

## REACTIONS OF GROUP IV ORGANOMETALLIC COMPOUNDS XVII\*. ADDITION REACTIONS OF HEPTAMETHYLDISILAZANE WITH BENZOYL ISO(THIO)CYANATE AND SUBSEQUENT ELIMINATIONS

ISAMU MATSUDA, KENJI ITOH AND YOSHIO ISHII

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

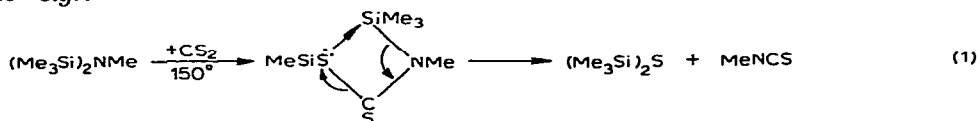
(Received June 18th, 1969)

### SUMMARY

Benzoyl isocyanate and isothiocyanate react with heptamethyldisilazane to give 1/1 adducts, which exist as mixtures of the isomers involving 1,3-transfer of trimethylsilyl groups. The adducts from benzoyl isothiocyanate decompose thermally by two  $\beta$ -elimination processes; one, at temperatures below 100°, gives methyl isothiocyanate, and the other, at 150°, gives trimethylsilyl isothiocyanate.

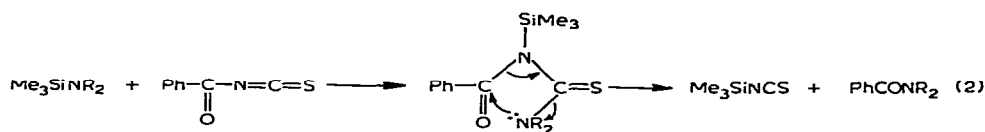
Migration of trimethylsilyl groups was confirmed by means of NMR measurements at various temperatures. This migration is important in determining the course of subsequent  $\beta$ -elimination reactions.

Heptamethyldisilazane,  $(\text{Me}_3\text{Si})_2\text{NMe}$ , is known to be only weakly nucleophilic because of the  $2p_\pi-3d_\pi$  interactions in the Si-N-Si linkages. It is known to undergo addition-elimination reactions with carbon disulphide or phenyl isothiocyanate<sup>2</sup> *e.g.*:



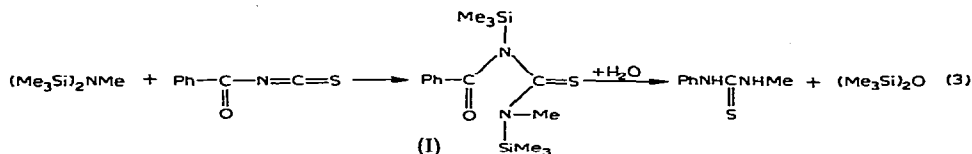
In this paper, the reactions of heptamethyldisilazane with benzoyl isocyanate and isothiocyanate are described and compared with reactions involving simple (trimethylsilyl)dialkylamines<sup>3</sup>.

When benzoyl isothiocyanate was added to heptamethyldisilazane, a viscous oily 1/1 adduct (I) was isolated. Adduct (I) was characterized by means of elementary analysis, NMR and IR spectrometry, and quantitative formation of desilylated *N*-methyl-*N'*-phenylthiourea on hydrolysis. The formation of a stable adduct, (I), at room temperature contrasts with the behaviour of (trimethylsilyl)dimethylamine<sup>3</sup>, which gives trimethylsilyl isothiocyanate and *N,N*-dialkylbenzamide as shown in eqn. (2).



\* For Part XVI see ref. 1.

This difference can be attributed to reduction of the nucleophilicity of nitrogen atom towards carbonyl group by  $p_\pi-d_\pi$  overlap in the adduct (I).



The proton magnetic resonance spectrum of (I) showed four kinds of trimethylsilyl and two kinds of *N*-methyl proton signals (Fig. 1), each set of which coalesced at higher temperature. This suggests the existence of two isomers which are interconvertible through the migration of trimethylsilyl groups.

