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THERMAL AND PHOTOCHEMICAL BEHAVIOR OF 2-SILA- AND GERMA-CYCLOPENTANONE[1]

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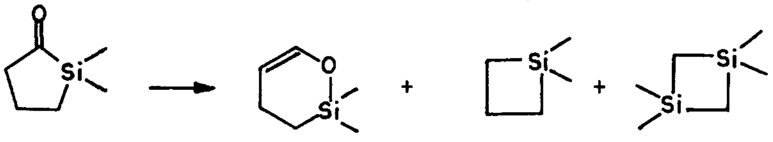
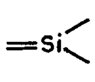
Abstract: Pyrolysis and photolysis of the first examples of five-membered ring sila and germa ketones 2 is reported. The photolysis of 2a leading to a cyclic acetal via a siloxycarbene is contrasted to the behavior of the germa analog 2b which gives ring cleavage via a ketene intermediate.

Acylsilanes exhibit a fascinating chemistry largely unravelled by Brook and coworkers.[2] The six membered ring silaketone 1 has been shown to rearrange photochemically or thermally to a ring enlarged siloxycarbene but the unavailability of the five-membered ring analog or of corresponding cyclic germyl analogs has prohibited a comparison. Our recent synthesis of 2-sila and 2-germacyclopentanone 2a and 2b via lithiated 1-methoxybutadiene[1] now permits a comparative study of the thermal and photo-chemistry of these cyclic metallo ketones.

Vapor phase pyrolysis of 2a at 550° led to a 50:50 mixture of products 3 and 4 in 60-80% yield. While 3 apparently arises by Si to O migration (Brook rearrangement)[2] with a subsequent 1,2-hydride shift of the resulting siloxy carbene (see 9), the silacyclobutane 4 is the result of a decarbonylation with C-Si bond formation. Normally only rearrangement rather than decarbonylation is observed in thermolysis of acylsilanes.[3]



2a 3 4 5



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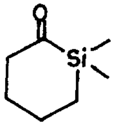

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At higher temperatures disilacyclobutane 5 was identified as a product as well. The distribution of products (detected by gc) as a function of pyrolysis tube temperature is illustrated in Fig. 1 (total yields 60-80%) and revealed that the disila product 5 had formed mainly at the expense of 4. This is consistent with a thermolysis of 4 to silaalkene 6, which then dimerizes to 5, a process that is well documented.[4] Indeed, when 4 was pyrolyzed at 680°C, 5 was the sole volatile product in over 90% yield. Thermal decomposition of the germyl analog 2b did not lead to volatile products corresponding to 3-5.

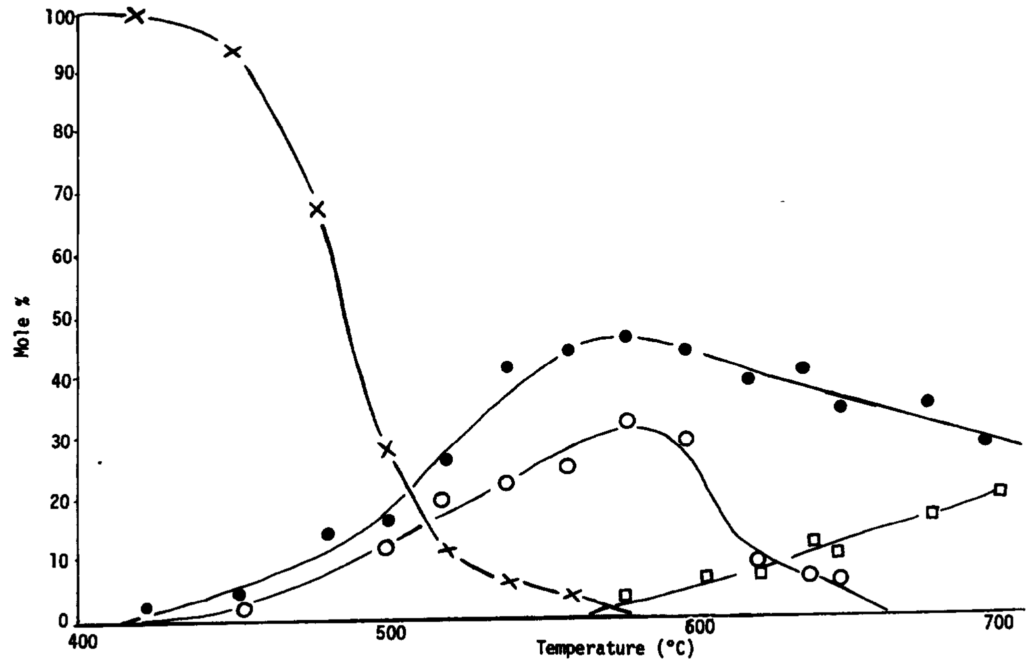
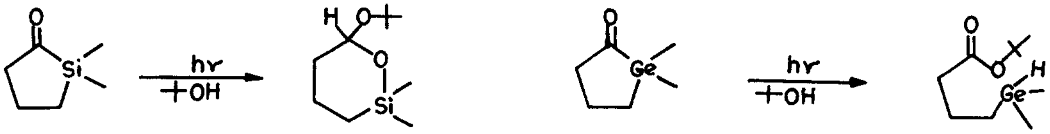


