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7-GERMANORBORNADIENES AND THEIR THERMAL CYCLOELIMINATIONS

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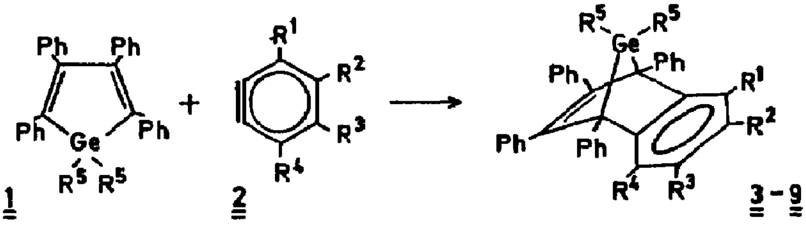
Summary: 7 new 7-germanorbornadienes, crystalline and stable at 25°C, have been prepared by Diels-Alder reaction. They decompose thermally via a two step mechanism with an intermediate biradical, forming the benzene derivative and germylenes, R_2Ge.

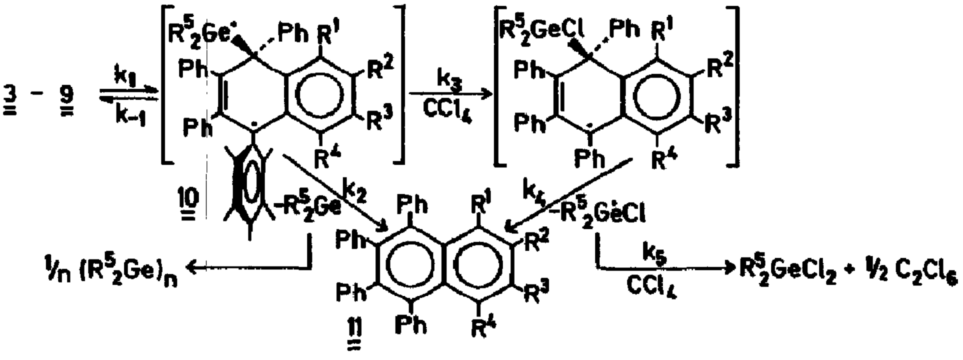
Carbenes[2] and carbene analogues[3-5] have been generated by thermolysis of norborn(adi)enes and their 7-hetero derivatives. This is an advantageous unimolecular reaction not needing any further reagents. Our good experience with a 7-dimethylstannanorbornene[4] giving stannylenes R_2Sn led us to the question, whether corresponding 7-germa compounds are in general accessible[6] and suitable to generate germylenes R_2Ge thermally. A one step mechanism is conceivable and allowed by orbital symmetry but is not necessarily the real procedure. Others have also to be considered, and it is one of the aims of the present investigation to clarify the mechanism of this cycloelimination.

Diels-Alder reaction of the germol 1 with dehydrobenzene and its methyl derivatives[7] 2 yield readily the colourless, well crystallised 7-germanorbornadienes 3-9. They all are stable at room temperature but exhibit remarkable differences in thermal stability, see table 1.



The unmethylated benzo derivative 3 gives cycloelimination at 70°C in CCl_4, following first order kinetics, $t_{1/2}$ = 40 min. Methyl groups in remote positions, see 4, 5, have no influence on this. On the other hand, by methylation in the benzo part of the molecule of one or two of the positions neighbouring the phenyl rings in the 1,4 positions, the thermal stability is raised considerably, giving e.g. $t_{1/2}$ = 7 hrs, 6. Additional methyl groups in 7 and 8 yield a more bulky and rigid ring of substituents around the benzo moiety, the thermal stability is raised drastically, $t_{1/2}$ = 70 or, resp., 120 hrs.

A clear conclusion concerning the mechanism is derived from this influence of position and number of the methyl groups: the cycloelimination of the germylene follows not a one step but a two step mechanism passing the intermediate biradical 10 [8,9].



