

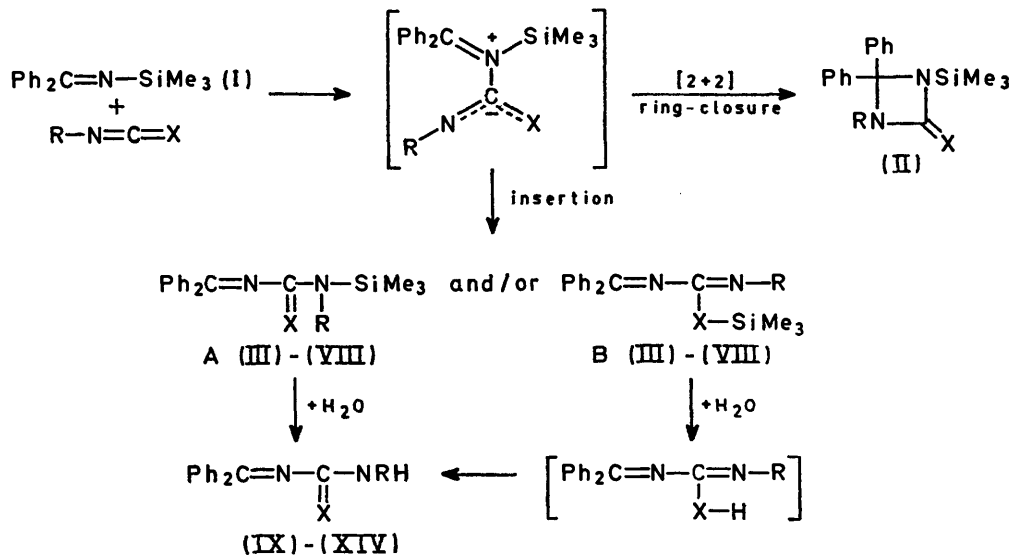
Reactions of Group IV Organometallic Compounds. Part XXVI.¹ Insertion Reactions of Isocyanates and Isothiocyanates to *N*-Trimethylsilyl-(diphenylmethylene)amine and Subsequent [4 + 2] Cycloadditions of Isocyanates with Their Adducts

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N-Trimethylsilyl(diphenylmethylene)amine reacted with 1 mol. equiv. of methyl, phenyl, or benzoyl isocyanate, and with the corresponding isothiocyanates, by the selective cleavage of the Si-N bond. The n.m.r. spectra of the 1:1 insertion product (III)—(VIII) showed the non-equivalency of trimethylsilyl proton signals at low temperature. The concept of 1,3-transfer of the trimethylsilyl group was preferred to that of hindered rotation about the C-N bond for the interpretation of these splittings. With 2 mol. equiv. of methyl or phenyl isocyanate, the silylamine gave the 1,3-substituted 3,4-dihydro-4,4-diphenyl-6-trimethylsilyloxy-1,3,5-triazin-2(1*H*)-ones (XVIII) by [4 + 2] cycloadditions of isocyanates with the imidate form (B) of the 1:1 adducts.

N-TRIMETHYLSILYL(DIPHENYLMETHYLENE)AMINE² (I) has two possible pathways for additions with unsaturated bonds: (i) insertion into the Si-N bond as with organosilylamides³⁻⁷ and (ii) [2 + 2] cycloaddition across the C=N bond of this imine to give four-membered ring compounds (II).⁸⁻¹⁰ The two possibilities for the reaction with isocyanates are summarized in Scheme 1.

imine (I) with an equimolar amount of isocyanate or isothiocyanate gave the 1:1 adducts (IV), (VI), and (VII). These adducts were identified by elemental analysis, and by i.r., n.m.r., and mass spectroscopy. Isolation of the adduct (III) with methyl isocyanate was unsuccessful, since the adduct reacted further to produce a mixture of 1:1 and 1:2 adducts. Some physical



SCHEME 1

We report that the insertion prevails over the [2 + 2] cycloaddition (see Scheme 1). The insertion products (III)—(VIII) exist as tautomers through the 1,3-transfer of the trimethylsilyl group. A new [4 + 2] cycloaddition of 1:1 adducts is also described.

