

7-SILANORBORNADIENES AND THEIR THERMAL CYCLOELIMINATIONS

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Summary: Thermolysis of 22 7-silanorbornadienes (18 of them are new) forming silylene R_2Si and the corresponding benzene derivatives is shown to be a two step reaction enhanced by higher stability of the intermediate biradical. Evidence for the latter is given by trapping and ESR experiments.

7-Silanorbornadienes² have been used as excellent thermal silylene sources. A one step mechanism has been considered in the literature³ and is allowed by orbital symmetry. But this is no indication for the reality of this process and has been regarded with caution recently⁴ since interference by a trifluoromethyl group prevented thermal silylene formation⁵ and pointed in this case to a biradical mechanism. No clear general interdependence of structural details of 7-silanorbornadienes and their thermal stability is known hitherto⁶. Some decompose at 300°C⁶, others at -50°C.

Since we gained some experience with 7-stanna⁷ and 7-germanorborn(adi)enes⁸ and their use for the generation of the heavier carbene analogues R_2Sn and R_2Ge , we prepared 17 new 7-silanorbornadienes and 1 aza analogue by Diels-Alder reactions, see tables 1+2, in order to reinvestigate the mechanism of the thermal cycloelimination, and to establish structural details important for the thermal stability.

The benzo derivatives 1 and 2 exhibit a quite different thermal stability depending on the nature of R^1-R^5 . They decompose below 0°C if R^1, R^4 , and R^5 are H, see 1a, c, d, giving the naphthalene and a Me_2Si polymer. Methyl or t-butyl groups in the remote position R^2 and R^3 , see 1c, d, do not alter this behaviour. But, methylation in the positions R^1 or R^1+R^4 , see 1b, e, f, produces a striking thermal stability even at 130°C and above. Since methyl groups can be regarded as chemically inert here, only steric influences can be taken into consideration for this effect. Things become meaningful, we think, only if one considers the rotation of the phenyl groups at C-1 and C-4. If R^1 or/and R^4 is methyl the rotation of the neighbouring phenyl groups at C-1 or/and C-4 is strongly hindered, the latter is more or less rigidly fixed into a position vertical

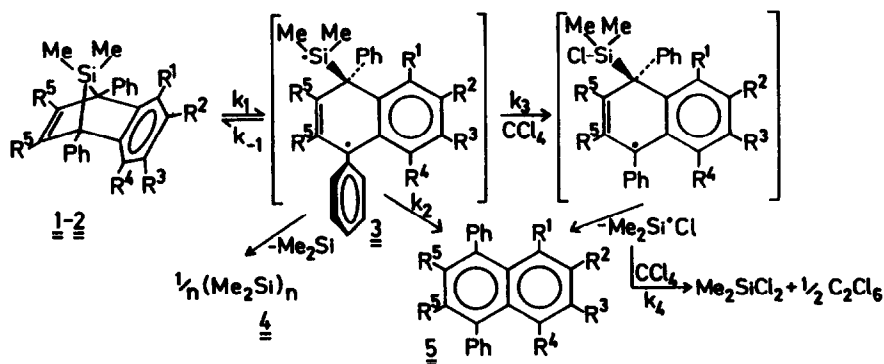
to the basic ring of the norbornadiene. The same effect is observed if the two H at C-5 and C-6 are replaced by the bulky phenyl rings, see 2a-f. Again, the thermal stability of the 7-silanorbornadiene is raised to above 220°C.

Table 1: 2,3-Benzo-7-silanorbornadienes 1, 2.

| | R ⁵ | R ¹ | R ² | R ³ | R ⁴ | Me ¹ | Me ² | R ¹ | R ² | R ³ | R ⁴ | Ph | mp°C | yield % |
|-----------|----------------|----------------|----------------|----------------|----------------|--|-----------------|----------------|----------------|----------------|----------------|-----|---------|---------|
| <u>1a</u> | H | H | H | H | H | 0.04 | 0.14 | - | - | - | - | - | Decomp. | <0°C |
| <u>1b</u> | H | Me | H | H | H | 0.10 | 0.18 | 1.7 | ← 6.7 | - 7.3 | → | | 151 | 54 |
| <u>1c</u> | H | H | Me | H | H | Decomp. <0°C. Only degradation products found. | | | | | | | | |
| <u>1d</u> | H | H | Me | Me | H | | | | | | | | | |
| <u>1e</u> | H | Me | Me | H | Me | -0.10 | 0.16 | 1.6 | 2.13 | 6.5 | 1.6 | 7.3 | 128 | 58 |
| <u>1f</u> | H | Me | Me | Me | Me | -0.18 | 0.05 | 1.6 | 2.05 | 2.05 | 1.6 | 7.3 | 199 | 50 |
| <u>2a</u> | Ph | H | H | H | H | -0.02 | 0.62 | ← | 6.4 | - 7.5 | → | | 234 | 75 |
| <u>2b</u> | Ph | Me | H | H | H | 0.00 | 0.62 | 2.33 | ← 6.2 | - 7.3 | → | | 212 | 65 |
| <u>2c</u> | Ph | H | Me | H | H | 0.00 | 0.61 | - | 2.37 | ← 6.5 | - 7.4 | → | 119 | 58 |
| <u>2d</u> | Ph | H | Me | Me | H | 0.00 | 0.58 | - | 2.26 | 2.26 | 6.4-7.3 | | 189 | 50 |
| <u>2e</u> | Ph | Me | Me | H | Me | -0.06 | 0.28 | 2.0 | 2.20 | - | 1.65 | 6.8 | 178 | 34 |
| <u>2f</u> | Ph | Me | Me | Me | Me | -0.06 | 0.16 | 1.94 | 2.24 | 2.24 | 1.94 | 6.9 | 223 | 51 |

