat. N-[(Diethylamino)dimethylsilyl]benzophenone imine and N-(chlorodimethylsilyl)benzophenone imine undergo thermal rearrangement giving bis(benzophenone-imino)dimethylsilane. The possible course of reaction may be written as follows:



Decomposition of N-(triethoxysilyl)benzophenone imine to tetraethoxysilane also took place during the distillation process.

Infrared spectra and structure

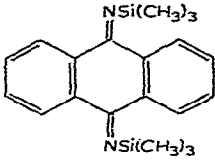
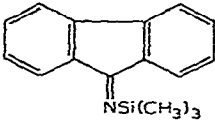
The infrared spectra are complex due to the presence of phenyl rings. Only the structurally characteristic bands are summarized in Table 1. The spectrum of N-(trimethylsilyl)benzophenone imine is shown in Fig. 1 as a typical example. An intense band near 1670 cm^{-1} is attributed to the C=N stretching vibration³. The

TABLE 1

CHARACTERISTIC INFRARED BANDS OF METAL-SUBSTITUTED KETIMINES (in cm^{-1})

$\nu(C=N)$ is C=N stretching; $\nu(M-N)$ is metal–nitrogen stretching; $\delta_{\text{sym}}(M-R)$ is symmetric deformation of M–CH₃, M–CH₂ or M–CH; $\rho(M-R)$ is methyl or methylene rocking and Si–C stretching.

Compound	$\nu(C=N)$	$\nu(M-N)$	$\delta_{\text{sym}}(M-R)$	$\rho(M-R)$	M–Ph
$(C_6H_5)_2C=NSi(CH_3)_3$	1642	907	1262, 1242	838, 757	
$(C_6H_5)_2C=NSi(CH_3)_2(CHCl_2)$	1645	907	1267, 1250	858, 786	
$(C_6H_5)_2C=NSi(C_2H_5)_3$	1657	900	1265	827, 735	
$(C_6H_5)_2C=NSi(\text{iso-}C_3H_7)_3$	1670	900	1255	820	
$(C_6H_5)_2C=NSi(n\text{-}C_4H_9)_3$	1655	900	1255	820, 755	
$(C_6H_5)_2C=NSi(C_6H_5)_3^a$	1662	905			1427, 1110
$(C_6H_5)_2C=NSi(CH_2C_6H_5)_3^b$	1658	908	1267	823	
$(C_6H_5)_2C=NSi(CH_3)_2(CH=CH_2)$	1640	908	1260, 1240	844, 780	
$(C_6H_5)_2C=NSi(CH_3)_2(CH_2CH=CH_2)$	1647	905	1266, 1246	855, 758	
$(C_6H_5)_2C=NSi(CH_3)_2[N(C_2H_5)_2]$	1653	904	1266, 1248	840, 781	
$(C_6H_5)_2C=NSi(CH_3)_2(OC_4H_9)$	1650	907	1263, 1248	856, 786	
$(p\text{-}ClC_6H_4)(C_6H_5)C=NSi(CH_3)_3$	1645	905	1246	838, 755	
$(m\text{-}ClC_6H_4)(C_6H_5)C=NSi(CH_3)_3$	1652	905 (sh)	1248	838, 758	
$(o\text{-}ClC_6H_4)(C_6H_5)C=NSi(CH_3)_3$	1658	925	1248	840, 755	
$(p\text{-}CH_3C_6H_4)(C_6H_5)C=NSi(CH_3)_3$	1643	905	1248	836, 755	
$(m\text{-}CH_3C_6H_4)(C_6H_5)C=NSi(CH_3)_3$	1650	910	1250	840, 757	
$(o\text{-}CH_3C_6H_4)(C_6H_5)C=NSi(CH_3)_3$	1641	921	1248	836, 754	
$(p\text{-}CH_3OC_6H_4)(C_6H_5)C=NSi(CH_3)_3$	1645	905	1248	838, 755	
$(p\text{-}CH_3C_6H_4)_2C=NSi(CH_3)_3$	1643	923	1248	835, 755	
$(o\text{-}CH_3C_6H_4)_2C=NSi(CH_3)_3$	1647	925	1250	840, 757	

Compound	$\nu(\text{C}=\text{N})$	$\nu(\text{M}-\text{N})$	$\delta_{\text{sym}}(\text{M}-\text{R})$	$\rho(\text{M}-\text{R})$	M-Ph
$(\text{C}_6\text{H}_5)_2\text{C}=\text{NGe}(\text{CH}_3)_3$	1630	?	1234	824, 758	
$(\text{C}_6\text{H}_5)_2\text{C}=\text{NSn}(\text{CH}_3)_3$	1613	?	1190	785, 775	
$(\text{C}_6\text{H}_5)_2\text{C}=\text{NC}(\text{C}_6\text{H}_5)_3^a$	1621				
$(\text{C}_6\text{H}_5)_2\text{C}=\text{NGe}(\text{C}_6\text{H}_5)_3^a$	1633	?			1425, 1092
$(\text{C}_6\text{H}_5)_2\text{C}=\text{NSn}(\text{C}_6\text{H}_5)_3^a$	1613	?			1425, 1072
$[(\text{C}_6\text{H}_5)_2\text{C}=\text{N}]_2\text{Si}(\text{CH}_3)_2^a$	1630	970	1264, 1245	854, 785	
$[(\text{C}_6\text{H}_5)_2\text{C}=\text{N}]_3\text{Si}(\text{CH}_3)^a$	1643	910	1258, 1245	852, 750	
$[(\text{C}_6\text{H}_5)_2\text{C}=\text{N}]_2\text{Si}(\text{C}_6\text{H}_5)_2^a$	1669	908			1422, 1106
$[(\text{C}_6\text{H}_5)_2\text{C}=\text{N}]_3\text{Si}(\text{C}_6\text{H}_5)^a$	1670	905			1423, 1104
	1678	905	1246	836, 754	
	1670	897	1246	831, 750	
$(\text{CF}_3)_2\text{C}=\text{NSi}(\text{CH}_3)_3$	1780	954	1260, 1235	854, 770	
$(\text{CF}_2\text{Cl})_2\text{C}=\text{NSi}(\text{CH}_3)_3$	1780	925	1250, 1240	850, 769	
$(\text{C}_6\text{H}_5)(\text{CH}_3)\text{C}=\text{NSi}(\text{CH}_3)_3$	1690	910	1250	840, 765	
$(\text{C}_6\text{H}_5)\text{HC}=\text{NSi}(\text{CH}_3)_3$	1660	910 (sh)	1250	845, 758	

^a Spectra obtained in mull of Kaydol oil. ^b Spectra obtained in carbon tetrachloride solution.

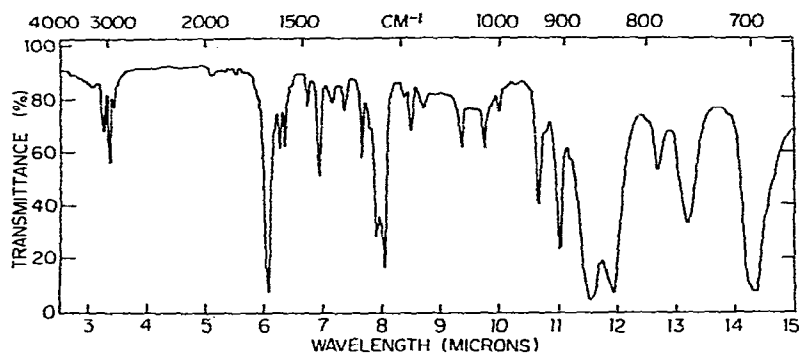


Fig. 1. The infrared spectrum of N-(trimethylsilyl)benzophenone imine.

familiar symmetric deformation band of the trimethylsilyl group appears at 1250 cm^{-1} . This band is intense and usually split into two components of unequal intensity due to vibrational interactions. In addition to the 1250 cm^{-1} band, two broad bands at 840 cm^{-1} and 750 cm^{-1} are always present, arising from the methyl rocking and the Si-C stretching vibrations⁴. Ketimines with other alkyl groups attached to silicon also have similar absorptions in these regions. Two sharp, narrow bands characteristic of phenyl groups on silicon occur invariantly at 1425 cm^{-1} and 1110 cm^{-1} ⁴.