RESULTS AND DISCUSSION

Insertions of N-Trimethylsilyl(diphenylmethylene)amine with Isocyanates or Isothiocyanates.—Treatment of the

¹ Part XXV, K. Itoh, S. Kato, and Y. Ishii, *J. Organometallic Chem.*, 1972, **34**, 293.

² L. H. Chan and E. G. Rochow, *J. Organometallic Chem.*, 1967, **9**, 231.

³ M. F. Lappert and B. Prokai, *Adv. Organometallic Chem.*, 1967, **5**, 225.

⁴ I. Matsuda, K. Itoh, and Y. Ishii, *J. Chem. Soc. (C)*, 1969, 701.

data for the new 1:1 adducts (III)—(VIII) and their desilylated derivatives (IX)—(XIV) are summarized in Tables 1 and 2.

I.r. spectra of the adducts (III)—(V) showed strong absorptions at *ca.* 1650 cm^{-1} , as expected for linear ureas. The mass spectra of (IV) and (VII) as well as of the desilylated products (IX)—(XIV) suggested the

⁵ I. Matsuda, K. Itoh, and Y. Ishii, *J. Organometallic Chem.*, 1969, **19**, 339.

⁶ I. Matsuda, K. Itoh, and Y. Ishii, *J. Chem. Soc. (C)*, 1971, 1850.

⁷ K. Itoh, N. Kato, S. Sakai, and Y. Ishii, *J. Chem. Soc. (C)*, 1969, 2005.

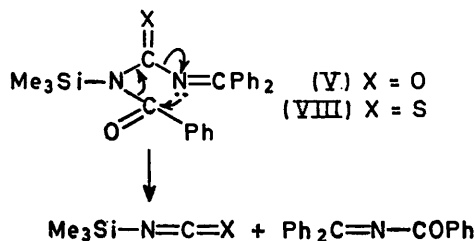
⁸ H. Ulrich, *Accounts Chem. Res.*, 1969, **2**, 186.

⁹ R. Richter and W. P. Trautwein, *Chem. Ber.*, 1969, **102**, 931, 938.

¹⁰ R. Neidlein and R. Bottler, *Arch. Pharm.*, 1969, **302**, 306.

presence of the fragment ions $\text{Ph}_2\text{C}=\text{N}^+=\text{C}=\text{X}$ and $\text{Ph}_2\text{C}=\text{N}^+$, thereby supporting the linear structure depicted in Scheme 1. The latter ion arises by elimination of $:\text{C}=\text{X}$ from the former, since the relative intensity of $\text{Ph}_2\text{C}=\text{N}^+$ increased at higher ionization potentials. The presence of $\pi \rightarrow \pi^*$ transitions at *ca.* 250 nm ($\log \epsilon$ 4) were ascribed to a conjugated $\text{X}=\text{C}=\text{N}=\text{CPh}_2$ linkage, and also supported the linear structure. Thus, spectroscopic evidence excluded the possibility of a [2 + 2] cycloadduct (II). Consequently, the 1:1 adducts have linear structures (III)—(VIII) and the insertion of isocyanate or isothiocyanate across the Si-N bond of $\text{Ph}_2\text{C}=\text{N}-\text{SiMe}_3$ was the predominant path, and migration of the Me_3Si moiety from the ammonium nitrogen atom to either the amino- or oxy-anion took place far more rapidly than the cyclization induced by

isomeric forms are possible; the amide (A) or imidate (B) form. These two forms are interconvertible by



SCHEME 2

1,3-transfer of the trimethylsilyl group. Such reversible isomerizations have been established for heterocumulene adducts with organosilylamines,⁴⁻⁷ phosphines,¹¹ or

