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REACTIONS OF GROUP IV ORGANOMETALLIC COMPOUNDS XVIII*. THE ADDITION REACTION OF THIOBENZOYL ISOCYANATE WITH GROUP IV (ORGANOMETALLYL)AMINES

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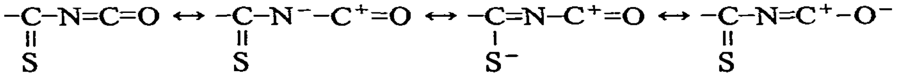
SUMMARY

Thiobenzoyl isocyanate forms 1/1 adducts with trimethylsilyl-, -germyl-, and -stannyldialkylamine. In the adducts from the silyl and germylamines, the trimethylmetal group can migrate between an oxygen and nitrogen atom. On the other hand, the adduct from the stannylamine prefers the *S*-metallated structure, which is consistent with the "softer" acid character of the tin compared with the silicon or germanium atom. The existence of intramolecular coordination of carbonyl oxygen with the trimethyltin group in a six-membered cycle structure, is suggested.

Thiobenzoyl isocyanate was recently prepared and reactions studied by Goerdeler *et al.*[2].

In the present work, this interesting heterocumulene was used as an acceptor in reactions with trimethylmetal(IV) amines.

The following canonical structures can be visualized for thiobenzoyl isocyanate, corresponding to three possible modes of addition. Two types of addition were actually identified[2]; (1), a 1,2-addition across the C=N bond (Ib) which is a well known mode of reaction with common isocyanates, and (2), a 1,4-addition reaction with unsaturated compounds to give cycloadducts. Because of its extreme instability, thiobenzoyl isocyanate was prepared *in situ* by the decarbonylative pyrolysis of 2-phenylthiazoline-4,5-dione in methylcyclohexane, and added immediately to (trimethylsilyl-, -germyl-, or -stannyldimethylamine.



$$-\underset{\underset{S}{\|}}{C}-N=C=O \leftrightarrow -\underset{\underset{S}{\|}}{C}-N^{-}-C^{+}=O \leftrightarrow -\underset{\underset{S^{-}}{|}}{C}=N-C^{+}=O \leftrightarrow -\underset{\underset{S}{\|}}{C}-N=C^{+}-O^{-}$$

(Ia) (Ib) (Ic) (Id)

Reaction took place instantaneously at room temperature with all four compounds, with the disappearance of characteristic red colour of thiobenzoyl isocyanate and of the infrared absorption at 2240 cm^{-1}. The 1/1 adducts were isolated

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* For Part XVII see ref. 1.

by evaporation of methylcyclohexane. Analytical results, infrared, and NMR spectrometric results of the 1/1 adducts, (II)–(V) are summarized in Tables 1, 2 and 3, respectively.

TABLE 1

ADDUCTS FROM THIOBENZOYL ISOCYANATE AND GROUP IV (ORGANOMETALLYL)AMINES

Adduct	Yield (%)	M.p. (°C)	Formula	Calcd.		Found	
				C	H	C	H
(II)	99	89.5–90.0	$C_{13}H_{20}N_2OSSi$	55.67	7.19	55.73	7.24
(III)	87	47.0–49.0[a]	$C_{13}H_{20}N_2OSGe$	48.02	6.22	48.42	6.54
(IV)	98	124.5–125.1	$C_{13}H_{20}N_2OSSn$	42.08	5.43	42.34	5.67
(V)	99	oil	$C_{15}H_{26}N_2OSSi_2$	53.21	7.74	52.81	7.46

[a] Adduct (III) was extremely hygroscopic.

TABLE 2

INFRARED SPECTRA OF ADDUCTS FROM THIOBENZOYL ISOCYANATE AND TRIMETHYLMETALLYLDIMETHYLAMINE IN CHLOROFORM

Compound	ν(C=O)	ν(C=N)	ν(C=S)	$\delta_{as}(CH_3\text{–}M)$	$\delta_{sym}(CH_3\text{–}M)$	ν(C–M)
(II, M=Si)	1695 vs	1575 vw	1330 s	1253 vs	845 vs	685 m
(III, M=Ge)	1695 vs	1580 vw	1328 s	1238 w	823 s	605 s
(IV, M=Sn)	1645 s	1590 s 1575 s	None	1160 s	760	530 m