All new compounds have been prepared in a 3 mmol scale at 20°C in THF and identified by mass spectrometry and NMR. ¹H-NMR data are given in δ(ppm) against TMS as internal standard. Yields are given for isolated compounds.

The only way we see to explain these new facts in accordance with Barton's⁵ and Maruca's⁶ findings, and the discussion by Gaspar⁴ is to assume an intermediate biradical 3, k_1 , i.e. a two step mechanism $k_1 + k_2$ for the splitting off of a silylene from the 7-silanorbornadiene, giving lastly the silylene polymer 4 and the corresponding naphthalene 5:

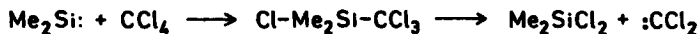


The "biradical mechanism" and the "silylene mechanism", therefore, are not contradictory, but the latter follows the former. Formation of the biradical 3, k_1 , is rate determining. There is strong analogy to carbene formation from norbornadienes⁹ and to germylene formation from 7-germanorbornadienes⁸. Both

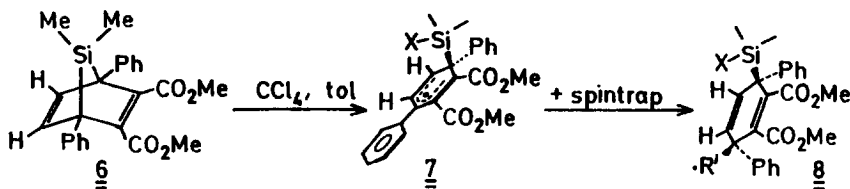
are two step reactions.

The biradical 3 is stabilised - and its lifetime should be prolonged - especially if the phenyl rings at C-1 and/or C-4 can take a position coplanar with the basic ring of the norbornadiene system, k_1 is enhanced. Then, trapping of 3 is possible, e.g. with CCl_4 , k_3 , giving lastly Me_2SiCl_2 and C_2Cl_6 , k_4 , found in high yields (GLC).

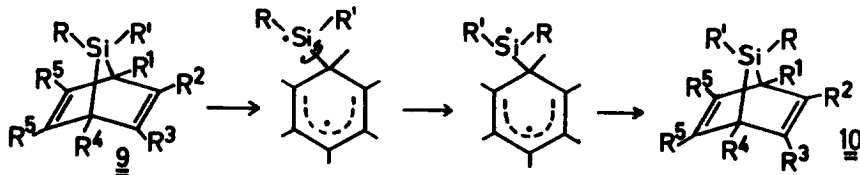
An alternative way, passing a free silylene and its insertion, can be excluded here, since no CCl_2 could be identified by excess cyclohexene:



Neither ESR nor CIDNP (generated by the back reaction of 3, k_{-1}) signals could be detected during thermolysis or photolysis of several 7-silanorbornadienes, e.g. 2a or 11 in benzene, diphenyl ether, or CCl_4 . This might be due to a lifetime of the corresponding biradicals 3 too short for ESR observation or by a permanent concentration too low. In order to gain higher radical concentrations (if there are any) we thermolysed 6 decomposing rapidly even at 28°C in CCl_4 or toluene. We observed a doublet split into a quintet. No Si centered radical can be detected. All data are in agreement with a cyclohexadienyl radical 7 ($\text{X} = \text{Cl}, \text{H}$) which can be assumed as the trapping product of the biradical 3 by means of the solvent, CCl_4 or toluene. This is confirmed by using the spin-traps $\text{MeN}(\text{O})=\text{CHPh}$ or $\text{tBuN}(\text{O})=\text{CHPh}$, both producing ESR spectra best interpreted as those of trapped cyclohexadienyl radicals 8.



