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DIMETHYL GERMYLENE INSERTION INTO A STRAINED C-Ge BOND AND MATRIX ISOLATION OF TETRAMETHYL DIGERMENE $Me_2Ge{=}GeMe_2$

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Summary: Free tetramethyl digermene $Me_2Ge{=}GeMe_2$ is generated thermally from molten 7,8-digerma bicyclooctadienes[2.2.2] which are obtained by germylene (Me_2Ge) insertion into the C-Ge bond of corresponding 7-germa norbornadienes. The structure of the digermene follows from MS, matrix IR and Raman spectroscopy.

The heavy analogues of alkenes C=C and disilenes Si=Si [2] are the digermenes, e.g. $Me_2Ge{=}GeMe_2$ 1, with the very interesting germanium germanium double bond, but a twenty years' search for them remained without success[3]. Only recently, a digermene with very bulky substituents has been identified in solution by UV, ^1H NMR, and an insertion product[4]. We have been faced with 1 during our work on heavy carbene analogues, especially R_2Ge [5] and R_2Sn [6], and we wish to report here the first generation of free 1, its matrix isolation, and its IR and Raman spectroscopy.

7-Dimethylgerma norbornadienes 2 proved in solution to be convenient thermal sources for free germylenes Me_2Ge, k_1 in Scheme 1, allowing smooth additions to π-systems, cycloadditions to 1,3-dienes, and insertions into σ-bonds[1,5]. Now we have found that they act in molten state as powerful germylene scavengers competing successfully with the rapid polymerization of germylenes by insertion into the highly strained C-Ge bond, k_2, forming benzo digerma bicyclooctadienes 3 in yields up to 60% depending on R and R^1-R^4, besides polygermanes 4 and the corresponding naphthalene, see Scheme 1. This insertion, k_2, might be exothermal and therefore rapid - see below - because 3 is much less strained than 2 as can be concluded from spheric models. The other way to 3 to be taken into consideration passing dimerization of Me_2Ge [7] forming 1, k_5, can be excluded because mixing of 2a (R= Ph, R^1-R^4=H) with another naphthalene in excess, e.g. Ph_4Me_3-naphthalene gives only 3a and no 3c: the Diels-Alder type addition, k_{-3}, is not possible, only the retro reaction, k_3, occurs. Table 1 gives the analytical data for compounds 3 obtained so far. If a compound 3 is thermolysed, the naphthalene and the polygermane 4, k_4, are found. With 3a, e. g., this is completed at 160°C within 4 hrs. Anthracene, however, known to be a better enophile than naphthalenes, in the molten mixture with 3a or 3c at 200°C gives the crystalline adduct 5, k_6. This is best interpreted as a trapping of transient digermene 1. The structure of 5 is backed by an independent synthesis, k_7. After we had finished this part of our work[1] a further independent synthesis of 5 has been published, k_8, together with another cycloaddition of 1 assumed to occur as a transient[8].

Scheme 1:

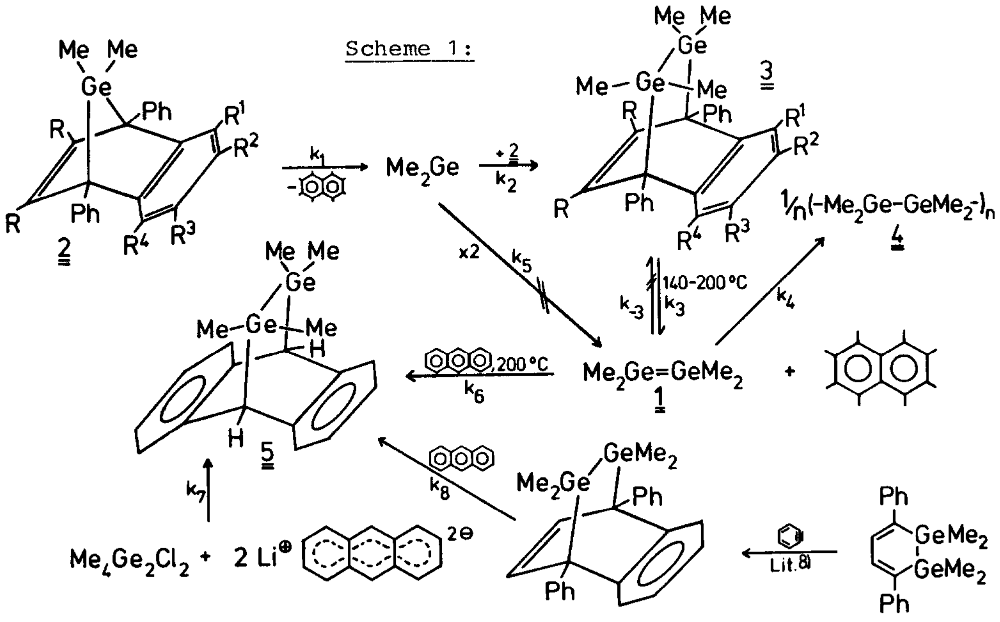


Table 1: Analytical Data for 7,8-Digerma-bicyclooctadienes[2.2.2]