Positions for the infrared bands associated with the symmetric deformation

and rocking modes of the methyl groups on germanium and tin, as well as the absorptions of the metal-phenyl links, have been established previously^{5,6} and are identified in our compounds accordingly.

A band in the 900 cm^{-1} region, observed throughout the spectra of all N-silyl ketimines prepared, is tentatively assigned to the silicon-nitrogen stretching mode. This assignment is in accord with the assignments made for silazanes ($900\text{--}1000\text{ cm}^{-1}$)⁷, azidotrimethylsilane (800 cm^{-1})⁸, and N-(trimethylsilyl)aniline (899 cm^{-1})⁹. The band representing Ge-N stretching appears as a shoulder at 796 cm^{-1} in azidotrimethylgermane⁸, and the Sn-N band occurs at 843 cm^{-1} in N-(trimethylstannyl)-aniline⁹. Corresponding bands are not apparent in the spectra of $(\text{C}_6\text{H}_5)_2\text{C}=\text{NGeR}_3$ and $(\text{C}_6\text{H}_5)_2\text{C}=\text{NSnR}_3$. Further study will be required for definite assignment of the Ge-N and Sn-N stretching frequencies in these compounds.

It is interesting to note that the C=N and Si-N stretching frequencies are rather independent of the nature of substituents on silicon.

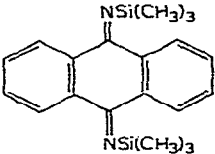
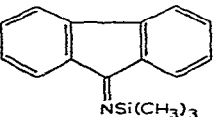
Ultraviolet spectra

The spectra of N-organosilyl-, germyl- and stannylbenzophenone imines in the usually accessible ultraviolet region consist of a long-wavelength band between $350\text{--}380\text{ m}\mu$ ($\epsilon \sim 10^2$), and a more intense short-wavelength absorption at about $250\text{ m}\mu$ ($\epsilon \sim 10^4$). The long-wavelength band, attributed to the $n \rightarrow \pi^*$ transition of a nonbonding electron on nitrogen, is characterized by its long wavelength, low intensity, and tendency to shift to shorter wavelength in polar solvents¹⁰. The short wavelength band corresponds to the $\pi \rightarrow \pi^*$ transition of the conjugate system, $(\text{C}_6\text{H}_5)_2\text{C}=\text{N}$. The spectrum of N-(trimethylsilyl)benzophenone imine is shown in Fig. 2, as a typical example, whereas the spectral data of all compounds prepared are recorded in Table 2.

TABLE 2

ULTRAVIOLET SPECTRA OF METAL-SUBSTITUTED KETIMINES

Group	Compound	$n \rightarrow \pi^*$ transition		$\pi \rightarrow \pi^*$ transition	
		$\lambda_{\text{max}}, \text{m}\mu$	ϵ	$\lambda, \text{m}\mu$	ϵ
I	$(\text{C}_6\text{H}_5)_2\text{C}=\text{NSi}(\text{CH}_3)_3$	364	77.8	243	1.63×10^4
	$(\text{C}_6\text{H}_5)_2\text{C}=\text{NSi}(\text{C}_2\text{H}_5)_3$	370	92.3	254	1.66×10^4
	$(\text{C}_6\text{H}_5)_2\text{C}=\text{NSi}(\text{iso-C}_3\text{H}_7)_3$	378	101.7	251	1.62×10^4
	$(\text{C}_6\text{H}_5)_2\text{C}=\text{NSi}(\text{n-C}_4\text{H}_9)_3$	370	93.5	252	1.64×10^4
	$(\text{C}_6\text{H}_5)_2\text{C}=\text{NSi}(\text{CH}_3)_2(\text{CHCl}_2)$	360	89.8	253	1.41×10^4
II	$(\text{C}_6\text{H}_5)_2\text{C}=\text{NSi}(\text{C}_6\text{H}_5)_3$	366	157.0	259	2.38×10^4
	$(\text{C}_6\text{H}_5)_2\text{C}=\text{NSi}(\text{CH}_2\text{C}_6\text{H}_5)_3$	368	114.0	254	1.86×10^4
	$(\text{C}_6\text{H}_5)_2\text{C}=\text{NSi}(\text{CH}_3)_2(\text{CH}=\text{CH}_2)$	363	76.3	242	1.43×10^4
	$(\text{C}_6\text{H}_5)_2\text{C}=\text{NSi}(\text{CH}_3)_2(\text{CH}_2\text{CH}=\text{CH}_2)$	364	89.3	246	1.46×10^4
	$(\text{C}_6\text{H}_5)_2\text{C}=\text{NSi}(\text{CH}_3)_2(\text{OC}_4\text{H}_9)$	365	96.2	250	1.52×10^4
	$(\text{C}_6\text{H}_5)_2\text{C}=\text{NSi}(\text{CH}_3)_2[\text{N}(\text{C}_2\text{H}_5)_2]$	360 (sh)	114.0	250	1.61×10^4
III	$(p\text{-ClC}_6\text{H}_4)(\text{C}_6\text{H}_5)\text{C}=\text{NSi}(\text{CH}_3)_3$	364	88.5	256	1.80×10^4
	$(m\text{-ClC}_6\text{H}_4)(\text{C}_6\text{H}_5)\text{C}=\text{NSi}(\text{CH}_3)_3$	364	70.9	248	1.52×10^4
	$(o\text{-ClC}_6\text{H}_4)(\text{C}_6\text{H}_5)\text{C}=\text{NSi}(\text{CH}_3)_3$	355	80.9	253	1.60×10^4
	$(p\text{-CH}_3\text{C}_6\text{H}_4)(\text{C}_6\text{H}_5)\text{C}=\text{NSi}(\text{CH}_3)_3$	360	87.9	254	1.81×10^4
	$(m\text{-CH}_3\text{C}_6\text{H}_4)(\text{C}_6\text{H}_5)\text{C}=\text{NSi}(\text{CH}_3)_3$	363	85.0	254	1.58×10^4

Group	Compound	$n \rightarrow \pi^*$ transition		$\pi \rightarrow \pi^*$ transition	
		$\lambda_{\max}$, m μ	ϵ	λ , m μ	ϵ
	$(o\text{-CH}_3\text{C}_6\text{H}_4)(\text{C}_6\text{H}_5)\text{C}=\text{NSi}(\text{CH}_3)_3$	360	73.6	253	1.60×10^4
	$(p\text{-CH}_3\text{OC}_6\text{H}_4)(\text{C}_6\text{H}_5)\text{C}=\text{NSi}(\text{CH}_3)_3$	357	104.7	274	1.51×10^4
	$(p\text{-CH}_3\text{C}_6\text{H}_4)_2\text{C}=\text{NSi}(\text{CH}_3)_3$	361	96.1	258	1.92×10^4
	$(o\text{-CH}_3\text{C}_6\text{H}_4)_2\text{C}=\text{NSi}(\text{CH}_3)_3$	355			
IV	$(\text{C}_6\text{H}_5)_2\text{C}=\text{NSi}(\text{CH}_3)_3$	364	77.8	243	1.63×10^4
	$(\text{C}_6\text{H}_5)_2\text{C}=\text{NGe}(\text{CH}_3)_3$	347	86.7	243	1.59×10^4
	$(\text{C}_6\text{H}_5)_2\text{C}=\text{NSn}(\text{CH}_3)_3$	361	94.3	233	1.38×10^4
	$(\text{C}_6\text{H}_5)_2\text{C}=\text{NC}(\text{C}_6\text{H}_5)_3$	305 (sh)	323.7	252	1.96×10^4
	$(\text{C}_6\text{H}_5)_2\text{C}=\text{NSi}(\text{C}_6\text{H}_5)_3$	366	157.0	259	2.38×10^4
	$(\text{C}_6\text{H}_5)_2\text{C}=\text{NGe}(\text{C}_6\text{H}_5)_3$	347	125.5	255	1.98×10^4
	$(\text{C}_6\text{H}_5)_2\text{C}=\text{NSn}(\text{C}_6\text{H}_5)_3$	358	113.5	222	2.48×10^4
	$(\text{C}_6\text{H}_5)_2\text{C}=\text{NPb}(\text{C}_6\text{H}_5)_3$	340 (sh)			
V	$(\text{C}_6\text{H}_5)_2\text{C}=\text{NSi}(\text{CH}_3)_3$	364	77.8	243	1.63×10^4
	$[(\text{C}_6\text{H}_5)_2\text{C}=\text{N}]_2\text{Si}(\text{CH}_3)_2$	364	202.8	250	2.83×10^4
	$[(\text{C}_6\text{H}_5)_2\text{C}=\text{N}]_3\text{Si}(\text{CH}_3)$	364	450.1	250	3.87×10^4
	$(\text{C}_6\text{H}_5)_2\text{C}=\text{NSi}(\text{C}_6\text{H}_5)_3$	366	157.0	259	2.38×10^4
	$[(\text{C}_6\text{H}_5)_2\text{C}=\text{N}]_2\text{Si}(\text{C}_6\text{H}_5)_2$	380	376.0	255	3.82×10^4
	$[(\text{C}_6\text{H}_5)_2\text{C}=\text{N}]_3\text{Si}(\text{C}_6\text{H}_5)$	371	574.7	252	4.32×10^4
VI	$(\text{C}_6\text{H}_5)(\text{CH}_3)\text{C}=\text{NSi}(\text{CH}_3)_3$	346	31.3 ^a	222	9.0×10^3
	$(\text{C}_6\text{H}_5)\text{HC}=\text{NSi}(\text{CH}_3)_3$	340		250	
	$(\text{CF}_3)_2\text{C}=\text{NSi}(\text{CH}_3)_3$	351		213	
	$(\text{CF}_2\text{Cl})_2\text{C}=\text{NSi}(\text{CH}_3)_3$	351	89.1	213	2.85×10^3
		424	322.0	292	2.50×10^4
		400	316.0	267 (sh)	1.98×10^4
		370	248.0	252	3.75×10^4
		352.5	306.0	299	9.35×10^3
				289	8.21×10^3
				265	2.08×10^3
				256	7.87×10^4
				248	5.70×10^4