CCl_4 enhances the thermolysis of 6 presumably by trapping the biradical 3, k_3 , thus preventing the back reaction k_{-1} . Another and more direct evidence for the existence of an intermediate between the 7-silanorbornadiene and the corresponding benzene + silylene would be the isomerization of a product with different substituents in position 7:



So we prepared 4 new 7-silanorbornadienes 9a-d, see table 2. In all cases the Diels-Alder synthesis was stereoselective, the different dienophiles attacking in the case of $\text{R} = \text{Me}$, $\text{R}' = \text{Cl}$ from the Cl-side, in the case of $\text{R} = \text{Ph}$, $\text{R}' = \text{Me}$ from the sterically less hindered Me-side. In every case, only one isomer was formed indicated by the Me-Si NMR value, see table 2. Both, heating 9a-c in

benzene or CCl_4 at 50°C or irradiation at 20°C , the latter also with 9d, produced the other isomer 10a-d. The original Me-Si NMR peak disappeared, and nearby a new one appeared, see table 2. No measurable retro-Diels-Alder reaction occurred under these conditions as checked by NMR and mass spectrometry. This proves that, prior to the final scission k_2 , a reversible one-bond breaking k_1 , k_{-1} takes place at relatively low temperatures.

Table 2: 7-Silanorbornadienes 6, 9-12

| | R | R' | R ¹ | R ² | R ³ | R ⁴ | R ⁵ | R | R' | R ² | R ³ | R ¹ | R ⁴ | R ⁵ | mp °C | yield % |
|------------|----|----|----------------|--------------------|--------------------|----------------|----------------|-------|-------|----------------|----------------|----------------|----------------|----------------|----------|-----------|
| <u>6</u> | Me | Me | Ph | CO ₂ Me | CO ₂ Me | Ph | H | 0.03 | 0.6 | 3.6 | 3.6 | ← 6.4-7.3 → | | | - | - |
| <u>9a</u> | Me | Cl | Ph | CO ₂ Me | CO ₂ Me | Ph | Ph | 0.73 | - | 3.6 | 3.6 | 6.4-7.7 | | | 178 | 37 |
| <u>9b</u> | Me | Cl | Ph | H | Ph | Ph | Ph | 0.70 | - | ← 6.3-7.2 → | | | | | 180 | 80 |
| <u>9c</u> | Ph | Me | Ph | CO ₂ Me | CO ₂ Me | Ph | Ph | * | 0.71 | 3.6 | 3.6 | 6.4-7.6 | | | 184 | 90 |
| <u>9d</u> | Ph | Me | Ph | H | Ph | Ph | Ph | * | 0.66 | ← 6.3-7.9 → | | | | | 207 | 76 |
| <u>10a</u> | Cl | Me | Ph | CO ₂ Me | CO ₂ Me | Ph | Ph | - | 0.08 | 3.61 | 3.61 | 6.4-7.6 | | | 179 | not detd. |
| <u>10b</u> | Cl | Me | Ph | H | Ph | Ph | Ph | - | 0.07 | ← 6.3-7.2 | | | | | 182 | not detd. |
| <u>10c</u> | Me | Ph | Ph | CO ₂ Me | CO ₂ Me | Ph | Ph | 1.06 | * | 3.36 | 3.36 | 6.4-7.6 | | | 210 | not detd. |
| <u>10d</u> | Me | Ph | Ph | H | Ph | Ph | Ph | 1.01 | | ← 6.3-7.9 → | | | | | 224 | not detd. |
| <u>11a</u> | Me | Me | H | Benzo | H | ** | | -0.16 | -0.16 | 6.77-7.27 | 3.75 | 3.75 | | * | 106 | 9 |
| <u>11b</u> | Me | Me | H | Benzo | Me | ** | | -0.25 | -0.25 | 6.8 | -7.3 | 3.6 | 1.79 | * | 150 | 2 |

*see aromatic protons

**benzo

Kinetic data¹⁰ support strongly the interdependence between structural details and thermal stability discussed above.

All new compounds 1,2,9,11 have been identified by mass spectrometry and ¹H-NMR δ (ppm). Yields are given (tables 1,2) for isolated pure compounds.

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References:

1. B. Mayer, Dissertation Univ. Dortmund, in preparation.
2. H. Gilman, S.G. Cottis, and W.H. Atwell, *J. Am. Chem. Soc.* **86**, 1956, 5584(1964).
3. P.P. Gaspar in W. Kirmse, *Carbene Chemistry*, Academic Press, New York, (1971).
4. P.P. Gaspar in M. Jones and R.A. Moss, *Reactive Intermediates*, 229 (1978).
5. T.J. Barton, J.C. Wittiac and C.L. Jutosh, *J. Am. Chem. Soc.* **94**, 6229(1972).
6. R. Maruca, R. Fischer, L. Roseman, and A. Gehring, *J. Organomet. Chem.* **49**, 139(1973).
7. W.P. Neumann, Ch. Grugel, and M. Schriewer, *Angew. Chem. Intern. Edit.* **18**, 543(1979).
8. W.P. Neumann and M. Schriewer, *Tetrahedron Letters*, 3273 (1980).
9. R.W. Hoffmann, *Angew. Chem.* **83**, 595(1971); *Angew. Chem. Internat. Edit.* **10**, 529(1971).
10. L.W. Groß, Diploma Thesis, Univ. Dortmund 1980.

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