TABLE 1

1:1 Adducts $\text{Ph}_2\text{C}=\text{N}-\text{C}(\text{X})=\text{NR}-\text{SiMe}_3$					Desilylated products			
R	X	M.p. (°C)	$\nu_{\text{max.}}/\text{cm}^{-1}$ ^a	τSiMe_3 ^a	M.p. (°C)	$\nu_{\text{max.}}/\text{cm}^{-1}$ ^b	$\lambda_{\text{max.}}(\text{EtOH})$ nm	
Me	O	(III)	<i>c</i>	1648, 1627	9.86 (IX)	187.5—189.5	1645	252
Ph	O	(IV)	118—119	1647	9.87 ^d (X)	159—160.5	1650, 1543	250
Bz	O	(V)	<i>c</i>	1672, 1631, 1581	9.80 (XI)	151—153	1711, 1659, 1631	243
Me	S	(VI)	<i>c</i>	1623, 1334	9.67 (XII)	170—171	1612, 1362	248
Ph	S	(VII)	125.5—127	1631, 1317	9.72 ^d (XIII)	132—133	1643 1362	258
Bz	S	(VIII)	<i>c</i>	1643, 1626, 1325	9.74 (XIV)	137—138	1705, 1255	260, 243

^a In CCl_4 solution. ^b KBr disc. ^c Oil. ^d In CDCl_3 solution.

TABLE 2

Analytical data

Compound	Molecular weight	Calc. (%)			Found (%)				
		Calc.	Found ^a	C	H	N	C	H	N
(IV)	$\text{C}_{25}\text{H}_{24}\text{N}_2\text{OSi}$	372	372	74.15	6.5	7.5	74.0	6.4	
(VI)	$\text{C}_{18}\text{H}_{22}\text{N}_2\text{SSi}$	342		63.1	6.5	8.2	62.85	6.4	
(VII)	$\text{C}_{25}\text{H}_{24}\text{N}_2\text{SSi}$	388	388	71.1	6.2	7.2	70.95	6.25	
(IX)	$\text{C}_{15}\text{H}_{14}\text{N}_2\text{O}$	238	238	75.6	5.9	11.75	75.6	5.95	11.8
(X)	$\text{C}_{20}\text{H}_{16}\text{N}_2\text{O}$	300	300	80.0	5.35	9.35	79.9	5.45	9.3
(XI)	$\text{C}_{21}\text{H}_{16}\text{N}_2\text{O}_2$	328	328	76.8	4.9	8.55	76.8	5.0	8.45
(XII)	$\text{C}_{15}\text{H}_{14}\text{N}_2\text{S}$	254	254	70.85	5.55	11.0	71.0	5.55	10.85
(XIII)	$\text{C}_{20}\text{H}_{16}\text{N}_2\text{S}$	316	316	75.9	5.1	8.85	75.9	5.2	8.9
(XIV)	$\text{C}_{21}\text{H}_{16}\text{N}_2\text{OS}$	344	344	73.25	4.7	8.15	73.45	4.9	8.0
(XVIII; R = Me)	$\text{C}_{20}\text{H}_{25}\text{N}_3\text{O}_2\text{Si}$	367	367	65.35	6.85	11.45	65.5	7.0	
(XVIII; R = Ph)	$\text{C}_{30}\text{H}_{29}\text{N}_3\text{O}_2\text{Si}$	491	491	73.3	5.95	8.55	73.25	6.15	
(XIX; R = Me)	$\text{C}_{17}\text{H}_{17}\text{N}_3\text{O}_2$	295	295	69.15	5.8	14.25	69.1	5.85	14.35
(XIX; R = Ph)	$\text{C}_{27}\text{H}_{21}\text{N}_3\text{O}_2$	412	412	73.25	4.45	8.85	73.2	4.6	8.8

^a By mass spectroscopy.

the nucleophilic attack of the amide anion on the carbonium ion.