^a Unusually low intensity for $n \rightarrow \pi^*$ band due to the presence of enamine.

West has suggested a model for the effect of metalloid substitution on the electronic transition of some simple chromophores¹¹. The qualitative energy level diagram of $\text{C}=\text{N}-\text{Si}$, according to West, is shown in Fig. 3. The diagram shows that silicon substituents on the nitrogen atom of the $\text{C}=\text{N}$ group decrease the energy required for $n \rightarrow \pi^*$ transition by their electropositive nature and by the $d_\pi-p_\pi$ interaction with the orbitals in the group. This can be illustrated by a comparison of the spectra of some N-silyl ketimines with those of the related organic ketimines (Table 3). Unlike silyl ketimines, the organic ketimines show only the high-intensity band below 300 m μ . Apparently the $n \rightarrow \pi^*$ band occurs at shorter wavelengths and therefore is

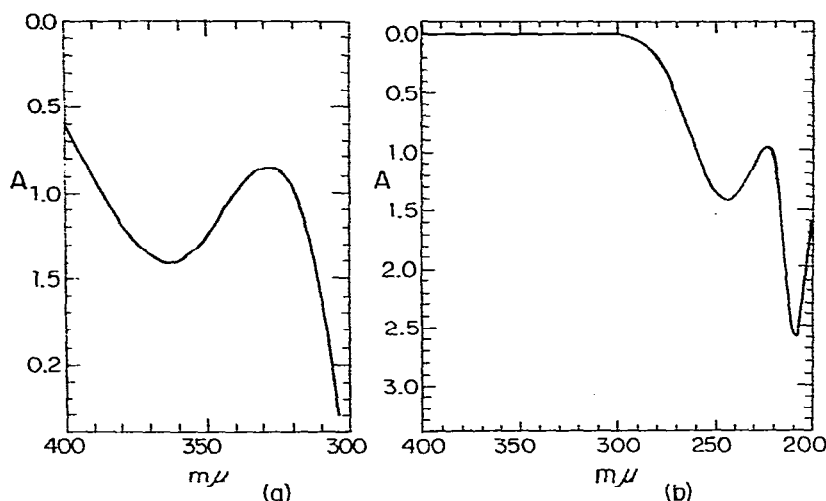


Fig. 2. The ultraviolet spectrum of N-(trimethylsilyl)benzophenone imine in (a) $1.81 \times 10^{-2} M$ (b) $8.75 \times 10^{-5} M$ solution in ether.

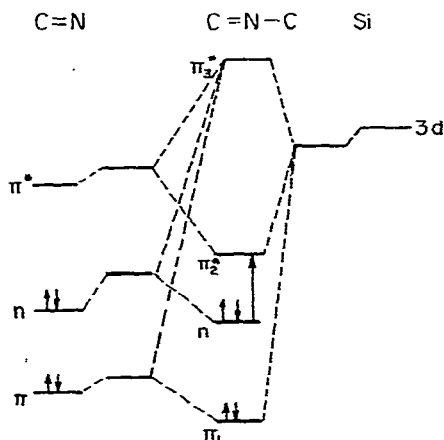


Fig. 3. Energy levels for the chromophore C=N-Si, showing the influence of the unfilled 3d orbitals of silicon.

hidden by the more intense $\pi \rightarrow \pi^*$ band. Assuming that the $n \rightarrow \pi^*$ transition in benzophenone and benzaldehyde imines occurs at about 250 $m\mu$, the bathochromic shift caused by silicon substitution in most silyl ketimines is thus 11,000–12,000 cm^{-1} .

The $\pi \rightarrow \pi^*$ transition is only slightly affected by the metalloid substitution. This may imply that the $d_\pi - \pi^*$ interaction is not a large effect. It should be taken into consideration, however, that this $\pi \rightarrow \pi^*$ transition is complex, for it involves the benzene rings as well as the C=N group. The excited state bonding may be less important here than for metal derivatives of simpler chromophores.

Effect of π -electron donating groups on silicon. In silylbenzophenone imines, if the nitrogen lone pair is involved in $d_\pi - p_\pi$ bonding with silicon, the substituents on silicon which are capable of donating π electrons would compete with the nitrogen lone pair for the vacant d orbitals of silicon and thereby weaken the π interaction

TABLE 3

COMPARISON OF UV SPECTRA OF ORGANOSILYL KETIMINES AND RELATED ORGANIC COMPOUNDS

Compound	$\lambda_{\max}$	$\log \epsilon_{\max}$	λ	$\log \epsilon$	Solvent	Ref.
$(\text{C}_6\text{H}_5)_2\text{C}=\text{NSi}(\text{CH}_3)_3$	364	1.89	243	4.21	Ether	12
$(\text{C}_6\text{H}_5)_2\text{C}=\text{NH}$			242		Ether	
$(\text{C}_6\text{H}_5)_2\text{C}=\text{NCH}_3$			246	4.2	Cyclohexane	
$(\text{C}_6\text{H}_5)_2\text{C}=\text{NCH}_2\text{C}_6\text{H}_5$			249	5.2	Ether	
$(\text{C}_6\text{H}_5)_2\text{C}=\text{NSi}(\text{C}_6\text{H}_5)_3$	366	2.20	259	4.38	Ether	
$(\text{C}_6\text{H}_5)_2\text{C}=\text{NC}(\text{C}_6\text{H}_5)_3$			305 (sh)	2.51	Ether	
			252	4.29		
$(\text{C}_6\text{H}_5)_3\text{HC}=\text{NSi}(\text{CH}_3)_3$	340		250		Ether	
$(\text{C}_6\text{H}_5)_3\text{HC}=\text{NCH}_3$			245	4.18	Ethanol	
$(\text{C}_6\text{H}_5)_3\text{HC}=\text{NC}_2\text{H}_5$			289	3.2	Ethanol	14
			280	3.3		
			246	4.3		
$(\text{C}_6\text{H}_5)_3\text{HC}=\text{NC}_6\text{H}_{11}$			245	4.06	Ethanol	15
			276	3.04		
			286	2.90		

between silicon and nitrogen. Consequently a shift might result in the $n \rightarrow \pi^*$ transition band.

In order to study this effect, silylbenzophenone imines containing π -electron donating substituents on silicon, such phenyl, vinyl, alkoxy and amino groups, were prepared and their spectra compared with that of N-(trimethylsilyl)benzophenone imine (Table 2, Group II). The spectral data indicate that there is no significant change in the $n \rightarrow \pi^*$ absorption maxima ($\lambda_{\max}$) caused by these π -electron donors. This lack of shift led to a reconsideration of the molecular structure of N-organosilylbenzophenone imines.

