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REACTIONS OF GROUP IV ORGANOMETALLIC COMPOUNDS

XXVIII*. THE INSERTION REACTIONS OF BENZOYL-tert-BUTYLCARBODIIMIDE WITH GROUP IV TRIMETHYLMETALLYLAMINES AND THE PREPARATION OF TRIMETHYL-SILYL- AND -GERMYL-tert-BUTYLCARBODIIMIDE

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Summary

The insertion reaction of benzoyl-tert-butylcarbodiimide with $Me_3M—NMe_2$ (M = Si, Ge and Sn) or $(Me_3M)_2NMe$ (M = Si and Sn) is described. The pyrolyses of 1/1 adducts by organosilyl- and organogermyl-amines gave the corresponding $Me_3M—N{=}C{=}N—CMe_3$ (M = Si and Ge) by elimination of *N,N*-disubstituted benzamides.

Introduction

The introduction of the electron-withdrawing benzoyl group into heterocumulene systems influences the structure of organometallic adducts, and the benzoyl group frequently induces facile elimination reactions of insertion products, as we have noted in the addition-elimination reactions of benzoyl isocyanate or isothiocyanate with Group IV organometallylamines [2—4]. As an extension of our previous studies on the benzoyl heterocumulene system, we describe below the insertion and subsequent elimination reactions of benzoyl-tert-butylcarbodiimide with Group IV organometallylamines of the type $Me_3M—NMe_2$ or $(Me_3M)_2NMe$.

Organometallic insertions of simple carbodiimides into B—C, Sn—N, Sn—O and Pb—O bonds were investigated by Lappert and coworkers [5]. Di-*p*-tolylcarbodiimide was mainly used, and the product was expected 1/1 adduct in most cases.

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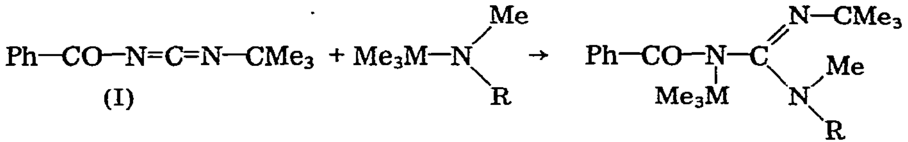
[*] For part XXVII see ref. 1.

Results and discussion

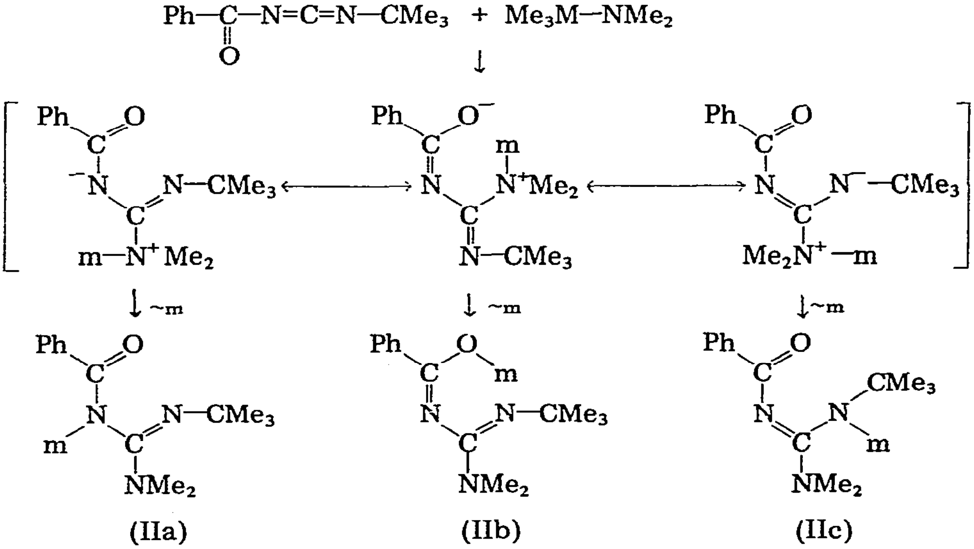
Insertion reactions of benzoyl-tert-butylcarbodiimide (I) with Group IV organometallylamines of the type $Me_3M—NMe_2$ (M = Si, Ge and Sn) and $(Me_3M)_2NMe$ (M = Si and Sn) took place exothermally at room temperature. Yields, infrared, and NMR spectra of the isolated insertion products (III)—(VII), are summarized in Table 1.



(III): M = Si, R = Me;
(IV): M = Si, R = Me_3Si;
(V): M = Ge, R = Me;
(VI): M = Sn, R = Me;
(VII): M = Sn, R = Me_3Sn.

The insertion reaction of $Me_3M—NMe_2$ must proceed by nucleophilic attack of the nitrogen atom followed by rapid migration of the organometallic moiety. There are three possible structures for the insertion products, corresponding to the three canonical forms shown in Scheme 1.