The latter is stabilized by benzyl mesomerism only when the phenyl ring in position 1 is coplanar with the basic ring of the norbornadiene system (the same conclusion has to be derived for the phenyl ring in position 4). If, instead, a vertical position of this phenyl ring (or these two rings, resp.) is caused by neighbouring methyl groups, 10 is no longer a benzyl radical, hence less stable, the 7-germa norbornadiene is made more stable by lack of a suitable kinetic way for the cycloelimination, k_1 is diminished. This effect reaches its maximum in the case of the tetramethylderivative 8: the phenyl rings in positions 1 and 4 are, as shown also by spheric models, rather rigidly fixed in a position vertical to the basic ring [10].

Thermolysis of 3 - 9 in benzene lastly yields the corresponding substituted naphthalene 11, k_2, and polygermane which is probably a following product of free germylenes, R_2Ge. The latter can be trapped in benzene in the presence of an excess of tolane or, resp., 2,3-dimethylbutadiene, yields: 58% and, resp., 90%:

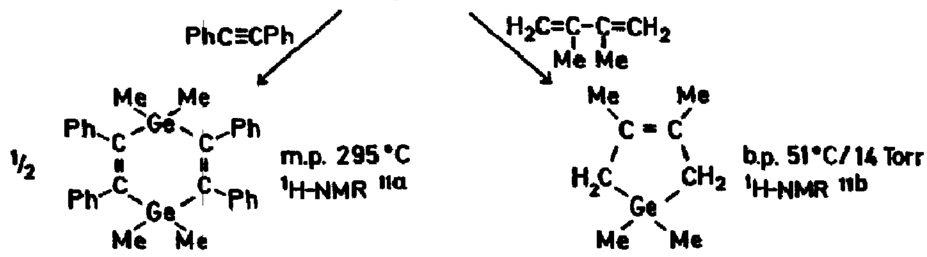


Table 1: Characterization of the 7-germanorbornadienes **3** - **9**

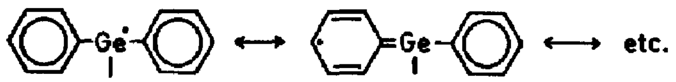
	R^1	R^2	R^3	R^4	R^5	^{1}H-NMR (CCl_4, values against TMS)	$t_{1/2}$,CCl_4 70°C,hrs.	Yield %	Decomp. °C
3	H	H	H	H	CH_3	0.2s; 0.88s (3 H each); 6.5-7.5 m (24 H)	0.67	65	138
4	H	CH_3	H	H	CH_3	0.2s; 0.83s; 2.32s (3 H each); 6.45-7.3 m (23 H)	0.67	65	120
5	H	CH_3	CH_3	H	CH_3	0.2s; 0.82s; (3 H each) 2.22s (6 H) 6.4-7.4 m (22)	0.67	65	140
6	H	H	H	CH_3	CH_3	0.2s; 0.62s; 2.3s (3 H each); 6.2-7.2 m (23 H)	7	70	152
7	CH_3	H	CH_3	CH_3	CH_3	0.23s; 0.50s; 1.65s, 2.0s; (3 H each) 6.3-7.3 m (21)	70	80	165
8	CH_3	CH_3	CH_3	CH_3	CH_3	0.16s; 0.43s (3 H each); 1.9s; 2.1 (6 H each) 6.4-7.2 m (20 H)	120	80	180
9	CH_3	H	CH_3	CH_3	Ph	1.62s; 1.92s; 2.28s (3 H each); 6.3-7.4 m (31 H)	4	70	160

In CCl_4 the norbornadiene disappears much more quickly. Apparently the very rapid scavenging, k_3, prevents the back reaction, k_{-1}. Therefore, in CCl_4 the slowest step k_1 is measured, see table 1. Consecutively, the germyl residue is split off as a radical releasing the corresponding naphthalene **11**, k_4, and is trapped by CCl_4, k_5. In any case, C_2Cl_6 and Me_2GeCl_2 are found in quantitative yields. (Consequently, in CCl_3Br mainly Me_2GeBr_2 is found, and no Me_2GeCl_2.) For the latter, an alternative way passing an insertion[12] had to be discussed:

$$Me_2Ge\colon + CCl_4 \longrightarrow Cl\text{-}Me_2Ge\text{-}CCl_3 \xrightarrow{\Delta} Me_2GeCl_2 + {:}CCl_2$$