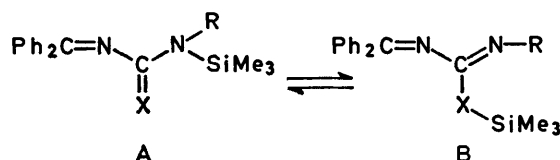
Distillation of the 1:1 adducts (V) and (VIII) caused decomposition to *NN*-(diphenylmethylene)benzamide and trimethylsilyl isocyanate or isothiocyanate. A possible mechanism is outlined in Scheme 2.

Spectroscopic Evidence for the 1,3-Transfer of the Trimethylsilyl Group.—Although the 1:1 adducts (III)—(VIII) were designated as linear structures, still two

¹¹ K. Itoh, M. Fukui, and Y. Ishii, *J. Chem. Soc. (C)*, 1969, 2002.

¹² K. Itoh, K. Matsuzaki, and Y. Ishii, *J. Chem. Soc. (C)*, 1968, 2709.

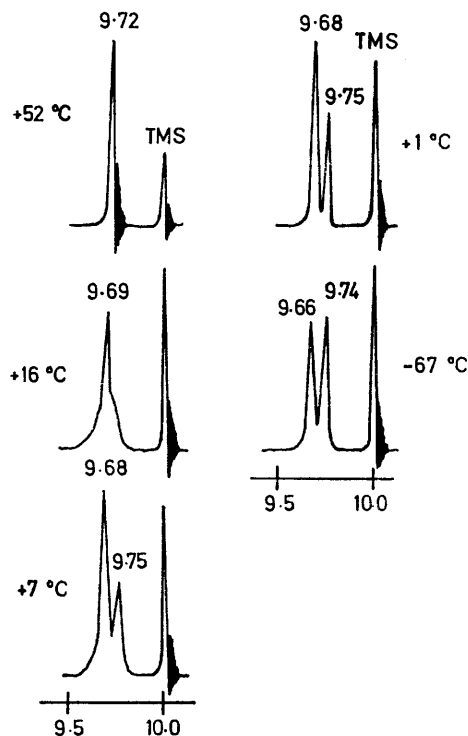
isomeric forms are possible; the amide (A) or imidate (B) form. These two forms are interconvertible by



The insertion products (V)—(VII) showed two separated trimethylsilyl proton signals at low temperature as

¹³ K. Itoh, M. Katsuda, and Y. Ishii, *J. Chem. Soc. (B)*, 1970, 302.

shown in the Figure. The results of variable temperature n.m.r. experiments are summarized in Table 3. The intensities of two signals varied with temperature.



N.m.r. spectra of diphenylmethylene(phenyl)(trimethylsilyl)thiourea (VII) at various temperature (in CDCl_3), with reference to tetramethylsilane (TMS)

This non-equivalency is ascribed to either the 1,3-transfer of the trimethylsilyl group or to the hindered rotation of amide structures.^{14,15} In the case of *N*-benzyl-*N*-methylformamide,¹⁶ the non-equivalent splitting of methylene and formyl protons was observed below 122 °C

Additional evidence for migration of the trimethylsilyl group in 1:1 adducts was obtained by mass spectroscopy. The mass spectra of the thiourea (VII) showed two independent series of fragmentation patterns from the two isomeric parent ions: (i) $[M^+ - \text{NPh}(\text{SiMe}_3)]$ ($\text{Ph}_2\text{C}=\text{N}=\text{C}=\text{S}$; relative intensity 31%) and (ii) $(M^+ - \text{S}\cdot\text{SiMe}_3)$ ($\text{Ph}-\text{N}=\text{C}=\text{N}^+=\text{CPh}_2$; 51%). These ions were considered to be the primary steps in fragmentations.