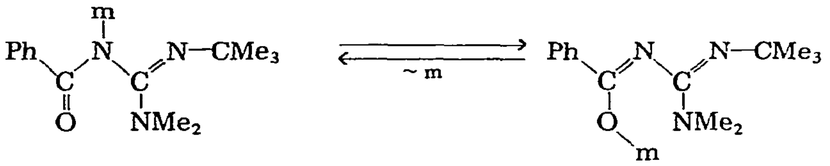
SCHEME 1



It has been reported that the addition of secondary amines (m = H) to (I) gave (IIc) [6]. However, the contribution of (IIc) is thought to be suppressed in the case of Group IV organometallylamines (m = Me_3Si, Me_3Ge and Me_3Sn) because two bulky tert-butyl- and trimethyl-metallyl groups are linked to the tertiary nitrogen atom in (IIc).

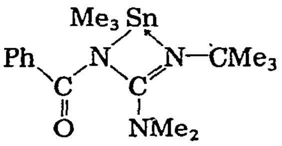
The PMR spectrum of the trimethylsilyl group in (III) (τ 9.64 ppm at 25°) separated below —30° into two singlets at τ 9.75 and 9.58 ppm. (intensity ratio 1/5). This suggests a migration of the trimethylsilyl group analogous to prototropy [7—9]. Thus, the adduct (III) is considered to be a mixture of the two isomers (IIIa) and (IIIb). The predominant isomer must be (IIIb), because the IR spectrum of (III) showed little absorption of the free carbonyl group around 1630 cm^{-1} and strong conjugated C=N stretching bands at 1573 and 1550 cm^{-1}. The ratio (IIIa)/(IIIb) was estimated to be 1/5 from the intensities of two CH_3—Si signals; τ 9.75 (minor isomer IIIa) and 9.58 ppm (major isomer IIIb) at —60°.

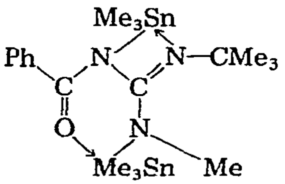
The existence of two isomers was also observed in the case of the organogermanium adduct (V). The interconversion between these two isomers is frozen even at room temperature; (Va) τ 9.40, 8.99 and 7.27 ppm; (Vb) τ 9.50, 8.77 and 7.12 ppm; isomer ratio (Va)/(Vb) = 10/1. The predominance of (Vb), and the assignment of the NMR signals were based on the appearance of a broad and strong carbonyl stretching frequency between 1620—1640 cm^{-1}, as well as that of a C=N band at 1612 cm^{-1}.

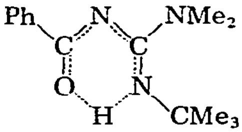


(IIIa): m = Me_3Si; (IIIb) (IIIa)/(IIIb) = 1/5
(Va): m = Me_3Ge; (Vb) (Va)/(Vb) = 10/1
(VIa): m = Me_3Sn — Only (VIa)

The infrared spectrum of the organotin adduct (VI) showed a strong carbonyl stretching frequency at 1630 cm^{-1}. The C=N stretching band shifted to lower frequency at 1550 cm^{-1}, indicating that coordination of the nitrogen atom to organotin moiety must be involved. Cryoscopy showed that (VI) was monomeric in benzene. The NMR spectrum did not show temperature dependence, and suggested the presence of the only one isomer. The depicted structure (VIa) is consistent with the above findings.


(VIa)


(VII)


(VIII)

The carbonyl stretching frequency was absent in the case of the 1/1 adduct from heptamethyldistannazane (VII). The NMR of (VII) showed temperature dependence; the two broad trimethyltin proton signals at room temperature became sharp at 0° with clear satellites (J^{117}Sn—C—H 52 and J^{119}Sn—C—H 56Hz).

TABLE 1

ADDITION OF BENZOYL-tert-BUTYLCARBODIIMIDE (I) TO GROUP IV ORGANOMETALLYLAMINES

Compound	Organometallyl-amine	Yield (%)	IR(CCl_4 soln.)(cm^{-1}) $\nu(C{=}O)$ and $\nu(C{=}N)$	PMR(CCl_4 soln.)(τ ppm)		
				CH_3—M	CH_3—C	CH_3—N
(III)	Me_3SiNMe_2	88	1607 s, 1573 s, 1550 s,	9.64	8.91	7.34
(IV)	$(Me_3Si)_2NMe$	63	1644 w, 1605 s, 1574 m	9.79, 9.60	8.92	7.61
(V)	Me_3GeNMe_2	95	1620—1640 s(br), 1612 s, 1572 m	9.50, 9.40	8.77, 8.99	7.12, 7.27
(VI)	Me_3SnNMe_2	89	1630 s, 1593 s, 1550 m	9.53	9.02	7.18
(VII)	$(Me_3Sn)_2NMe$	96	1594 s, 1578 s, 1562 s	9.74, 9.52	9.03	7.38