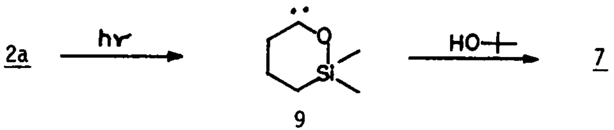
FIGURE I. THERMAL DECOMPOSITION OF 32a AT 1 MILLITORR (INITIAL) FROM 400°C to 700°C. 2a : (× × ×); 2: (● ● ●); 4:(○ ○ ○); 5: (□ □ □)

Photolysis of 1,1-dimethyl-1-sila-2-cyclopentanone (2a) in 0.05-0.2 M t-butyl alcohol led to complete disappearance of 2a and isolation by preparative gc of cyclic acetal 7 in 50% yield Under similar conditions, irradiation of the germaketone 2b (to ca. 75% completion) led to t-butyl-2-methyl-2-germa-6-hexanoate (8) in 40% yield.[5] Minor amounts (ca. 10-15%) of other products were observed but were not identified. Irradiation to complete disappearance of 2b lowered the overall yield of 8 under these conditions.



2a 7 2b 8

While photolysis of both 2a and 2b lead to solvent incorporation, the adducts differed considerably in structure. The formation of 7 from 2a can be envisaged as arising from attack of solvent on a cyclic siloxycarbene (9) in analogy to the 2-silacyclohexanone 1 which gave a seven membered ring acetal on photolysis in alcohol, and therefore resembles the pyrolysis process.



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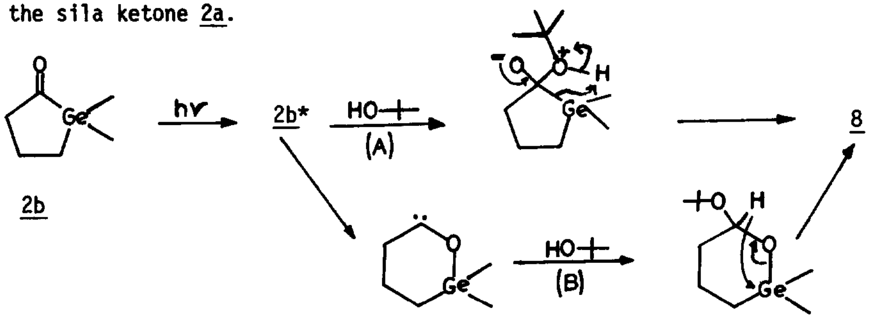
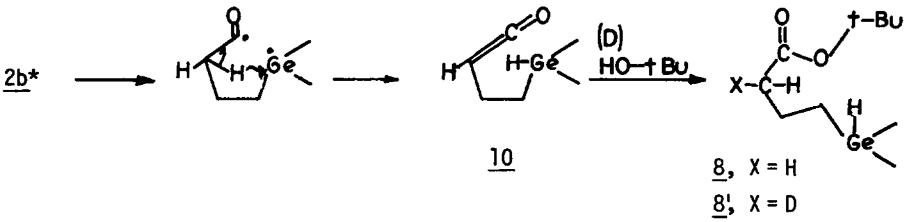
One of several pathways could be responsible for the formation of the ester product (8) from the photolysis of 2b. In principle, attack of solvent on the excited ketone could lead to 8 prior (A) or after (B) a rearrangement process (Scheme I). Process B would be analogous to the behavior of the sila ketone 2a.

Scheme I



These pathways have the common feature that the hydroxylic proton in the solvent terminates as the germanium-bound proton in the product (8). An alternative pathway involves hydrogen abstraction after acylgermanium bond cleavage leading to a ketene intermediate (10) which on addition of alcohol produces 8 (Scheme II).

Scheme II



This process is well known in the photochemistry of substituted cyclopentanones.[6] The hydroxylic proton of the solvent terminates in the position alpha to the ester moiety by this pathway. When we carried out the reaction in t-butyl alcohol-OD the deuteron is found alpha to the ester function in the product 8'.[7] Incorporation of deuteron into other positions was not observed. Hence, it is the ketene pathway (Scheme II) which is most likely to be responsible for the formation of 8 from 2b. Thus, whereas acylsilanes appear to rearrange efficiently to siloxycarbenes, the analogous process for acylgermanes remains to be documented.