Cyclizations with an Excess of Isocyanate.—When the imine (I) was treated with 2 mol. equiv. of isocyanate, white crystalline products were obtained. Analytical, i.r., n.m.r., and mass spectroscopic results established that the products were 1:2 adducts. The same products were also obtained quantitatively when the 1:1 adduct (IV) was treated with a further 1 mol. equiv. of isocyanate. Four possible structures must be considered as a result of the four modes of reaction: (i) the stepwise insertion of isocyanates into Si-N bond of the amides (III) and (IV) to give linear 1:2 adducts (XV); (ii) [2 + 2] cycloaddition between C=N bond of (III) or (IV) and isocyanate to give diazetidines (XVI); (iii) [4 + 2] cycloaddition of the amide (A) with isocyanate to give the oxadiazines (XVII); and (iv) [4 + 2] cycloaddition of the imidates (B) to give the triazines (XVIII).

The linear 1:2 adduct (XV) was excluded since the conjugated $\pi \rightarrow \pi^*$ transitions of $\text{Ph}_2\text{C}:\text{N}\cdot\text{CO}\cdot$ linkage disappeared completely. Other spectroscopic data were not sufficient to distinguish between the three remaining structures. Acidic hydrolysis of the desilylated 1:2 adduct (R = Ph) was conclusive. Hydrolysis of the desilylated 1:2 adducts with phenyl isocyanate in the presence of hydrochloric acid gave *NN'*-diphenylurea (70%), benzophenone (35%), and ammonium chloride (41%). The formation of *NN'*-diphenylurea can only be explained by (XIX; R = Ph): both (XVI) and

TABLE 3
Variable temperature n.m.r. study of 1:1 adducts

Compound	Coalescence temp. (°C)	Chem. shifts Me_3Si (τ temp.)		Relative intensity ratio A : B	
		0 °C	-50 °C	0 °C	-50 °C
(V)	24	9.79, 9.86 (-66°) ^a	9.79 (30°) ^a	4.8	3.4
(VI)	30	9.61, 9.68 (-67°) ^a	9.67 (79°) ^a	2	2
(VII)	17	9.66, 9.74 (-67°) ^b	9.72 (52°) ^b	0.63	0.91

^a In trichloroethylene solution. ^b In CDCl_3 solution.

and the temperature dependence of their relative intensities was negligible. For compounds (V) and (VII), the ratio of the relative intensity of two kinds of trimethylsilyl groups was temperature dependent. Considering literature reports,^{17,18} the splitting of the trimethylsilyl protons are ascribed to the migration of the trimethylsilyl group. Adducts (VI) and (VII) are the first examples of the complete splitting of trimethylsilyl proton signals in silylthioamide \rightleftharpoons silylthioimide equilibria.

¹⁴ W. E. Stewart and T. H. Siddall, *tert.*, *Chem. Rev.*, 1970, **70**, 517.

¹⁵ T. H. Siddall, *tert.*, and W. E. Stewart, *J. Org. Chem.*, 1967, **32**, 3261.

(XVII) should give *N*-phenylurea. If structure (XVII) is correct, the compound should readily react with hydroxide ion or aniline by cleavage of lactone rings, with acetic anhydride at amino-protons, and with picric acid to form the corresponding picrate at the basic nitrogen atoms in amidine linkage. However, the hydrolysis products of 1:2 adducts did not react with above reagents. The i.r. spectrum is consistent with structure (XIX; R = Ph): the carbonyl stretching frequencies at 1730 and 1660 cm^{-1} were similar to those

¹⁶ H. S. Gutowsky, J. Jonas, and T. H. Siddall, *tert.*, *J. Amer. Chem. Soc.*, 1967, **89**, 4300.

¹⁷ J. F. Klebe, *Accounts Chem. Res.*, 1970, **3**, 299.

¹⁸ J. Pump and E. G. Rochow, *Chem. Ber.*, 1964, **97**, 627.

of reported 1,3,5-triazinones⁹ (1720 and 1680 cm^{-1}). Consequently, the structure of 1:2 adducts was concluded to be (XVIII). Formation of the triazines (XVIII) is explained by a [4 + 2] cycloaddition between *O*-silylimidate (B), (III) and (IV), and the second molecule

methylsilyl groups is a useful technique in organic synthesis, which may be extended to include these new [4 + 2] cycloadditions.