TABLE 3

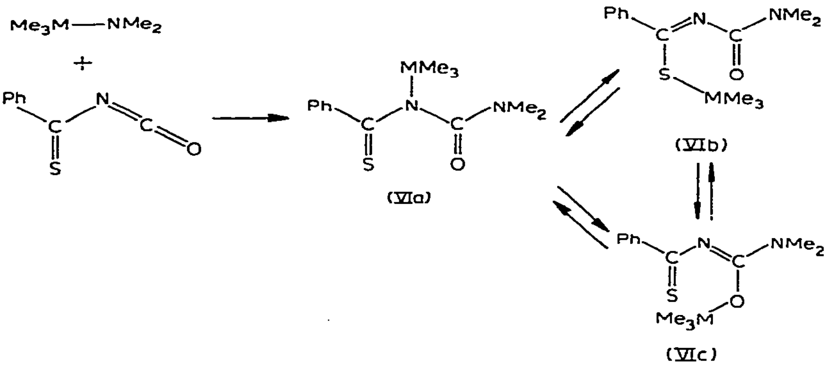
NMR SPECTRA OF ADDUCTS

Solvent: trichloroethylene for (II) and (III), methylene chloride for (IV).

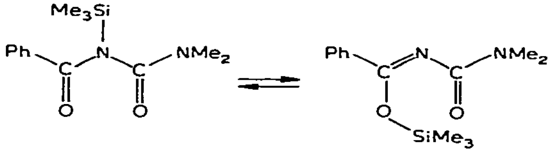
Compound	$(CH_3)_3M$	$(CH_3)_2N$	C_6H_5	Coalescence temp. (°C)
(II, M=Si)	9.64 s	6.99 s	2.75 1.95 m	+12
(III, M=Ge)	9.43 s	7.17 s	2.60 2.14	+16
(IV, M=Sn)	9.52 s	7.17 7.10	2.60 2.28 m	+38

Three structures, (VIa)–(VIc), can be considered, of which could occur interconversions through migration of the trimethylmetal group. Such migration is important and well established in the case of the trimethylsilyl group[3–7].

The infrared spectra of (II, M=Si) and (III, M=Ge) in chloroform showed two strong absorption bands ascribed to the stretching frequency of C=O and C=S bonds. Structure (VIa), in which the nitrogen atom is metallated, may thus be predominant in the case of M=Si and Ge.



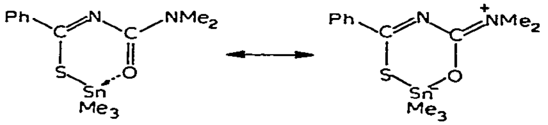
The adduct from the reaction between benzoyl isocyanate and (trimethylsilyl)-dimethylamine was previously found to exist as a mixture resulting from the following equilibrium, involving 1,3-transfer of the trimethylsilyl group between a nitrogen and an oxygen atom[5].



The difference between the adduct (VIc, M = Si) and that from benzoyl isocyanate could be ascribed to the affinity of the silicon atom (a typical "hard" acid) for an oxygen atom rather than for a sulphur atom.

On the other hand, structure (VIb) was predominant in the case of the 1/1 adduct (IV, M = Sn) as indicated by the absence of ν(C=S) around 1330 cm^{-1} and the appearance of a strong absorption of ν(C=N). The tin atom which is "softer" in character than silicon or germanium, is known to prefer a sulphur atom[8,9] so the predominance of structure (VIb) in (IV, M = Sn) is reasonable.

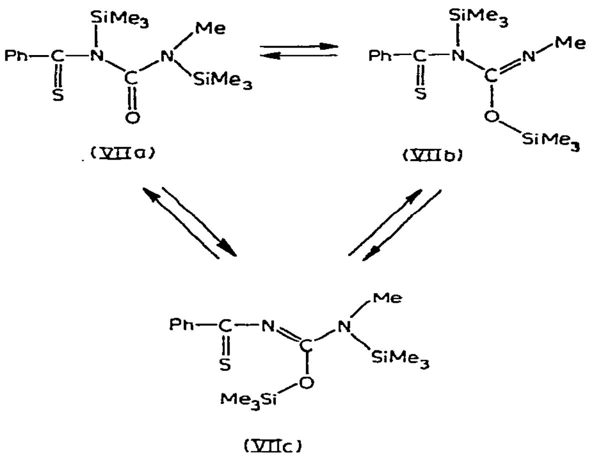
It was interesting that the carbonyl stretching vibration of the 1/1 adduct (IV, M = Sn) ν(C=O) 1645 cm^{-1}, was considerable shifted with that in the analogous adduct (II, M = Si) and (III, M = Ge) (ν(C=O) 1695 cm^{-1}). This fact indicates a strong intramolecular coordination of carbonyl oxygen to the trimethyltin moiety as follows:



Much greater stability towards hydrolysis compared with their silicon or germanium adducts is also consistent with such intramolecular coordination to form a stable six-membered ring, with the thiobenzoyl isocyanate unit behaving as a chelate. Stronger coordination in the solid was indicated by infrared measurements in KBr discs; in this case ν(C=O) absorption was found at 1605 cm^{-1}.