The $d_{\pi}-p_{\pi}$ interaction in the Si-N bond should be strongest when the C=N-Si linkage is linear, since the overlap between the nonbonding orbital of pure p character and the $3d$ orbital is greatest. The interaction is much weakened in a bent structure, when the nonbonding orbital acquires some s character and is directed away from the d orbital. In this case the energy of n level is not significantly changed by the variation of the π -electron-donating nature of the substituents on silicon. For reasons not yet understood, it seems that the nature of the groups attached to silicon has little influence on its ability to interact with the antibonding orbital (π^*) in the excited state. As a result, $\lambda_{\max}$ remains constant.

The postulate of a bent C=N-Si linkage is supported by studies of other structurally related compounds. Bis(trimethylsilyl)carbodiimide, $(\text{CH}_3)_3\text{SiN}=\text{C}=\text{NSi}(\text{CH}_3)_3$ ¹⁶, will not have a dipole moment if the C=N-Si linkage is linear. On the other hand, if it is bent, both of its stereoisomeric forms are expected to have a dipole moment. The dipole moment was measured and found to be 1.3 debye units. Furthermore, the molecular structure of trimethylsilyl isothiocyanate and trimethylsilyl isocyanate have been determined by electron diffraction¹⁷. The angles at the nitrogen atom were found to be 154° and 150° , respectively.

Ultraviolet spectra of compounds having more than one ketimine group on silicon.

When one or more methyl groups in N-(trimethylsilyl)benzophenone imine is replaced by another ketimine group, the $n \rightarrow \pi^*$ absorption maximum remains at 364 m μ (Table 2, Group V). This is consistent with the observations on the spectra of silyl ketimines with π donors on silicon, for ketimine groups are also capable of donating electrons from the π -system of the C=N bond. However, in the series of phenyl compounds, $[(C_6H_5)_2C=N]_xSi(C_6H_5)_{4-x}$ (where $x = 1, 2$ and 3), the λ_{max} values vary in a random fashion. This finding cannot yet be explained.

The inductive effect of substituents on silicon. In order to study the inductive effect on λ_{max} alone, various alkyl groups were introduced on the silicon atom. Their ultraviolet spectral data (Table 2, Group I) show that the absorption maximum shifts to longer wavelength when the alkyl group becomes more electron releasing. A plot of the λ_{max} against Taft's electronegativity value¹⁸ of the corresponding alkyl group indicates a linear relationship (Fig. 4).

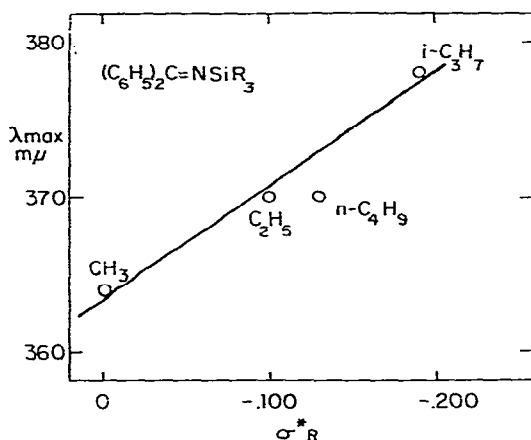


Fig. 4. Correlation of the long-wavelength absorption maximum λ_{max} with Taft's electronegativity value σ^*_R of the substituent groups R for the compounds $(C_6H_5)_2C=NSiR_3$.

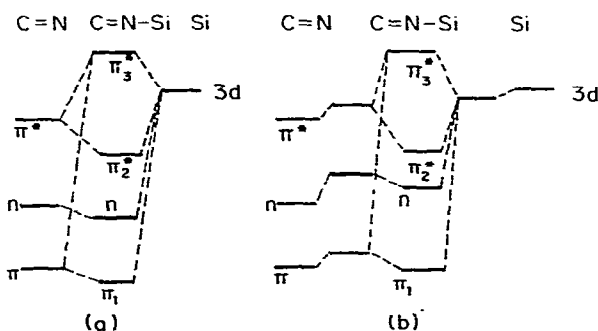


Fig. 5. Energy levels for C=N-Si (a) resonance effect alone (b) inductive and resonance effect of silicon substitution.

The inductive effect on the energy level for the chromophore C=N-Si is illustrated in Fig. 5. An electropositive group bonded to nitrogen causes the C=N group to be richer in electronic charge, while the reverse is true for the substituent.

Hence the positive inductive effect decreases the ionization potential and raises the levels of π^* , n and π . The n level is raised more than the other two levels, for silicon is directly attached to nitrogen. On the other hand, the $3d$ level is lowered. Since the π^* and $3d$ levels shift in opposite directions, better matching in energy of these two levels produce greater resonance interaction. The result is that π_2^* is not much changed by the inductive effect. With the π_2^* level remaining essentially constant and the n level raised, the energy required for the $n \rightarrow \pi^*$ transition is decreased, and a red shift results. This accounts for the shift of $\lambda_{\max}$ to longer wavelengths with increasingly electropositive alkyl groups on silicon.

Benzophenone imines containing other Group IV elements. Spectral data for the compounds $(\text{C}_6\text{H}_5)_2\text{C}=\text{MR}_3$ ($\text{R} = \text{CH}_3$ or C_6H_5) display a rather irregular variation in $\lambda_{\max}$ values (Table 2, Group IV). To study their data, two factors should be considered: the relative ability of π interaction of the individual elements, and their inductive effect.

Previous studies have shown that the relative order of π bonding is $\text{Si} > \text{Ge} > \text{Sn} \gg \text{Pb}$ and $\text{C}^{19,20,8}$. If this is true in the $\text{C}=\text{N}-\text{M}$ system, the amount of π^* lowering should decrease in the same order. Since the $\text{C}=\text{N}-\text{M}$ linkage is bent, the interaction of $3d$ orbitals with n will be small. The n level therefore is assumed to be essentially unchanged. In this way, the $n \rightarrow \pi^*$ transition band should shift to shorter wavelengths from silicon to germanium to tin compounds, and should occur at even shorter wavelengths in lead and carbon compounds (Fig. 6b).

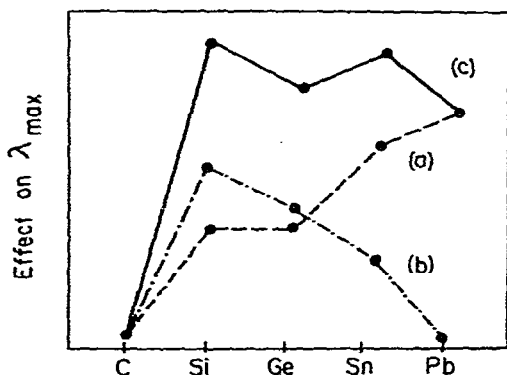


Fig. 6. The influence of (a) electronegativity — (b) π -interaction - - - on the $\lambda_{\max}$ value of $(\text{C}_6\text{H}_5)_2\text{C}=\text{NMR}_3$ compounds, and (c) the resultant of these two factors —.

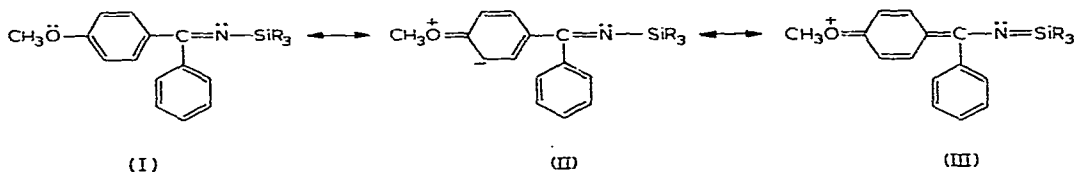
It has been noted that $\lambda_{\max}$ shifts to longer wavelength with electropositive substituents on nitrogen. Of the Group IV elements, silicon and germanium are more electropositive than carbon, while tin and lead are most electropositive and $\text{N}-\text{Sn}$ and $\text{N}-\text{Pb}$ bonds become more ionic. Therefore the $\lambda_{\max}$ value may be expected to increase in the following order: $\text{C} < \text{Si} \sim \text{Ge} < \text{Sn} < \text{Pb}$ (Fig. 6a).

The resultant of these two effects is shown in Fig. 6c, which accounts for the observed variation of the $\lambda_{\max}$ values in both series of ketimine compounds containing Group IV elements.