EXPERIMENTAL

All reactions were carried out under argon. N.m.r. spectra were measured (with tetramethylsilane as an internal standard) with Japan Electron Optics C-60 HL. I.r. spectra were recorded with Japan Spectroscopic Co. Ltd. IR-S and DS-403G spectrometers. Mass spectra were recorded with Japan Electron Optics JMS-01SG or Hitachi RMS-4 instruments.

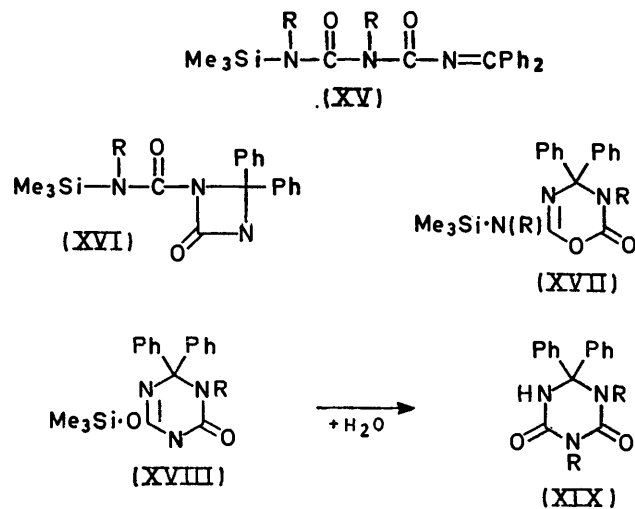
N-Trimethylsilyl(diphenylmethylene)amine (I).—The preparation was a modification of Rochow's method.² Benzonitrile (58 g, 0.56 mol) was added dropwise to phenylmagnesium bromide (0.58 mol) in diethyl ether (400 ml) with gentle refluxing. A few min after addition, a pale yellow solid precipitated. After heating under reflux for 3 h, chlorotrimethylsilane (55 g, 0.51 mol) was added dropwise to the mixture, which turned orange. The heating was continued for 3 h, and then the mixture was filtered. After removal of the solvent, distillation of the residue under reduced pressure gave the yellow oily imine (I) (78 g, 61%), b.p. 70–71° at 0.01 mmHg.

Equimolar Reactions.—(a) *Methyl isocyanate.* A mixture of the foregoing imine (1.99 g, 7.85 mmol) and methyl isocyanate (0.50 g, 8.60 mmol) was kept for ca. 12 h at room temperature without solvent. After the disappearance of the $\nu(\text{N}=\text{C}=\text{O})$ absorption in the i.r., distillation under reduced pressure gave a viscous liquid (1.90 g), b.p. 90–130° at 0.15 mmHg. The oil was a mixture of the 1:1 (III) and the 1:2 adduct (XVIII; R = Me) (ca. 3:1). Pure diphenylmethylene(methyl)trimethylsilylurea (III) could not be obtained under various conditions. The desilylated diphenylmethylene(methyl)urea (IX), obtained by exposure to atmospheric moisture, was isolated by recrystallization from ethyl acetate.