TABLE 2

TRIMETHYLSILYL- AND TRIMETHYLGERMYL-tert-BUTYLCARBODIIMIDE

Starting compound	Me_3M—N=C=N—CMe_3							Yield(%) Ph—CO—N(R)Me
	Compound	Yield(%)	B.p. (°C/mmHg)	IR(cm^{-1}) $\nu(N{=}C{=}N)$	NMR(τ ppm in CCl_4)		Analysis found (calcd.)(%)	
					CH_3—M	CH_3—C	C	
(III)	(IX: M = Si)	68	152/760	2144	9.83	8.75	56.53 (56.41)	R = Me: 53
(IV)	(IX: M = Si)	82					10.53 (10.65)	R = Me_3Si: 65
(V)	(X: M = Ge)	75	76/18	2125(sh) 2099	9.56	8.78	44.92 (44.73) 8.58 (8.44)	R = Me: 80

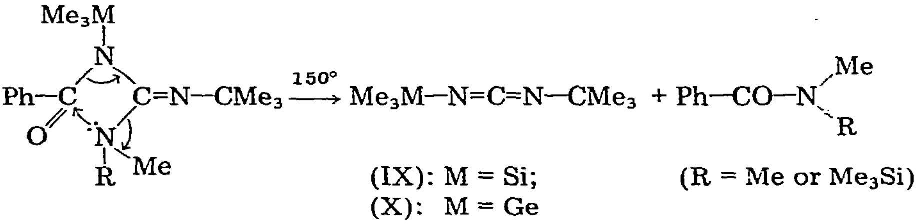
The presence of satellites also in the CH_3—N proton signal (J 29 Hz) suggested that one of the two trimethyltin groups must be bonded to the methylamino group. The molecular weight showed that compound (VII) is monomeric in benzene. These results are compatible with intramolecular coordination of the carbonyl oxygen to tin as in (VII). When the NMR spectra were measured above 50°, the two trimethyltin proton signals had coalesced to a singlet. This indicates that there is intermolecular exchange of the organotin moieties at elevated temperature.

Hydrolysis of (III), (V) and (VI) gave (VIII). The infrared spectrum of (VIII) showed absorptions at 1605, 1582 and 1548 cm^{-1}. The low frequency shift of the C=O and C=N absorptions is ascribed to the intramolecular hydrogen bond.

It is interesting that the contribution of the structure (a) increases on descending the Periodic Table ($a/b = 0.2$ for Si, 10 for Ge and ∞ for Sn). This sequence corresponds to the sequence of stability of the metal—oxygen bonds involved in the structure (b).

Pyrolyses of adducts: A formation of trimethylmetallyl-tert-butyl-carbodiimides

The thermal decomposition of the two organosilicon adducts (III) and (IV) and the organogermanium adduct (V) occurs at 150°. The products are the corresponding trimethylmetallyl-tert-butylcarbodiimide; $Me_3M—N=C=N—CMe_3$ (IX: M = Si) and (X: M = Ge) and *N,N*-disubstituted benzamide; Ph—CO—NMe—R [R = Me for the decomposition of (III) and (V) and R = Me_3Si for that of (IV)]. Yields, boiling points and spectral data are summarized in Table 2.



(IX): M = Si;
(X): M = Ge

(R = Me or Me_3Si)

(III): M = Si, R = Me;
(IV): M = Si, R = Me_3Si;
(V): M = Ge, R = Me

This type of addition-elimination is characteristic of benzoyl heterocumulene system [2, 3] and provides a method of preparing new asymmetric carbodiimides containing different Group IV elements. Unfortunately, the pyrolysis of organotin adducts (VI) and (VII) induced a disproportionation of organotin groups to give tetramethyltin and non-characterizable residues. Although symmetric bis(organosilyl)carbodiimides [10] and bis(trimethylstannyl)carbodiimide [11] have been reported, there are very few examples of organometallic carbodiimides containing different elements. We have, however, previously reported the preparation of phenyltrimethylsilylcarbodiimide [12] by the reaction of *N*-phenylisocyanide dichloride with lithium bis(trimethylsilyl)amide.

Experimental

All reactions were performed under argon. Elemental analyses were undertaken by the Alfred Bernhardt Mikroanalytisches Laboratorium at Engelskirchen, West Germany. NMR spectra were measured on a JEOL-C60HL spectrometer with tetramethylsilane as internal standard. The preparation of benzoyl-tert-butylcarbodiimide has been described previously [6].