It is interesting that the electrostatic values for electronegativity of C, Si, Ge, Sn and Pb^{21} lead to the same qualitative variation of $\lambda_{\max}$ values of the inductive effect alone is considered, i.e., if the role of π bonding is diminished, or even eliminated.

Effect of ring-substituents

The $n \rightarrow \pi^*$ transition in benzophenone imine involves the transfer of electronic charge from nitrogen to carbon. Ring substituents which are able to supply electrons to the π -system by resonance raise the energy of the excited state relative to the energy of the ground state and therefore cause a blue shift of the absorption maximum. This intramolecular blue shift, though not a large effect, has been observed when Cl, CH_3 and OCH_3 groups are introduced into the phenyl ring in *para* and *ortho* positions (Table 2, Group III). The structure (III) postulated below contributes to the ground state. Such a structure is made possible by the vacant $3d$ orbitals on silicon.

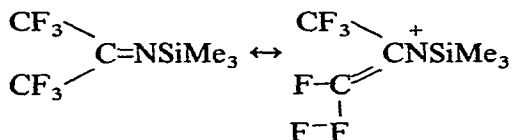


The relative order of resonance effect on λ_{max} is found to be $\text{CH}_3\text{O} > \text{CH}_3 > \text{Cl}$. A substituent in the *ortho* position has a stronger effect than one in the *para* position, perhaps because a steric effect is involved. *Meta*-substituents can only exert an inductive effect, which seems to be negligible as indicated by the unchanged λ_{max} value.

Conjugation effect

The spectral data in Table 2 (Group VI) for silyl ketimines derived from various ketones show that the $n \rightarrow \pi^*$ absorption maximum moves to longer wavelength with increasing degree of conjugation. Silyl ketimines of anthraquinone, fluorenone and benzophenone absorb in the highest wavelengths. The λ_{max} values decrease in the series $(\text{C}_6\text{H}_5)_2\text{C}=\text{NSiMe}_3 > (\text{C}_6\text{H}_5)\text{CH}_3\text{C}=\text{NSiMe}_3 > (\text{C}_6\text{H}_5)\text{HC}=\text{N-SiMe}_3$. Although the absorption maximum of a pure aliphatic silyl ketimine is not available the ketimine-amine equilibrium mixture of $(\text{C}_4\text{H}_9)(\text{C}_2\text{H}_5)\text{C}=\text{NSiMe}_3$ is colorless, indicating a low λ_{max} .

N-silylhexafluoroacetone imine and -tetrafluorodichloroacetone imine are pale yellow in color and absorb at higher wavelengths than the unsubstituted alkyl ketimines. Their λ_{max} values are comparable to those of the ketimines of benzophenone. This can be explained by the ability of a CF_3 group to enter into resonance interaction with the orbital in the $\text{C}=\text{N}$ bond. The resonance model, similar to the one postulated for (trifluoromethyl)benzene, is written below:



Intensity and d_π - p_π bonding

Although π -electron donating substituents on silicon have little influence on the $n \rightarrow \pi^*$ transition energy, they do affect the *intensity* of the absorption band. The intensity is enhanced by butoxy and diethylamino groups, and more markedly by three phenyl groups. The same effect is more pronounced in the two series of compounds, $[(\text{C}_6\text{H}_5)_2\text{C}=\text{N}]_x\text{SiR}_{4-x}$ ($\text{R} = \text{CH}_3$ and C_6H_5 , $x = 1, 2$ and 3). (Table 2).

When the number of ketimine groups on silicon is increased to two and three, the intensity is enhanced considerably more than two-fold and three-fold. (The intensity ratios for the methyl and phenyl compounds are 1:2.6:5.8 and 1:2.5:3.7, respectively.) Although steric factors may be important, our tentative interpretation is that intensity bears a relationship with $d_{\pi}-p_{\pi}$ bonding between silicon and nitrogen.

A $n \rightarrow \pi^*$ transition can be either allowed or forbidden by local symmetry¹⁰. The intensity of this transition for organosilyl ketimines clearly depends on the geometry of the C=N-Si linkage. For $n \rightarrow \pi^*$ transition, the intensity I can be expressed (with approximations) as follows²²:

$$\sqrt{I} \propto \sqrt{D} = \int \psi_i M \psi_f d\tau = \int n M \pi^* d\tau$$

where ψ_i is the orbital from which an electron is excited, ψ_f the orbital to which it is excited, D is the dipole strength, and M the dipole moment vector.

From symmetry considerations, excitation of an electron in a linear C=N-Si linkage from an n orbital of pure p character (p_y) to a π^* orbital formed from p_z orbitals is forbidden (Fig. 7a), and the integral vanishes. On the other hand, when the linkage is bent to 120° at nitrogen, (Fig. 7b), $n \rightarrow \pi^*$ transition from a nonbonding

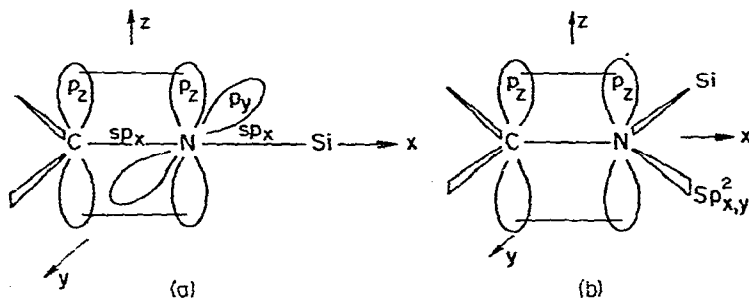


Fig. 7. The σ -bond skeleton and π -atomic orbitals in (a) linear C=N-Si linkage (b) bent C=N-Si linkage.

orbital of sp^2 hybrid is allowed, for the integral has a non-vanishing value. It is therefore believed that intensity varies with the bond angle ($\angle \text{CNSi}$), and very probably decreases when the angle increases from 120° to 180° .

On the other hand, the CNSi angle is closely related to the amount of $d_{\pi}-p_{\pi}$ interaction between the nitrogen lone pair and a silicon $3d$ orbital. The interaction is strongest when the C=N-Si linkage is linear and decreases with smaller CNSi angle. Thus the intensity of the $n \rightarrow \pi^*$ transition would increase when the nitrogen is less involved in $d_{\pi}-p_{\pi}$ bonding with silicon. For this reason, the π -donating substituents, competing with the nitrogen lone pair for the d orbital of silicon and thus weakening the amount of $d_{\pi}-p_{\pi}$ bonding in the Si-N bond which is originally small due to the bent structure, cause an enhancement in intensity.

Conclusion. The electronic spectra of ketimine derivatives of the Group IV elements are complex because at least three effects of the metals are involved:

- (1) The inductive effect: the electropositive nature of the metal raises the energy of π^* , π and, in particular, n . It therefore influences the availability of the nitrogen lone pair.
- (2) The π interaction between the empty d orbitals of the metal and the π system

in the C=N bond: the energies of both π^* and π levels are lowered by this effect. This interaction is much stronger with π^* than with π , and is referred to by West as "the excited state π interaction".

(3) The π interaction between the empty d orbitals of the metal and the lone pair on nitrogen: this "ground state π interaction" causes a lowering of the energy of the n level.

The result of these three effects combined is to produce a bathochromic shift of the $n \rightarrow \pi^*$ transition band. For most silylbenzophenone imines, a displacement of approximately $12,000 \text{ cm}^{-1}$ was observed. The $\pi \rightarrow \pi^*$ transition is complex, for it is due to the conjugated system involving the benzene rings and the C=N bond.

The $n \rightarrow \pi^*$ absorption maximum of silylbenzophenone imine is rather insensitive to the π electron donating substituents on silicon. This finding leads to the postulate of a bent structure for C=N-Si linkage and the conclusion that multiple bonding between silicon and nitrogen is small.

Since the ground state π interaction is small, the variation of the absorption maxima of silicon, germanium and tin compounds can be understood on the basis of the other two factors: the relative amount of excited state π bonding ($\text{Si} > \text{Ge} > \text{Sn} \gg \text{Pb}$ and C) and the inductive electron-releasing effect. The order of the change in their λ_{max} values reflects the balance of these two effects.

Lastly, the intensity of absorption corresponding to the $n \rightarrow \pi^*$ transition is low. It increases with decreasing $d_{\pi}-p_{\pi}$ bonding in the Si-N bond and is a sensitive indication of molecular geometry.