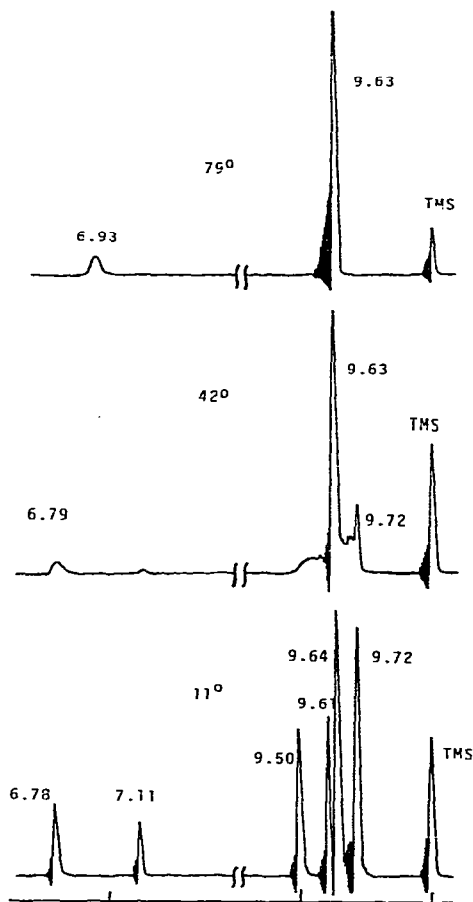
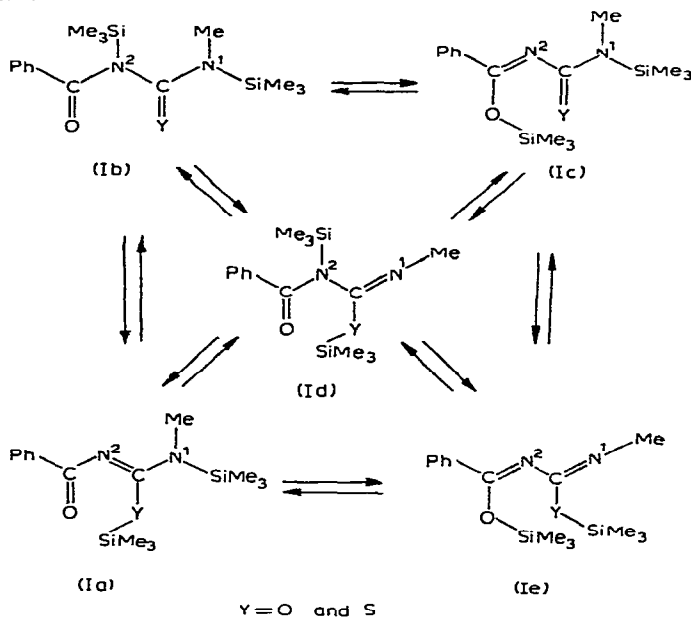


Fig. 1. NMR spectra of adduct (I) from the reaction of heptamethyldisilazane with benzoyl isothiocyanate at various temperatures (solvent trichloroethylene).

Five possible isomers, (Ia)–(Ie), interconvertible through random 1,3-transfer of trimethylsilyl groups could be formulated for the adduct (I) between heptamethyldisilazane and benzoyl isothiocyanate (see Scheme 1). Since the trimethylsilyl group