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References and Notes

1. For the previous paper see J. A. Soderquist and A. Hassner, J. Org. Chem., 45, in press (1980)

2. A. G. Brook, Accts. Chem. Res., 7, 77 (1974) and references cited therein.

3. W. Ando and A. Sakaguchi, J. Organometal. Chem., 133, 219 (1977).

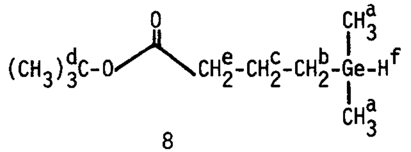
4. (a) M. C.Flowers and L. E. Gusel'nikov, J. Chem. Soc. B, 419 (1968).
   (b) T. J. Barton, G. Marquardt and J. A. Kilgour, J. Organometal. Chem., 85, 317 (1975).
   (c) R. F. Cunico, ibid., 83, 65 (1974).

5. The structure of 7 was determined from the following spectroscopic data:

   Nmr (CCl_4): δ = 0.04 (s, 3H); 0.16 (s, 3H); 0.55 (m, 2H); 1.20 (s, 9H); 1.40-2.20 (m, 4H); 5.03 (m, 1H). Ir (tf): 2970 (s); 2930 (s); 2875 (m); 1735 (w); 1475 (sh); 1460 (m); 1435 (m); 1395 (s); 1365 (s); 1255 (s); 1200 (s); 1155, 1140, 1115 (s); 1070 (m); 1040, 1015 (s); 985 (s); 950 (s); 915 (s); 840 (s); 798 (s); 780 (m); 735 (w); 705 (w); 680 (m). ms: m/e = 202 (8); 1827 (2); 174 (2); 159 (8); 147 (43); 146 (35); 145 (20); 131 (56); 129 (83); 118 (89); 103 (100); 101 (53); 77 (19); 75 (32); 73 (27); 59 (12); 58 (9); 57 (69); 43 (11).

   The structure of 8 was elucidated from:

   Nmr (CCl_4): δ = 0.22 (d, 6H), J = 3.0 Hz; 0.79 (m, 2H); 1.1-1.9 (m, 2H); 1.42 (s, 9H); 2.5 (t, 2H), J = 6.6 Hz; 3.80 (m, 1H) order: a, b, c, d, e, f, see below).



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   Treatment of 8 with $Eu(fod)_3$ gave $\Delta\delta$'s: e > d ∿ c > b > f > a. Double resonance experiments together with $Eu(fod)_3$ allowed the following coupling constants to be measured. $J_{af} = J_{bf} = 3.0$ Hz; $J_{bc} = 8.4$ Hz; $J_{ce} = 6.6$ Hz.

   Ir (tf): 2980 (s); 2940, 2920 (s); 2030 (s); 1730 (s); 1480, 1455, 1420 (w); 1395 (m); 1370 (s); 1315 (w); 1290 (w); 1270, 1260, 1250, 1220 (m); 1170, 1160 (bs); 1125 (bm); 1055, 1040, 1025, 1110, 985, 975, 950, 905, 890 (w); 845, 835 (bs); 785, 760, 730 (w). The relative intensities of the 2980, 2030, and 1730 cm^{-1} peaks are ca. 1:1:2. ms: m/e = 248 (0); 190 (42); 175 (97); 147 (47); 121 (74); 105 (37); 71 (35); 57 (100); 41 (26). For peaks of 105 or larger only the peaks containing the Ge-74 isotope are given.

6. (a) G. Quinkert, B. Wegmund and E. Blanke, Tetrahedron Lett., 221 (1962).
   (b) J. D. Coyle, J. Chem. Soc. B., 1736 (1971).
   (c) See also "Excited States in Organic Chemistry," J. A. Barltrop and J. D. Doyle, John Wiley and Sons, New York (1975).

7. In $DOBu^t$ solvent the product 8'showed ir absorbances virtually identical to the non-deuterated product. The CH, GeH and C=O absorbance cited above had the same relative intensities as for 8. However, the ms of 8' was different from 8 in the 191, 176, 148 and 72 replaced the peaks at 190,147 and 71 absorbances. The unaffected absorbances at m/e = 121, 105, 57 and 41 seem likely to be due to the Me_2GeOH^+, Me_2GeH^+, Me_3C^+ and $C_3H_5^+$ formulations which do not contain deuterium label. The 360 MHz spectrum of 8' is $CDCl_3$ (δ = 0.21 (d, 6H); J = 3.3 Hz; 3.81 (m, 1H); J = 8.4 Hz, J = 2.9 Hz; 1.45 (s, 9H); 167 (m, 2H); 2.24 (t, 1H); J = 7.4 Hz, 3.81 (m, 1H) J = 3.3 Hz) revealed that this label was alpha to the ester in the e position of 8.

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