This could, however, be excluded because no 7,7-dichloronorcarane is formed by excess cyclohexene, hence no dichloro carbene is present. In CCl_4 no polygermane is found. Therefore, **10** is scavanged quantitatively[14], k_3, and germylene formation, k_2, is suppressed fully under these conditions.

Additional evidence for the existence of the biradical **10** comes from the enhancement of the thermolysis by replacement of the methyl groups in position 7 by phenyl groups in **9**. The partial double bond character of the C-Ge-bond, as shown by other examples[13], apparently contributes to the stabilization of **10** and enhances therefore the degradation of **9**, see table 1. Analogue influences have been demonstrated earlier in the case of corresponding 7-carbon compounds[2].



Since better stabilization of **10** causes a more rapid degradation of the corresponding 7-germanorbornadienes **3**-**9**, transition states for the splitting, k_1, close to the biradical **10** have to be assumed.

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REFERENCES

1. M. Schriewer, Dissertation Univ. Dortmund, in preparation.
2. Review: R.W. Hoffmann, Angew. Chem. 83, 595 (1971);Angew. Chem.Internat. Edit. Engl. 10, 529 (1971).
3. a) H. Gilman, S.G. Cottis, and W. H. Atwell, J. Am. Chem. Soc. 86, 1596, 5584 (1964); b) G. Märkl, H. Hauptmann, Tetrahedron Lett. 1968, 3257; c) I.G.M. Campbell, R.C. Cookson, M.B. Hocking, A.N. Hughes, J. Chem. Soc. 1965, 2184.
4. Ch. Grugel, W.P. Neumann, and M. Schriewer, Angew. Chem. 91, 577 (1979); Angew. Chem. Internat. Edit. Engl. 10, 529 (1979).
5. K. Kuno, K. Kobayashi, M. Kawanisi, S. Kozima and T. Hitomi, J. Organometal. Chem. 137, 349 (1977).
6. The only derivative knwon hithereto, 7.7-dimethyl-2.3 bis (carboxymethyl)-1,4,5,6-tetraphenyl-7-germanorbornadiene, decomposes even at 0°C: J.G. Zavistoski and J.J. Zuckerman, J. Am. Chem. Soc. 90, 6612 (1968).
7. Compounds 2 have been generated from the corresponding fluoro brom benzene and Mg in THF at 20°C, in the case of Me_4-2 from the dibromo derivative.
8. By means of other arguments it has been shown earlier that carbene formation from norbornadienes takes place also via a two step mechanism[2].
9. Thermolysis of analogue 7-silanorbornadienes also exhibits a two step mechanism: L.W. Groß, B. Mayer and W.P. Neumann, unpublished.
10. The molecule of 6 is bulkier than those of 3-5. Besides, only one way for the formation of a benzyl radical is available, splitting of the bond between C-4 and Ge, diminishing the probability of C-Ge splitting (k_1).
11. Identical with samples prepared by indipendent ways: a) M.E. Volpin, Yu. D. Koreshkov, V.G. Dulova and D.N. Kursanov, Tetrahedron Lett. 18, (1962) 107; b) P. Mazerolles and G. Manuel, Bull. Soc. Chim. Fr. (1966), 327.
12. M. Massol, J. Barrau, and J. Satgé, Inorg. Nucl. Chem. Lett. 7, 895 (1971).
13. a)H. Sakurai, K. Mochida, and M. Kira, J. Organometal. Chem. 124, 235 (1977); b) Review: L.E. Gusel'nikov and N.S. Nametkin, Chem. Rev. 79, 529 (1979).
14. M. Lehnig, F. Werner, and W.P. Neumann, J. Organometal. Chem. 97, 375 (1975).

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