EXPERIMENTAL

Spectroscopic measurements

Ultraviolet spectra were obtained in ether solution on a Cary Recording Spectrometer, using a pair of 1 cm quartz cells. The long wavelength absorption was generally measured at a concentration of $2 \times 10^{-2} \text{ M}$. The solution was then diluted one-hundred-fold for the measurements of the more intense absorption below $300 \text{ m}\mu$.

Infrared spectra were recorded on Perkin Elmer Model 137B (Infracord), Model 237, and Model 21 spectrometers using sodium chloride discs. For liquid compounds, pure samples were used. For solids, the spectra were taken either in carbon tetrachloride solution or in Kaydol.

All new compounds were identified by proton magnetic resonance spectra measured in carbon tetrachloride solution on a Varian A-60 NMR spectrometer. Tetramethylsilane was used as the calibrating standard.

Analyses

Elemental analyses were carried out either by the Schwarzkopf Microanalytical Laboratory, N.Y., or in the laboratory of the Institut für Anorganische Chemie der Technischen Hochschule, Graz, Austria, through the courtesy of Professor Ulrich Wannagat (Table 4).

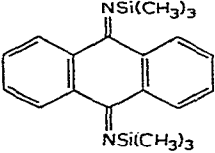
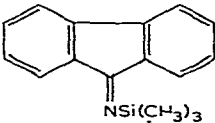
Molecular weights

The Beckmann freezing-point depression method was employed, with cyclohexane as solvent ($K_f = 20.45$). This method usually gave results which were 5 to

TABLE 4

ANALYTICAL RESULTS OF NEW SILYL KETIMINES PREPARED

Compound		% C	% H	% N	% Si	Mol. wt.
$(C_6H_5)_2C=NSi(C_2H_5)_3$	Calcd.	77.23	8.53	4.74	9.50	295.46
	Found	76.74	8.43	4.66	9.96	280
$(C_6H_5)_2C=NSi(iso-C_3H_7)_3$	Calcd.	77.28	9.26	4.15	8.31	
	Found	77.50	9.02	4.81	8.92	
$(C_6H_5)_2C=NSi(n-C_4H_9)_3$	Calcd.	79.09	9.82	3.69	7.39	
	Found	78.75	9.53	3.70	7.29	
$(C_6H_5)_2C=NSi(CH_3)_2(CHCl_2)$	Calcd.	59.63	5.32	4.35	8.71	
	Found	58.86	5.08	4.77	9.75	
$(C_6H_5)_2C=NSi(C_6H_5)_3$	Calcd.	84.75	5.74	3.21	6.38	439.58
	Found	83.49	5.33	3.50	7.56	426.2
$(C_6H_5)_2C=NSi(CH_2C_6H_5)_3$	Calcd.	84.80	6.50	2.91	5.84	
	Found	84.67	6.45	2.65	7.05	
$(C_6H_5)_2C=NSi(CH_3)_2(CH=CH_2)$	Calcd.	76.93	7.22	5.28	10.57	265.39
	Found	78.82	7.10	5.78	7.88	248
$(C_6H_5)_2C=NSi(CH_3)_2(CH_2CH=CH_2)$	Calcd.	77.37	7.58	5.01	10.04	
	Found	78.88	7.46	4.90	8.52	
$(C_6H_5)_2C=NSi(CH_3)_2[N(C_2H_5)_2]$	Calcd.	73.50	8.44	9.02	9.03	310.47
	Found	72.77	8.31	9.13	9.76	303
$(C_6H_5)_2C=NSi(CH_3)_2(OC_4H_9)$	Calcd.	73.26	8.10	4.50	9.00	311.46
	Found	72.47	7.96	5.24	9.40	294
$(p-ClC_6H_4)(C_6H_5)C=NSi(CH_3)_3$	Calcd.	66.76	6.30	4.87	9.75	287.83
	Found	66.51	5.82	4.84	7.76	278.1
$(m-ClC_6H_4)(C_6H_5)C=NSi(CH_3)_3$	Calcd.	66.76	6.30	4.87	9.75	287.83
	Found	66.81	5.89	4.72	8.49	268.8
$(o-ClC_6H_4)(C_6H_5)C=NSi(CH_3)_3$	Calcd.	66.76	6.30	4.87	9.75	287.83
	Found	66.70	6.00	4.64	8.83	277
$(p-CH_3C_6H_4)(C_6H_5)C=NSi(CH_3)_3$	Calcd.	76.35	7.92	5.24	10.49	267.41
	Found	75.84	7.51	5.90	9.87	253.5
$(m-CH_3C_6H_4)(C_6H_5)C=NSi(CH_3)_3$	Calcd.	76.35	7.92	5.24	10.49	267.41
	Found	76.97	7.56	4.76	9.85	260.8
$(o-CH_3C_6H_4)(C_6H_5)C=NSi(CH_3)_3$	Calcd.	76.35	7.92	5.24	10.49	267.41
	Found	77.30	7.84	5.34	9.95	262.1
$(p-CH_3OC_6H_4)(C_6H_5)C=NSi(CH_3)_3$	Calcd.	72.04	7.47	4.94	9.90	283.41
	Found	73.22	7.28	5.32	9.30	271.6
$(p-CH_3C_6H_4)_2C=NSi(CH_3)_3$	Calcd.	76.81	8.23	4.98	9.97	
	Found	77.61	7.82	4.99	9.67	
$(C_6H_5)_2C=NGe(CH_3)_3$	Calcd.	64.50	6.43	4.70	24.37 ^a	
	Found	64.43	6.61	4.88	24.43	
$(C_6H_5)_2C=NSn(CH_3)_3$	Calcd.	55.86	5.57	4.07	34.54 ^b	344.02
	Found	55.38	5.32	3.88	33.80	318
$(C_6H_5)_2C=NC(C_6H_5)_3$	Calcd.	90.74	5.95	3.31		
	Found	89.60	5.33	3.32		
$(C_6H_5)_2C=NGe(C_6H_5)_3$	Calcd.	76.90	5.21	2.89	15.06 ^a	484.12
	Found	76.03	5.07	2.87	15.28	442.3
$(C_6H_5)_2C=NSn(C_6H_5)_3$	Calcd.	70.21	4.75	2.64	22.39 ^b	
	Found	68.34	4.67	1.64	23.42	
$[(C_6H_5)_2C=N]_2Si(CH_3)_2$	Calcd.	80.36	6.28	6.69	6.70	
	Found	78.74	6.26	6.89	7.80	
$[(C_6H_5)_2C=N]_3Si(CH_3)$	Calcd.	82.30	5.70	7.20	4.81	583.75
	Found	82.43	6.98	7.20	3.51	503
$[(C_6H_5)_2C=N]_2Si(C_6H_5)_2$	Calcd.	84.09	5.57	5.16	5.17	542.70
	Found	84.16	5.67	5.23	5.08	550

Compound		% C	% H	% N	% Si	Mol. wt.
$[(C_6H_5)_2C=N]_3Si(C_6H_5)$	Calcd.	83.68	5.46	6.51	4.34	645.81
	Found	83.70	5.39	6.47	4.79	585
$(C_6H_5)(CH_3)C=NSi(CH_3)_3$	Calcd.	69.00	8.94	7.31	14.68	191.31
	Found	69.02	8.87	7.65	14.80	188
$(CF_3)_2C=NSi(CH_3)_3$	Calcd.	30.38	3.82	5.90	11.83	
	Found	30.37	3.74	6.10	11.93	
$(CF_2Cl)_2C=NSi(CH_3)_3$	Calcd.	26.68	3.36	5.19	10.38	270.12
	Found	26.97	3.48	5.47	10.74	262.5
	Calcd.	68.53	7.48	7.99	16.02	
	Found	68.30	7.57	7.88	15.43	
	Calcd.	76.45	6.82		11.16	
	Found	77.34	7.25		11.90	

^a Germanium analysis. ^b Tin analysis.

10% too low. Some determinations were made in the Institut für Anorganische Chemie of Graz, using an ebullioscopic method.

Chemical preparation

The solvents used in the preparation (benzene, ether, petroleum ether and ligroin) were all dried by sodium wire. All reactions were carried out in an atmosphere of prepurified and dried nitrogen. All liquid compounds prepared were purified by repeated fractional distillation, using a 30 cm Vigreux column.