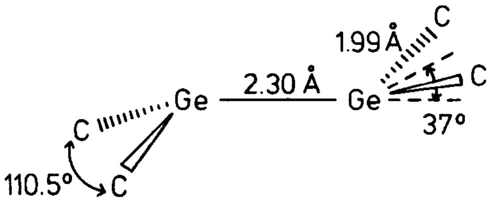
						yield		dec.	^{1}H NMR			
No.	R	R^1	R^2	R^3	R^4	NMR	isol.	(°C)	solv.	Me - Ge	Me - Aryl	Ph
3a	Ph	H	H	H	H	50%	24%	156-160	a	0.07^c 0.93^c	-	$6.59\text{-}7.31^d$
									b	0.13^c 0.89^c	-	-
3b	Ph	Me	H	H	H	50%	4%	k	b	0.12^e 0.23^e 0.88^e 0.93^e	1.68^e	-
3c	Ph	Me	Me	H	Me	60%	25%	183	a	0.12^e 0.17^e 0.92^e 1.0^e	1.42^c 2.1^e	$6.2\ \text{-}7.5^f$
									b	0.17^e 0.22^e 0.95^e 1.0^e	1.62^e 1.67^e 2.03^e	-
3d	Ph	Me	Me	Me	Me	60%	20%	215-220	a	0.15^c 0.97^c	1.38^c 2.07^c	$6.1\ \text{-}7.4^g$
									b	0.22^c 1.03^c	1.66^c 2.05^c	-
3e	H	Me	Me	H	Me	k	k	k	a	0.23^e 0.25^e 0.52^e 0.57^e	1.4^c 2.03^e	k
5	Benzo	H	H	H	H	k	59%	173-175	a	0.07^h	-	$6.98^{i,j}$

a) in CCl_4; b) in benzene; c) s, 6H; d) m, 24H; e) s, 3H; f) m, 21H; g) m, 20H; h) s, 12H; i) s, 8H; j) 4.03 (t-CH, s, 2H); k) not determined. For the isolated compounds, correct elemental analyses have been obtained.

These results give evidence for a transient particle like **1**, but no proof for its occurrence in free state, of course. Further good arguments, however, are provided by mass spectrometry. If a sample of crystalline **2a** is heated in the probe of a mass spectrometer (Varian CH 7, 16 eV, 150-200°C), exclusively two particles can be observed, the naphthalene (base peak), m/e = 432, and Me_4Ge_2, m/e = 206, with the typical isotope pattern for 2 Ge atoms in this particle. Neither Me_2Ge nor Me_6Ge_3 nor higher oligogermanes are visible. With an apparatus of higher sensitivity (Finnigan MAT 8200, 70 eV), besides, M^+ of **2a** can be seen (0.11%), m/e = 536, and, interestingly, M^+ of **3a**, too, m/e = 638 (0.065%), but again no Me_2Ge and no higher germanes. This indicates that trapping of Me_2Ge by **2**, k_2, is more efficient, i.e. rapid, than diffusing into the gas phase, even in the high vacuum of a mass spectrometer.

This encouraged us to try a matrix isolation of whatever might come out from thermolysis of **2a** in the solid state or melt. Using a special matrix technique[9] and experience of former work[10], we recorded (thermolysis at 140-175°C) in an argon matrix at first much naphthalene, partly obscuring the expected vibrations. Lastly, we could separate it by condensing it on the way.

Then, good IR spectra have been obtained in argon matrix, and intense Raman spectra both in argon and nitrogen matrices at 5K. They show, besides the CH_3 vibrations, clearly the skeletal ones to be postulated for **1**: ν_{Ge-Ge} (only Ra) and the four ν_{C-Ge} (2 Raman active and 2 IR active, see Table 2[11]). By chance, an ab initio study of a Ge-Ge double bond in digermene H_4Ge_2 has just been published[12] showing a bent structure of the molecule. This enabled us to establish a normal coordinate analysis of Me_4Ge_2 and to calculate the vibrations, see Table 2. Whereas a planar model gave insufficient approximations, the following trans-bent geometry (C_{2h}), in accordance with the theory[12] led to the best agreement with the measured frequencies:



ν_{Ge-Ge} (Ra, 404 cm^{-1}) is much higher than in the case of the single-bonded digermane $Me_3Ge-GeMe_3$ (275 cm^{-1}). This means that the digermene $Me_2Ge=GeMe_2$ **1** can really be written with a double bond like the disilene $Me_2Si=SiMe_2$ and the olefin $Me_2C=CMe_2$. It is bent, and dipolar or biradical forms give, if any, only minor contributions. With this respect **1** can be regarded as a dienophile undergoing also Diels-Alder reactions, e.g. k_6.

Table 2: Skeletal Vibrations of the Isolated Tetramethyl Digermene 1, $Me_2Ge{=}GeMe_2$, (Symmetry C_{2h}), Calculated and Observed (cm^{-1})[11]

	Raman[a)]				IR[a)]		
Assignment	Obs. Ar	Obs. N_2	Calc.	Representation	Obs. Ar	Calc.	Representation
ν (Ge-C)	591	589	588	B_g	598	593	A_u
	580	580	576	A_g	568	564	B_u
ν (Ge-Ge)	404	405	401	A_g	b)		
δ (GeGeC)	235	234	232	B_g			
δ (CGeC)	200	198	206	A_g			

a) IR and Raman measurements could be performed down to 400, resp. 190 cm^{-1}.- b) There is no band near 400 cm^{-1} in the IR as to be postulated.

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11) A complete report of the spectroscopic measurements and calculations will be published elsewhere. Me groups are assumed tetrahedral, with C-H =1.09 Å.

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