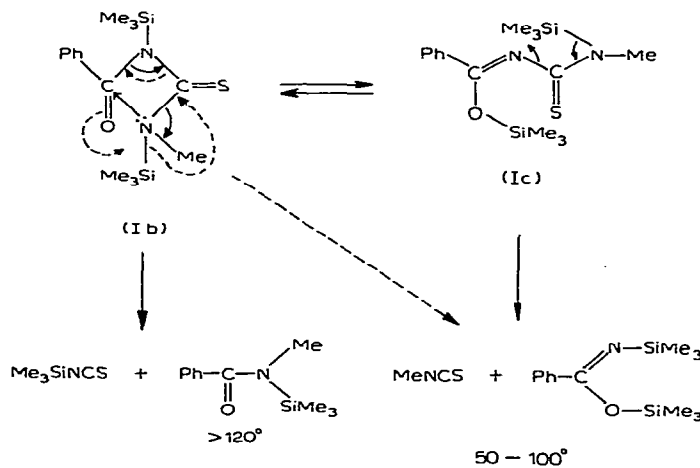
SCHEME 1



behaves as a typical "hard" acid, structures (Ia), (Id), and (Ie), in which silicon is linked to the "soft" sulphur atom, can be ruled out<sup>4</sup>, leaving isomers (Ib) and (Ic) as possibilities.

Adduct (I) decomposed in two ways depending on the temperature. At lower temperatures it gives methyl isothiocyanate and *N,O*-bis(trimethylsilyl) benzimidate, and at higher temperatures it gives trimethylsilyl isothiocyanate and *N*-methyl-*N*-(trimethylsilyl)benzamide, as shown in Table 1.

The results indicate the following addition-elimination reaction mechanism:



Below  $100^\circ$  methyl isothiocyanate is the predominant decomposition product, and thus, structure (Ic) is probably preferred at these temperatures. Thus the proton

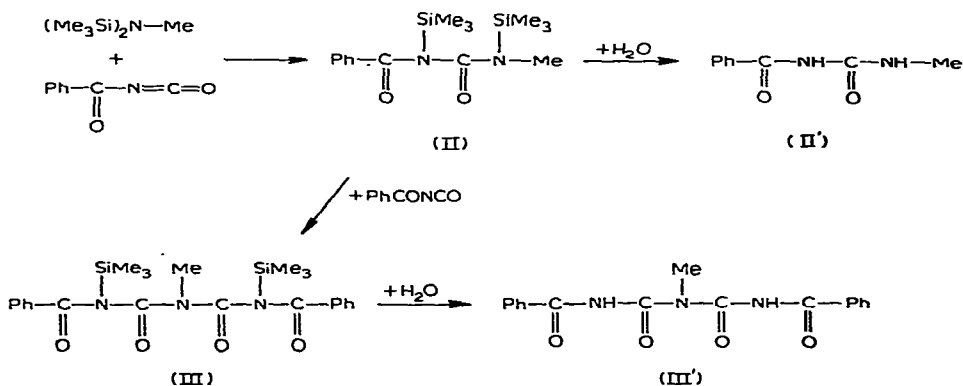
TABLE I

THERMAL DECOMPOSITION PRODUCTS FROM ADDUCT (I) AT VARIOUS TEMPERATURE

Temp. (°C)	Time (h)	(MeNCS)/(Me <sub>3</sub> SiNCS)
50	27	only MeNCS
100	17	4.8
120	17	1.4
150	18	0.23

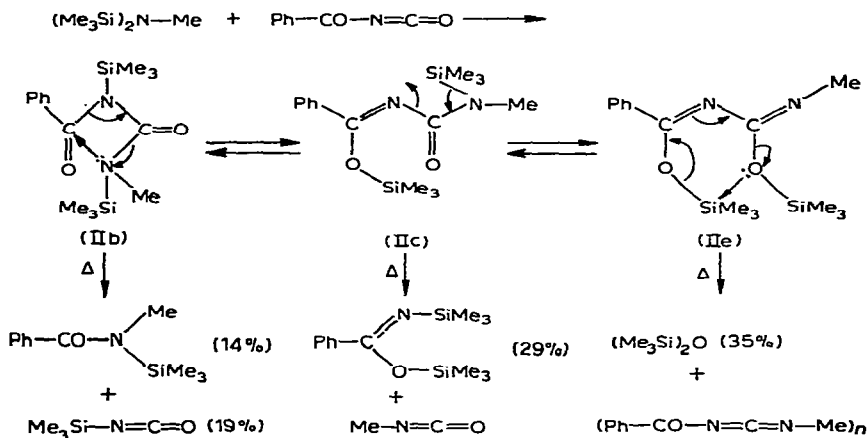
signals at  $\tau$  9.72, 9.64, and 6.78 in Fig. 1 can be ascribed to structure (Ic), and a ratio of (Ic)/(Ib) of 1.5/1 at 11° can be estimated from the relative peak intensities.