N-(Trimethylsilyl)benzophenone imine. This compound can be prepared from the reaction of benzophenone and bis(trimethylsilyl)amide according to the procedure of Krüger *et al.*¹

An alternative synthetic method is described as follows: A 1-liter 3-necked flask was fitted with a motor stirrer, a reflux condenser, and a dropping funnel. The reflux condenser was equipped with a drying tube filled with Drierite, and the dropping funnel carried the nitrogen inlet tube. Three hundred and fifty ml of anhydrous ether and 6.9 g (1 g-atom) of lithium shot were placed in the flask. A solution of 79 g (0.5 mole) of bromobenzene in ether was made up in the dropping funnel, one-fifth of which was added quickly to the stirred mixture. A small crystal of iodine was added to initiate the reaction. When the reaction set in, the remaining bromobenzene was added dropwise. In about two hours, almost all the lithium was consumed. An ether solution of 51.5 g (0.5 mole) of benzonitrile was then added slowly, and the reaction mixture immediately changed to red in color, with evolution of heat. This was immediately followed by the addition of 54 g (0.5 mole) of trimethylchlorosilane, whereupon lithium chloride separated and the color of the reaction mixture changed to orange. Stirring was continued overnight. The ether was then distilled off and replaced by benzene, from which lithium halides (50.3 g) were removed easily by filtra-

tion. *N*-(Trimethylsilyl)benzophenone imine distilled at 138°/3 mm; yield 70.5 g (55.4%).

N-[(Dichloromethyl)dimethylsilyl]benzophenone imine (b.p. 148–150°/4 mm), *N*-(triethylsilyl)benzophenone imine (b.p. 121°/0.07 mm), *N*-(tri-*n*-butylsilyl)benzophenone imine (b.p. 157°/0.1 mm) and *N*-(triisopropylsilyl)benzophenone imine (b.p. 141°/0.08 mm) were prepared from equimolar mixtures of benzophenone imine lithium and the corresponding trialkylchlorosilane, according to the procedure described above. During the preparation of the triisopropyl compound, no apparent reaction took place between the two reactants in ether solution, perhaps due to the bulkiness of the isopropyl group, until about half of the ether was removed by distillation and replaced by dry tetrahydrofuran.

N-(Triphenylsilyl)benzophenone imine. The synthesis was carried out with 0.1 mole of triphenylchlorosilane. The product was crystallized from the final reaction residue in 29.2% yield (12.8 g), using ligroin as solvent. The yellow crystals melted at 124–126° after four recrystallizations.

N-(Tribenzylsilyl)benzophenone imine. This compound was prepared from 0.075 mole of tribenzylchlorosilane and the usual lithium reagent. A viscous yellow oil distilled at 230–266°/4 mm and solidified on standing overnight. The yield was 9.6 g (26.6%). The solid was purified by recrystallization from ligroin (m.p. 96–98°).

Reaction of 0.2 mole of benzophenone imine lithium and 0.2 mole of the corresponding organochlorosilane yielded the following silyl ketimines, which distilled as yellow oils: *N*-(vinyl dimethylsilyl)benzophenone imine (b.p. 109–117°/3 mm), *N*-(allyl dimethylsilyl)benzophenone imine (b.p. 148–150°/5 mm) and *N*-(*n*-butoxy dimethylsilyl)benzophenone imine (144–145°/0.5 mm).

N-[(Diethylamino)dimethylsilyl]benzophenone imine. (Diethylamino)dimethylchlorosilane was obtained from the reaction of diethylamine and dimethyldichlorosilane. One-fifth mole of the chlorosilane was allowed to react with benzophenone imine lithium. Fractional distillation gave the product, boiling at 131°/0.15 mm. It was found that excessive heating during the distillation would cause the conversion of the liquid product to a yellow solid, which was identified as (dibenzophenone imino)dimethylsilane.

N-(Triethoxysilyl)benzophenone imine. One-half mole of triethoxychlorosilane, prepared from ethanol and silicon tetrachloride²³, was added to benzophenone imine lithium solution. Reaction proceeded in the usual manner. Fractional distillation gave two major fractions of products: 41.5°/2.8 mm (35 g) and 117–118°/0.7 mm (10 g). The lower boiling fraction was redistilled at 167° at atmospheric pressure and was identified to be tetraethoxysilane by NMR and infrared spectra. The infrared spectrum of the higher boiling fraction was very similar to that of benzophenone imine, (C₆H₅)₂C=NH.

In a repeated experiment to prepare the same compound, 20.5 g of yellow oil distilled at 129°/0.6 mm. The product gave the correct NMR signals for (triethoxysilyl)benzophenone imine, but on further purification with a fractionation column the compound seemed to decompose thermally and only tetraethoxysilane and benzophenone imine were collected.

N-(Chlorodimethylsilyl)benzophenone imine. One-fifth mole of benzophenone imine lithium in ether was added slowly to 0.2 mole of dimethyldichlorosilane over a period of one hour. The final residue of the reaction mixture was fractionated. During distillation, the boiling liquid in the stillpot became increasingly viscous,

darkened in color and solidified on cooling. The yellow solid thus obtained was recrystallized from ligroin (m.p. 124–128°) and was found to be (dibenzophenone-imino)dimethylsilane.

N-(Trimethylsilyl)-*p*-chlorobenzophenone imine. Phenyllithium solution, prepared from 1.4 g (0.2 g-atom) of lithium shot and 15.7 g (0.1 mole) of bromobenzene, was filtered through glass wool into a dropping funnel, from which it was added dropwise to an ether solution of *p*-chlorobenzonitrile cooled in ice bath. The solution was then brought to room temperature, and to it 10.9 g (0.1 mole) of trimethylchlorosilane was added. The reaction mixture was then stirred overnight and worked up in the usual manner. The yellow liquid product distilled at 118°/0.17 mm.

The *m*- and *o*-chloro analogs, obtained by the same method distilled at 115°/0.1 mm and 115°/0.15 mm respectively.

N-(Trimethylsilyl)-*p*-methylbenzophenone imine. This compound was prepared from 23.8 g (0.1 mole + 30 %) of sodium bis(trimethylsilyl)amide and 19.6 g (0.1 mole) of *p*-methylbenzophenone in 29.6 % yield, following the same procedure for benzophenone described by Krüger¹. The yellow product boils at 117°/0.2 mm.

N-(Trimethylsilyl)-*o*-methylbenzophenone imine. *o*-Tolyllithium was obtained from the reaction of 0.1 mole of bromotoluene and 0.2 g-atom of lithium shot according to the method of Gilman *et al.*²⁴. The lithium reagent was then allowed to react with 10.3 g (0.1 mole) of benzonitrile to give *p*-methylbenzophenone imine lithium, to which 10.85 g (0.1 mole) of trimethylchlorosilane was added. Sixteen grams (61 %) of the silyl ketimine distilled at 105°/0.2 mm.

The *m*-methyl derivative (b.p. 112°/0.2 mm) was prepared in the same way as the *ortho* compound.

N-(Trimethylsilyl)-*p,p'*-dimethylbenzophenone imine. This compound was obtained from 0.1 mole of *p*-tolyllithium, 0.1 mole of *p*-methylbenzonitrile and 0.1 mole of trimethylchlorosilane. A yield of 20.8 g (73.8 %) of the compound was obtained. (B.p. 117°/0.1 mm)

N-(Trimethylgermyl)benzophenone imine. Trimethylgermanium chloride (12.9 g, 0.84 mole), obtained from the reaction of methylmagnesium chloride and dimethylgermanium dichloride²⁵, was allowed to react with 0.84 mole of benzophenone imine lithium according to the method developed for the silicon analog. Fractionation gave the germyl ketimine at 109–110°/0.17 mm.

N-(Triphenylgermyl)benzophenone imine. Tetraphenylgermanium was prepared from the phenyl Grignard reagent and germanium tetrachloride. The compound was converted to triphenylgermanium bromide by the action of bromine²⁶.

Phenyllithium, prepared from 1.4 g (0.2 g-atom) of lithium and 15.7 (0.1 mole) of bromobenzene, was filtered through glass wool under nitrogen atmosphere. By the method of direct acid-titration, the yield was found to be 0.085 mole. Of this, 0.0575 mole was allowed to react with 5.95 g (0.0575 mole) of benzonitrile to give benzophenone imine lithium, which was added to the refluxing ether solution of 0.0575 mole of triphenylgermanium bromide. Next day, when the reaction was complete, the solution was clear and orange in color. After all the solvent and lithium bromide were removed, the viscous residue was refluxed with ligroin and filtered while hot with a filtering funnel fitted with sintered-glass plate, under nitrogen atmosphere. Yellow crystals of germyl ketimine separated on standing. The pure compound melts at 127–132°.