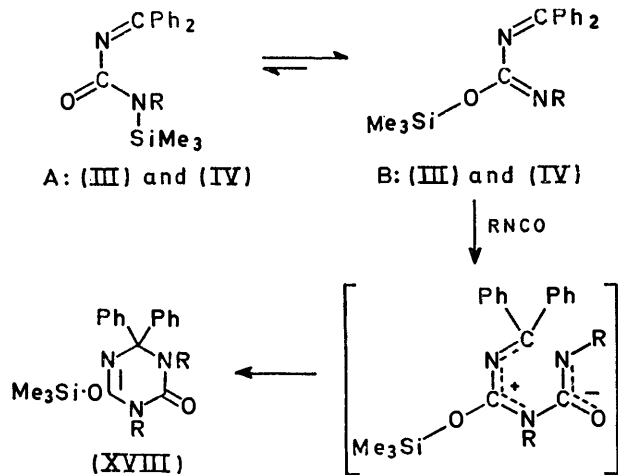
(b) *Phenyl isocyanate.* When phenyl isocyanate (0.92 g, 7.70 mmol) was added to a benzene solution of the imine (I) (2.00 g, 7.90 mmol), a slightly exothermic reaction ensued. After 0.5 h, evaporation gave the very hygroscopic *N*-phenylurea (IV), nearly quantitatively, m.p. 118–119° [from benzene-*n*-hexane (1:1)]. Hydrolysis of the *N*-phenylurea (IV) gave needles of diphenylmethylene(phenyl)urea (X), m.p. 159–160.5° [from chloroform-*n*-hexane (1:1)].

(c) *Benzoyl isocyanate.* Benzoyl isocyanate (1.06 g, 7.15 mmol) was added dropwise to a carbon tetrachloride solution of the imine (I) (1.68 g, 6.62 mmol) with ice-cooling. Evaporation left benzoyl(diphenylmethylene)trimethylsilylurea (V), a hygroscopic oil. It was too unstable to be distilled. Characterization was carried out by desilylation to benzoyl(diphenylmethylene)urea (XI), which was recrystallized from ethyl acetate.

(d) *Methyl isothiocyanate.* A mixture of the imine (I) (2.03 g, 8.02 mmol) and methyl isothiocyanate (0.84 g, 11.5 mmol) was kept overnight at 80 °C in an ampoule. Diphenylmethylene(methyl)(trimethylsilyl)thiourea (VI), a brown oil, was obtained by the removal of the excess of methyl isothiocyanate. Hydrolysis of the thiourea (VI)



of isocyanate (see Scheme 3). This conclusion is supported by the spectroscopic evidence for the existence of *O*-silylimidates (B). It is noteworthy that the triazinedione (XIX) could not be prepared either by the direct reaction of diphenylmethyleneamine (I) with 2 mol. equiv. of isocyanate, or by the interaction of desilylated products (IX) and (X) with isocyanate.



SCHEME 3

Introduction of trimethylsilyl group would increase the proportion of the reactive imidate form (B), (III) and (IV), because of the strong Si-O bond. Thus, [4 + 2] cycloaddition to give (XVIII) occurred, readily. Displacement of keto \rightleftharpoons enol¹⁹⁻²² or amide \rightleftharpoons imidate^{4,6,22} equilibria by the introduction of tri-

¹⁹ H. O. House, L. J. Czuba, M. Gall, and H. D. Olmstead, *J. Org. Chem.*, 1969, **34**, 2324.

²⁰ G. Stork and P. F. Hudrlik, *J. Amer. Chem. Soc.*, 1968, **90**, 4462, 4464.

²¹ L. Birkofer, A. Ritter, and H. Vernalahen, *Chem. Ber.*, 1966, **99**, 2518.

²² L. Birkofer, 'Newer Method of Preparative Organic Chemistry,' Verlag Chem., Academic Press, vol. 5, 1968, p. 211; *Angew. Chem.*, 1965, **77**, 414.

gave diphenylmethylen(methyl)thiourea (XII), pale yellow needles (recrystallized from ethanol).

(e) *Phenyl isothiocyanate*. A mixture of the imine (I) (1.03 g, 4.07 mmol) and phenyl isothiocyanate (1.19 g, 8.80 mmol) in benzene (2 ml) was kept for 1 day at ca. 90 °C in an ampoule. Yellow-orange needles separated on cooling. Filtration and washing with a small portion of n-hexane gave pure diphenylmethylen(phenyl)(trimethylsilyl)thiourea (VII), m.p. 125.5–127° [from benzene–n-hexane (1:1)]. Hydrolysis of the phenylthiourea (VII) gave yellow prisms, m.p. 132–133° (from benzene).