Benzoyl isocyanate inserts stepwise into the Si-N bonds of heptamethyldisilazane to give the 1/1 adduct, (II), and the symmetrical 1/2 adduct (III), in 73% and 85% yield, respectively.



The NMR spectrum of the adduct (II) showed four kinds of trimethylsilyl proton at  $\tau$  9.77, 9.71, 9.67 and 9.62, and two kinds of *N*-methyl proton at  $\tau$  7.35 and 7.18 at  $-50^\circ$ , so that at least two isomers are possible even at this low temperature.

## SCHEME 2

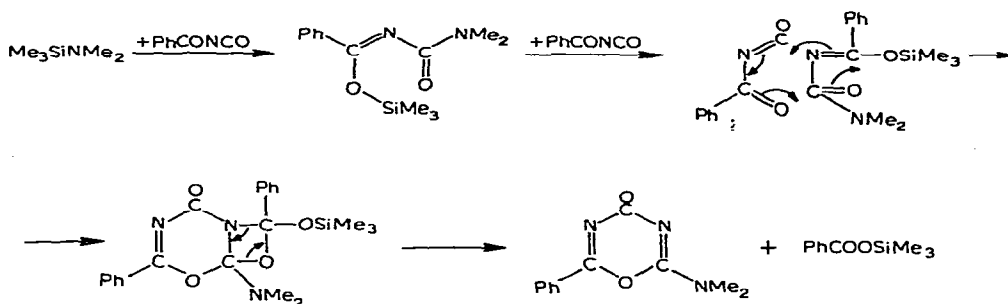


In this case ( $Y = O$  in above mentioned scheme), all possible sites have "hard" character (two oxygen and two nitrogen atoms), consequently, assignment of possible isomers is much more difficult than with adduct (I).

Pyrolysis of the 1/1 adduct (II) above  $150^\circ$  gave hexamethyldisiloxane (35%), trimethylsilyl isocyanate (19%), *N*-methyl-*N*-(trimethylsilyl)benzamide (14%), *N,O*-bis(trimethylsilyl) benzimidate (29%), and an unidentified residue which showed *N*-methyl and benzoyl proton signals. Pyrolysis in the presence of benzoyl isocyanate gave 1-methyl-3,5-dibenzoyl isocyanurate, the cycloadduct from one mole of methyl isocyanate and two moles of benzoyl isocyanate, and this suggests that methyl isocyanate is formed in the pyrolysis of adduct (II).

The products could be accounted for by reaction scheme 2, involving three possible isomers (IIb), (IIc), and (IIe).

As previously mentioned, stepwise insertion gives the symmetrical 1/2 adduct (III), the structure of which was confirmed by means of mass spectrum fragmentations. This is analogous to the result with phenyl isocyanate<sup>5,6</sup>, and markedly different from that from the reaction of benzoyl isocyanate with (trimethylsilyl)dimethylamine<sup>3</sup>. In the last case, an unexpected oxadiazine formation was observed.



## EXPERIMENTAL

All reactions were carried out under argon. Infrared and NMR spectra were recorded with Nippon Bunko IR-S, and Japan Electron Optics C-60 spectrometer, respectively.

Heptamethyldisilazane<sup>7</sup>, benzoyl isocyanate<sup>8</sup>, and benzoyl isothiocyanate<sup>9</sup> were prepared by reported methods.

### Reaction of heptamethyldisilazane with benzoyl isothiocyanate to give 1/1 adduct (I)

Heptamethyldisilazane (0.70 g, 4.3 mmole) was added to benzoyl isothiocyanate (0.76 g, 4.3 mmole) at room temperature and the mixture was kept at  $15^\circ$  for 36 h in an ampoule. After evaporation of mixture at  $10^{-5}$  mmHg for 3 h, the brown 1/1 adduct (I) was isolated in 100% yield. (Found: C, 53.18; H, 7.65.  $\text{C}_{15}\text{H}_{26}\text{N}_2\text{OSSi}_2$  calcd.: C, 53.21; H, 7.74%.) IR:  $\nu_{\text{max}}$   $1643\text{ cm}^{-1}$ . NMR (trichloroethylene):  $\tau$  9.64, 9.61, 9.50; 7.13, 6.78.