N-(Trimethylstannyl)benzophenone imine. Johnson's method was employed to prepare trimethyltin chloride²⁷. Reaction of 62.6 g (0.285 mole) of dimethyltin dichloride and 20.9 g (0.095 mole) of methylaluminum sesquichloride yielded 32.2 g of trimethyltin chloride.

N-Trimethylstannyl ketimine was obtained from 0.1 mole of benzophenone imine lithium and 0.1 mole of trimethyltin chloride. The product distilled at 121°/0.15 mm as a yellow oil, which solidified upon standing.

N-(Triphenylstannyl)benzophenone imine. The imino lithium reagent (0.06 mole) was allowed to react with 23.1 g (0.06 mole) of triphenyltin chloride. Moisture was carefully excluded during the crystallization process. Precipitation of the product from the ligroin solution was initiated by the addition of a few crystals of the germanium analog. The product obtained from the fourth recrystallization melted at 78–88° and appeared to be very sensitive toward atmospheric moisture. Bis(trimethyltin) oxide (m.p. 119–123°) was isolated when the recrystallization was not carried out under dry nitrogen.

N-(Triphenylplumbyl)benzophenone imine. The attempt to isolate pure crystals of this compound from the reaction mixture of triphenyllead chloride and benzophenone imine lithium was unsuccessful. A white solid believed to be triphenyllead oxide was the major product obtained. On this white solid, only a small amount of yellow crystals deposited after prolonged standing. Their ultraviolet absorption at 340 μ (shoulder) suggest that the crystals might be *N*-(triphenylplumbyl)benzophenone imine.

N-(Triphenylmethyl)benzophenone imine. A solution containing 0.08 mole of benzophenone imine lithium reacted readily with 0.08 mole of triphenylchloromethane to give the triphenylmethyl ketimine in 29% yield. The product was recrystallized from a mixture of ligroin and benzene (m.p. 161–162°).

Bis(benzophenone-imino)dimethylsilane. This compound was obtained as product of thermal rearrangement of *N*-(chlorodimethylsilyl)benzophenone imine and *N*-[(diethylamino)dimethylsilyl]benzophenone imine. Another method is the reaction of benzophenone imine lithium and dimethyldichlorosilane in 2:1 molar ratio.

Tris(benzophenone-imino)methylsilane. A solution of 0.24 mole of the lithium reagent was allowed to react with 0.08 mole of methyltrichlorosilane. The compound was crystallized under nitrogen atmosphere (m.p. 114–117°).

Bis(benzophenone-imino)diphenylsilane (m.p. 108–109°) and *tris*(benzophenone-imino)phenylsilane (m.p. 142–143°) were prepared in like manner. An attempt to isolate tetrakis(benzophenone-imino)silane from a reaction mixture of 0.08 mole of benzophenone imine lithium and 0.32 mole of silicon tetrachloride was not successful.

N,N'-Bis(trimethylsilyl)anthraquinone diimine. The compound was prepared from the reaction 47.7 g (0.2 mole + 30%) of sodium bis(trimethylsilyl)amide and 20.8 g (0.1 mole) of anthraquinone. Trimethylchlorosilane (28.3 g, 0.2 mole + 30%) was added at the completion of the reaction. A yield of 14 g (39.5%) of the orange-red compound distilled at 171–173°/0.4 mm, which solidified on cooling. The solid was recrystallized from ligroin (m.p. 118–120°).

N-(Trimethylsilyl)fluorenone imine. This compound was prepared from bis(trimethylsilyl)amide and fluorenone in 61% yield. The yellow product distilled at 129°/0.5 mm and solidified at room temperature.

N-(Trimethylsilyl)-1,1,2,2-tetrafluoro-1,2-dichloroacetone imine. A solution of 47.7 g (0.2 mole + 30 %) of sodium bis(trimethylsilyl)amide in 150 ml of ether was added dropwise to a stirred solution of 39.8 g (0.2 mole) of tetrafluorodichloroacetone (b.p. 46°) in 400 ml of ether over a period of 105 min. During the course of addition, the color of the reaction mixture changed from pale yellow to brown. Stirring continued for 11 h, after which 28.3 g (0.2 mole + 30 %) of trimethylchlorosilane was added and the mixture was refluxed for 4 h. Ether was distilled and replaced by petroleum ether (38–54°) to facilitate filtration of sodium chloride. A fraction of the yellow liquid distilled at 141–142° (9.6 g, 14%). The compound was further purified by vapor phase chromatography (Aerograph Model 700), using a carbowax column. Higher boiling products (64–108°/16 mm) were not investigated further.

N-(Trimethylsilyl)hexafluoroacetone imine. A 1-liter three-necked flask (A) was fitted with a motor stirrer, a dropping funnel bearing a nitrogen inlet tube and a reflux condenser. The reflux condenser was connected to a second 1-liter 3-necked flask (B) equipped with a motor stirrer and a dry ice condenser, at the outlet of which a trap immersed in a dry ice/acetone bath was placed. In flask (A), 20 g of phosphorus pentoxide and 80 g of concentrated sulfuric acid were mixed*. To the mixture previously cooled to 60°, 52.55 g (0.27 mole) of hexafluoroacetone sesquihydrate, $(\text{CF}_3)_2\text{C}=\text{O} \cdot 1.6 \text{ H}_2\text{O}$, (Du Pont) was added dropwise. Gaseous hexafluoroacetone (b.p. –28°) which flashed off immediately was passed into flask (B), where it was dissolved in 400 ml of ether kept at dry ice/acetone temperature. On the completion of dehydration, flask (A) and its assembly were removed. A solution of 49.5 g (0.27 mole) of sodium bis(trimethylsilyl)amide in 200 ml of ether was added slowly to the solution of hexafluoroacetone while its temperature was brought to 0° with an ice bath. After stirring for 20 h, the reaction was fractionated to give a yellow liquid at 83–91°. It was further purified by vapor phase chromatography, using a carbowax column. The column temperature was set at 37–40°. One-tenth ml samples were injected each time and the pure product was collected in a receiver kept at dry ice/acetone temperature. The higher-boiling products of the reaction were not investigated.

N-(Trimethylsilyl)acetophenone imine. One-half mole of phenyllithium solution was added to 0.5 mole of acetonitrile in ether, followed by 54 g (0.5 mole) of trimethylchlorosilane. The yellow liquid product, which distilled at 124–126°/22 mm, was obtained in 28.4 % yield. NMR spectrum $\delta(\text{Ph})$ 7–8 ppm (complex), $\delta(=\text{CH}_2)$ 4.07 ppm (doublet), $\delta(\text{C}-\text{CH}_3)$ 2.33 ppm, $\delta(\text{Si}-\text{CH}_3)$ 0.2 ppm, $\delta(\text{N}-\text{H})$ 2.8 ppm (appeared only at temperature lower than –15°).

Dipole moment of bis(trimethylsilyl)carbodiimide

The compound was prepared according to the method of Pump and Wannagat¹⁶. Its dipole moment was measured in benzene solution by the heterodyne beat method using the apparatus built and described by Osthoff²⁸. Four solutions were prepared whose molar fractions of solute were 0.02605; 0.01739, 0.01012 and 0.00505. The best approximation to induced polarization ($P_E + P_A$) in the Debye equation was obtained by the molar refraction of the pure solute, while the total polarization P was evaluated according to the method of Halverstadt and Kumler^{29,30}. Using the Debye equation, the dipole moment was calculated to be 1.31 debye units.

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SUMMARY

Twenty eight silyl ketimines and several germanium and tin analogs have been prepared by the action of sodium bis(trimethylsilyl)amide on non-enolizable ketones or the reaction of lithium derivatives of ketimines with organosilicon chlorides. Their electronic spectra, the $n \rightarrow \pi^*$ transition in particular, have been investigated to study the $d_{\pi}-p_{\pi}$ interaction between the empty d orbitals of silicon and the π system of the C=N bond. The spectral data indicate a bent structure for C=N-Si linkage and hence very little multiple bonding in the Si-N bond.

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