(f) *Benzoyl isothiocyanate*. Benzoyl isothiocyanate (0.89 g, 5.37 mmol) was added dropwise to the imine (I) (1.18 g, 4.66 mmol) at room temperature. Usual work-up gave the benzoylthiourea (VIII), a brown-orange oil, which was too unstable to be purified by distillation. Hydrolysis gave the yellow desilylated thiourea (XIV), m.p. 134.5–136° [from benzene–n-hexane (2:1)].

Annulations.—(a) *3,4-Dihydro-1,3-dimethyl-4,4-diphenyl-6-trimethylsilyloxy-1,3,5-triazin-2(1H)-one* (XVIII; R = Me). A mixture of the imine (I) (1.55 g, 6.12 mmol) and methyl isocyanate (0.75 g, 13.35 mmol) was kept for 1 day at room temperature; it solidified. After removal of the excess of methyl isocyanate (crude yield; quantitative), recrystallization gave prisms of the *triazinone* (90%), m.p. 133.5–135° [from benzene–n-hexane (1:1)], τ (CDCl₃) 9.73 (Me₃Si) and 7.33 and 6.91 (NMe), ν_{\max} (CCl₄) 1693 and 1668 cm⁻¹.

Hydrolysis of the triazinone gave hexahydro-1,3-dimethyl-6,6-diphenyl-1,3,5-triazine-2,4-dione (XIX; R = Me) (92%), prisms, m.p. 238–239° (from ethanol), τ (CDCl₃) 7.28 and 7.03 (NMe), ν_{\max} (KBr) 1723 and 1648 cm⁻¹.

(b) *3,4-Dihydro-1,3,4,4-tetraphenyl-6-trimethylsilyloxy-*

1,3,5-triazin-2(1H)-one (XVIII; R = Ph). (i) Phenyl isocyanate (1.75 g, 14.6 mmol) was added dropwise to the imine (I) (1.56 g, 6.15 mmol) in benzene (2 ml) with a slightly exothermic reaction. n-Hexane was added, and the mixture was kept for 30 min at room temperature. Removal of the solvent left needles of the triazinone (80%), m.p. 142–145° [from benzene–n-hexane (1:1)], τ (CDCl₃) 9.88 (Me₃Si), ν_{\max} (CDCl₃) 1702 and 1664 cm⁻¹.

(ii) Phenyl isocyanate (0.76 g, 6.35 mmol) was added to the benzene solution (5 ml) of 1:1 adduct (IV) (2.43 g, 6.55 mmol). After keeping the mixture for 6 h at room temperature, the ν (N=C=O) absorption in the i.r. disappeared. Removal of the solvent and recrystallization [from benzene–n-hexane (1:1)] gave needles of the triazinone (XVIII; R = Ph) (2.35 g, 4.78 mmol; 75%).

Hydrolysis of the triazinone, as usual, gave white needles of hexahydro-1,3,6,6-tetraphenyl-1,3,5-triazine-2,4-dione (XIX; R = Ph) (90%), m.p. 215–216° (from ethanol–benzene), ν_{\max} (KBr) 1730 and 1657 cm⁻¹.

Hydrolysis of the Triazine-2,4-dione (XIX; R = Ph) *with Hydrochloric Acid*.—The triazinedione (0.63 g, 1.51 mmol) was dissolved in ethanol (30 ml) and conc. hydrochloric acid (21 ml) was added. The solution was heated under reflux for 4 days. The mixture was extracted several times by chloroform. Evaporation of the chloroform left a residue which was separated into benzophenone (0.10 g; 35%) and NN'-diphenylurea (0.23 g; 70%) by using the difference of solubility in diethyl ether. Ammonium chloride (0.03 g; 41%) was obtained by evaporating the aqueous layer.

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