**Hydrolysis.** Adduct (I) was quantitatively hydrolyzed into *N*-benzoyl-*N'*-methylthiourea; m.p.  $147.8\text{--}149.0^\circ$  (ethanol),  $\nu(\text{C}=\text{O})$   $1672\text{ cm}^{-1}$ . (Found: C, 55.43; H, 4.83; N, 14.15.  $\text{C}_9\text{H}_{10}\text{N}_2\text{OS}$  calcd.: C, 55.65; H, 5.19; N, 14.42%.)

**Pyrolysis.** Adduct (I) was pyrolyzed in sealed tubes at temperatures between 50–150°. Vacuum distillation gave methyl isothiocyanate [ $\nu_{\max}$  2140  $\text{cm}^{-1}$ ;  $\tau(\text{CH}_3)$  6.67 in  $\text{CCl}_4$ ] and trimethylsilyl isothiocyanate [ $\nu_{\max}$  2080  $\text{cm}^{-1}$ ;  $\tau(\text{SiCH}_3)$  9.68 in  $\text{CCl}_4$ ], collected in a dry ice/acetone trap, *N,O*-bis(trimethylsilyl) benzimidate [b.p. 77–81°/0.5 mm;  $\nu_{\max}$  1695  $\text{cm}^{-1}$ ;  $\tau(\text{SiCH}_3)$  9.89 and 9.71 in  $\text{CCl}_4$ ], and *N*-methyl-*N'*-(trimethylsilyl)benzamide [b.p. 87–89°/0.9 mm;  $\nu_{\max}$  1665  $\text{cm}^{-1}$ ;  $\tau(\text{NCH}_3)$  7.24, 6.98 and  $\tau(\text{SiCH}_3)$  9.79 in  $\text{CCl}_4$ ].

All these products were identified by the comparison of their NMR and IR spectra with those of authentic specimens. The effect of temperature on the product ratio was estimated from NMR peak intensities in the mixture of trimethylsilyl isothiocyanate and methyl isothiocyanate trapped at  $-78^\circ$  under  $10^{-3}$  mmHg. Results are given in Table 1.

*Reaction of heptamethyldisilazane with benzoyl isocyanate to give adduct (II)*

When benzoyl isocyanate (1.13 g, 7.69 mmole) was gradually added to heptamethyldisilazane (1.41 g, 8.05 mmole) at room temperature, reaction took place exothermally. The mixture was kept at 75° for 2 h under reduced pressure, and 1/1 adduct (II) was then isolated by vacuum distillation [b.p. 105–108°/0.2 mm;  $\nu_{\max}$  1661, 1630  $\text{cm}^{-1}$ ,  $\tau(\text{NCH}_3)$  7.29,  $\tau(\text{SiCH}_3)$  9.75 and 9.66 in trichloroethylene] in 75% yield. (Found: C, 55.63; H, 7.66.  $\text{C}_{15}\text{H}_{26}\text{N}_2\text{O}_2\text{Si}$  calcd.: C, 55.86; H, 8.13%.)

**Hydrolysis.** Hydrolysis of (II) gave white needles of *N*-benzoyl-*N'*-methylurea (II'), m.p. 165–166° (from ethanol). (Found: C, 60.27; H, 5.83; N, 15.95.  $\text{C}_9\text{H}_{10}\text{N}_2\text{O}_2$  calcd.: C, 60.66; H, 5.66; N, 15.72%.)