Reaction of Me_3SiNMe_2 with benzoyl-tert-butylcarbodiimide (I)

Benzoyl-tert-butylcarbodiimide (I; 2.38 g, 11.8 mmol) was gradually added to Me_3SiNMe_2 (1.65 g, 14.0 mmol). Reaction proceeded exothermally at room temperature. After evolution of heat ceased the 1/1 adduct (III) was isolated by distillation under reduced pressure in 88% yield: (III); b.p. 97—100°/0.1 mmHg. (Found: C, 64.07; H, 8.98. $C_{17}H_{29}N_3OSi$ calcd.: C, 63.90; H, 9.15%.)

The hydrolysis of (III) was performed with atmospheric moisture to give *N*-benzoyl-*N'*-tert-butyl-*N''*,*N''*-dimethylguanidine (VIII) in quantitative yield. (VIII), m.p. 180°. (Found: C, 67.98; H, 8.56. $C_{14}H_{21}N_3O$ calcd.: C, 68.08; H, 8.69%.) IR(ν_{max}):1605, 1582 and 1548 cm^{-1}. NMR: τ(CH_3—C) 8.56 and (CH_3—N) 7.01 ppm.

Reaction of $(Me_3Si)_2NMe$ with (I)

A mixture of heptamethyldisilazane (0.98 g, 5.56 mmol) and (I) (0.90 g, 4.44 mmol) was heated at 95° for 3 days in an ampoule. Distillation gave the 1/1 adduct (IV) in 63% yield. (IV): b.p. 97—98°/0.06 mmHg. (Found: C, 60.60; H, 9.45. $C_{19}H_{35}N_3OSi_2$ calcd.: C, 60.42; H, 9.34%.)

Reaction of Me_3GeNMe_2 with (I)

A carbon tetrachloride (2 ml) solution of Me_3GeNMe_2 (0.79 g, 4.89 mmol) was gradually added to (I) (0.89 g, 4.41 mmol) at room temperature. After heat evolution had ceased, carbon tetrachloride and excess Me_3GeNMe_2 were evaporated off under reduced pressure. The 1/1 adduct (V) was isolated as a pale yellow oil in 95% yield. Attempts to purify the adduct (V) by vacuum distillation failed because thermal decomposition took place. (Found: C, 55.91; H, 7.85. $C_{17}H_{29}N_3OGe$ calcd.: C, 56.09; H, 8.03%.)

Reaction of Me_3SnNMe_2 and $(Me_3Sn)_2NMe$ with (I)

Carbodiimide (I) (0.94 g, 4.65 mmol) was gradually added to an n-hexane (2 ml) solution of Me_3SnNMe_2 (1.07 g, 5.13 mmol). After a few minutes, the 1/1 adduct (VI) precipitated as white needles in 89% yield. Recrystallization was from n-hexane. (VI): m.p. 68—69°. (Found: C, 49.93; H, 7.23. $C_{17}H_{29}N_3OSn$ calcd.: C, 49.79; H, 7.13%.)

The 1/1 adduct (VII) was similarly prepared by the addition of (I) (1.05 g, 5.19 mmol) to heptamethyldistannazane (1.95 g, 5.46 mmol) in 96% yield. (VII): m.p. 67—69°, C, 40.74; H, 6.29. $C_{19}H_{35}N_3OSn_2$ calcd.: C, 40.83; H, 6.31%.) The spectroscopic data for the 1/1 adducts are summarized in Table 1.

Thermal decomposition of (III), (IV) and (V); preparation of trimethylsilyl- or trimethylgermyl-tert-butylcarbodiimide (IX and X)

(a). The pyrolysis of (III) is described as an example. The 1/1 adduct (III) (1.27 g, 3.98 mmol) was kept in a sealed tube at 150° for 24 h. The mixture was distilled under reduced pressure with a Dry-Ice/acetone trap attached. Crude trimethylsilyl-tert-butylcarbodiimide (IX) was collected in the trap (0.46 g, 68%), and *N,N*-dimethylbenzamide was obtained as distillate (0.31 g, 53%; b.p. 90°/0.1 mmHg). The crude (IX) was purified by distillation (b.p. 152°/760 mmHg). The pyrolysis of (IV) and (V) was performed in the similar manner. Analytical and spectral data are listed in Table 2.

(b). The mixture of heptamethyldisilazane (0.98g, 5.57 mmol) and (I) (1.08 g, 5.36 mmol) was kept in a sealed tube at 150° for 17 h. The mixture was distilled under reduced pressure. Crude (IX) was collected in Dry-Ice/acetone trap (0.75 g; 82%). The fraction at b.p. 55—58°/0.2 mmHg was *N*-methyl-*N*-trimethylsilylbenzamide (0.72 g; 65%). Trimethylgermyl-tert-butylcarbodiimide (X) was prepared similarly from equimolar amounts of (I) and Me_3GeNMe_2 at 150°.

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