The higher coalescence temperature for the proton signal of the dimethylamino group for (IV, M = Sn) than for (II, M = Si) and (III, M = Ge) (see Table 3) can be accounted for by intramolecular coordination.

For the adduct, (V), from heptamethyldisilazane, the range of structures is more complex, because four sites, NMe, N, O, and S, are possibly available to the two trimethylsilyl groups. However, *S*-silylated structures can be reasonably ruled out because of the "hard" acid character of silicon, and thus three structures (VIIa), (VIIb), and (VIIc) remain to be considered.



In carbon tetrachloride, the ν(C=O) absorption at 1710 cm^{-1} was extremely weak. Consequently, structures (VIIb) and (VIIc), which are stable *O*-silylated forms, predominate over (VIIa), and this conclusion is supported by the appearance of a strong ν(C=N) absorption at 1615 cm^{-1}. At present, it is difficult to determine whether structure (VIIb) or (VIIc) predominates.

EXPERIMENTAL

Infrared and NMR spectra were measured with Jasco-DSG-403G and Jeol-C-60 spectrometers, respectively.

Thiobenzoyl isocyanate was prepared by pyrolysis of 2-phenylthiazoline-4,5-dione[2] in methylcyclohexane at 105–110°, and was characterized by infrared spectrometry. The theoretical amount of carbon monoxide was evolved in the pyrolysis.

Reaction of thiobenzoyl isocyanate with (trimethylsilyl)dimethylamine

2-Phenylthiazoline-4,5-dione (1.02 g, 5.33 mmole) was suspended in 5 ml of methylcyclohexane and pyrolyzed as above. The solution was added to 0.90 ml (9.2 mmoles) of (trimethylsilyl)dimethylamine, an exothermal reaction occurred and the colour changed from red to deep yellow. Evaporation of volatile materials under reduced pressure left 1.46 g (98%) of the 1/1 adduct (II). Analytical and spectrometric results are given in Tables 1–3. Hydrolysis was readily brought about by atmospheric moisture, and gave *N*-thiobenzoyl-*N'*,*N'*-dimethylurea in quantitative yield. The product was recrystallized from carbon tetrachloride, m.p. 88.0–89.0°. (Found: C, 57.97; H, 5.81; N, 13.09. $C_{10}H_{12}N_2OS$ calcd.; C, 57.67; H, 5.81; N, 13.45%.) IR (KBr disk): ν(C=O) 1670, ν(C=S) 1330 cm^{-1}. NMR (CCl_4): τ 7.12 s (NCH_3, 6 H), τ 2.64, 1.95 m (C_6H_5, 5 H).

Reaction of thiobenzoyl isocyanate with (trimethylgermyl)dimethylamine

Thiobenzoyl isocyanate, formed from 68.7 mg (0.36 mmoles) of 2-phenylthiazoline-4,5-dione, was added dropwise to (trimethylgermyl)dimethylamine, as described for the silicon analogue, to give the adduct in 87% yield. It was identified by elemental analysis (Table 1) and spectroscopy (Tables 2, 3). Hydrolysis of the adduct (III), with atmospheric moisture gave *N*-thiobenzoyl-*N'*,*N'*-dimethylurea quantitatively.

Reaction of thiobenzoyl isocyanate with (trimethylstannyl)dimethylamine

The analogous procedure with 585 mg (3.05 mmole) of 2-phenylthiazoline-4,5-dione and 660 mg (3.2 mmole) of (trimethylstannyl)dimethylamine gave the adduct (IV) in 98% yield. It was recrystallized from benzene, and had m.p. 124.5–125.1°. Analytical and spectroscopic results are included in Tables 1–3. It was stable to hydrolysis when exposed to the air for one week at room temperature.

Reaction of thiobenzoyl isocyanate with heptamethyldisilazane

The adduct (V) was isolated quantitatively when 125 mg (0.65 mmole) of 2-phenylthiazoline-4,5-dione was pyrolyzed and the product added to heptamethyldisilazane (0.70 mmole) at room temperature. Evaporation of the solvent gave the adduct (V) as a viscous oil. Analytical and spectroscopic results are given in Tables 1–3. It was readily hydrolyzed to give *N*-methyl-*N'*-thiobenzoylurea in quantitative yield; m.p. 143.5–143.9° (ethanol). (Found: C, 55.48; H, 4.96; N, 14.12. $C_9H_{10}N_2OS$ calcd.: C, 55.65; H, 5.19; N, 14.42%.) IR (KBr disk) ν(C=O) 1705, ν(C=S) 1360 cm^{-1}.

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