**Pyrolysis.** Pyrolysis was carried out in sealed ampoule under argon, for 18 h at 160–170°. Distillation gave hexamethyldisiloxane (35%), trimethylsilyl isocyanate (19%), *N,O*-bis(trimethylsilyl) benzimidate (29%), and *N*-methyl-*N'*-(trimethylsilyl)benzamide (14%). The unidentified residue, which showed benzoyl and *N*-methyl proton signals, could not be distilled.

*Reaction of heptamethyldisilazane with benzoyl isocyanate in 1/2 molar ratio to give adduct (III), and its desilylated biuret (III')*

When benzoyl isocyanate (1.94 g; 13.2 mmoles) was gradually added to heptamethyldisilazane (1.15 g, 6.54 mmole) at room temperature, 1/2 adduct (III) was obtained with evolution of heat. (Found: C, 58.65; H, 6.78.  $\text{C}_{23}\text{H}_{30}\text{N}_3\text{O}_4\text{Si}_2$  calcd.: C, 58.82; H, 6.65%.)  $\nu_{\max}$  1705, 1663  $\text{cm}^{-1}$ ;  $\tau(\text{SiCH}_3)$  9.83, 9.66 and  $\tau(\text{NCH}_3)$  6.89 in trichloroethylene.

**Hydrolysis.** Hydrolysis of adduct (III), gave *N,N'*-dibenzoyl-*N'*-methylbiuret (III') in 85% yield, m.p. 128–129° (ethanol),  $\nu(\text{C}=\text{O})$  1792  $\text{cm}^{-1}$ . (Found: C, 62.88; H, 4.73; N, 12.93.  $\text{C}_{17}\text{H}_{15}\text{N}_3\text{O}_4$  calcd.: C, 62.76; H, 4.65; N, 12.92%.)

*Formation of 1-methyl-3,5-dibenzoyl isocyanurate from 1/3 molar reaction of heptamethyldisilazane with benzoyl isocyanate*

Benzoyl isocyanate (1.65 g, 11.2 mmole) was added to heptamethyldisilazane (0.62 g, 3.5 mmoles) at room temperature, and the mixture was kept at room temperature for one week. The pale yellow solid obtained by evaporation of volatile materials under reduced pressure was washed with benzene to give the colourless

1-methyl-3,5-dibenzoyl isocyanurate in 8% yield, m.p. 202° (from ethanol);  $\nu_{\max}$  1741, 1705  $\text{cm}^{-1}$ ;  $\tau(\text{NCH}_3)$  6.60 in  $\text{CDCl}_3$ . (Found: C, 61.39; H, 3.68; N, 11.86.  $\text{C}_{18}\text{H}_{13}\text{N}_3\text{O}_5$  calcd.: C, 61.54; H, 3.73; N, 11.96%.)

## REFERENCES

- 1 K. ITOH, I. MATSUDA AND Y. ISHII, *Tetrahedron Lett.*, (1969) 2675.
- 2 K. ITOH, I. K. LEE, I. MATSUDA, S. SAKAI AND Y. ISHII, *Tetrahedron Lett.*, (1967) 2667.
- 3 I. MATSUDA, K. ITOH AND Y. ISHII, *J. Chem. Soc., C*, (1969) 701.
- 4 K. ITOH, K. MATSUZAKI AND Y. ISHII, *J. Chem. Soc., C*, (1968) 2709.
- 5 J. F. KLEBE, J. B. BUSH, JR., AND J. E. LYONS, *J. Amer. Chem. Soc.*, 86 (1964) 4400.
- 6 D. Y. ZHINKIN, M. M. MORGUNOVA, K. K. POPKOV AND K. A. ANDRIANOV, *Dokl. Akad. Nauk SSSR*, 158 (1964) 641.
- 7 R. C. OSTHOFF AND S. W. KANTOR, *Inorg. Synt.*, 5 (1957) 58.
- 8 A. J. SPEZIALE AND L. R. SMITH, *J. Org. Chem.*, 27 (1962) 3742.
- 9 J. B. JOHNSON AND L. H. CHERNOFF, *J. Amer. Chem. Soc.*, 34 (1912) 165.

*J. Organometal. Chem.*, 19 (1969) 339-345