

## The First Reversible Thermal Dissociation of Digermanes $R_3Ge-GeR_3$ giving Germyl Radicals $R_3Ge\cdot$ , and of Disilanes $R_3Si-SiR_3$ giving Silyl Radicals $R_3Si\cdot$

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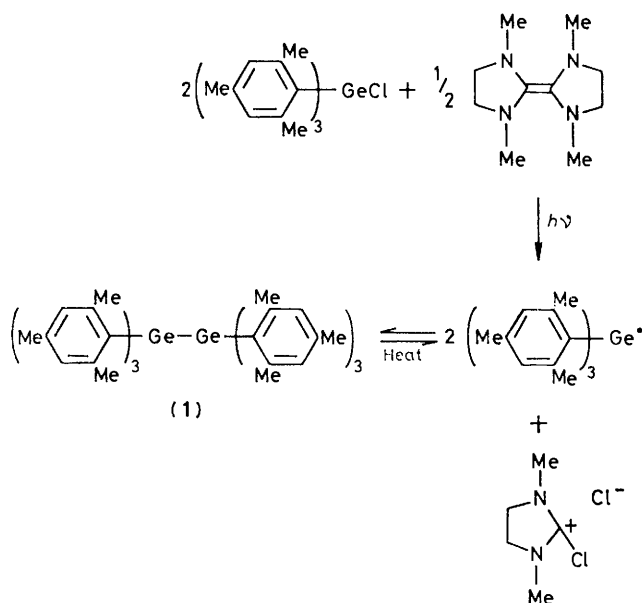
The Ge-Ge bond in hexamesityldigermane dissociates reversibly between  $-12$  and  $+53$  °C ( $\Delta H_{diss.}$   $87 \pm 8$  kJ/mol), and the Si-Si bond in hexamesityldisilane behaves analogously between  $-60$  and  $-20$  °C; above these temperatures, irreversible reactions of the radicals occur.

The carbon-carbon bond can dissociate radically by the sole influence of the steric effect of bulky substituents.<sup>1</sup> Since similar behaviour has been found recently for the analogous tin-tin bond even at room temperature,<sup>2</sup> it was of special interest to investigate the corresponding Ge-Ge and Si-Si bonds in this respect.

From our experience with distannanes<sup>2</sup> the mesityl substituent was thought to be bulky enough to cause dissociation. In order to prepare the unknown hexamesityldigermane (1) we used trimesitylgermyl chloride and Lappert's procedure<sup>3</sup> but only succeeded when we irradiated the reaction mixture at  $-70$  °C in toluene (TQ 150 high-pressure quartz lamp (Scheme 1). Compound (1) could be isolated and purified by evaporating the light petroleum solution at  $20$  °C giving crystals, decomp.  $142$  °C, and was identified by  $^1H$  n.m.r. and i.r. spectroscopy, and elemental analysis. It dissociates reversibly, in decalin or toluene solutions of the pure compound, between  $-12$  and  $+53$  °C giving the known e.s.r. signal of the trimesitylgermyl radical.<sup>3,4</sup> Above  $53$  °C irreversible degradation occurs giving polymers, compounds containing Ge-H groups, and other compounds. From the e.s.r. intensity of the radical  $\Delta H_{diss.}$  (Ge-Ge) was found to be  $87 \pm 8$  kJ/mol. For an unstrained Ge-Ge bond, e.g. in  $Ph_3Ge-GePh_3$ , values of about  $243$  kJ/mol have been observed.<sup>5</sup>

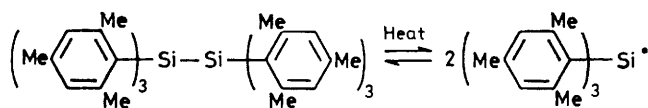
We were unable to prepare (1) by the usual methods from the triarylgermyl hydride with  $(Bu^tO)_2$  photolytically or with azobisisobutyronitrile, from the methoxide with  $(Me_3Si)_2Hg$ , from the chloride with a Na/K or Na/Hg alloy, or from the aryl bromide with  $GeI_2$  and 1,2-dibromoethane.<sup>6</sup>

Hexakis-(2,4,6-triethylphenyl)digermane could also be prepared as above (only in solution hitherto). It dissociates



Scheme 1

reversibly between  $-80$  and  $+10$  °C (above  $10$  °C irreversible degradation occurs), and from the e.s.r. spectrum (singlet,  $g$  2.0080)  $\Delta H_{diss.}$  (Ge-Ge) is  $44 \pm 8$  kJ/mol. Both the temperature range and  $\Delta H_{diss.}$  indicate the stronger steric strain in this digermane caused by the bulkier ethyl-substituted aryl residues.



Scheme 2

These results encouraged us to study the silicon analogue but many more side reactions of silyl radicals with aromatic compounds had to be taken into account<sup>7</sup> besides the recombination of silyl radicals. After many unsuccessful attempts<sup>8</sup> we generated the trimesitylsilyl radical from pure trimesitylsilyl chloride following Lappert's procedure<sup>3</sup> in principle, but irradiating the mixture in toluene at  $-80^{\circ}\text{C}$ .<sup>†</sup> At  $-60^{\circ}\text{C}$  the e.s.r. spectrum of the radical can be recorded. It is nicely resolved (at least 100 lines);  $g$  2.0035 (2.0027<sup>3</sup>),  $a_{\text{CH}_3}^{\text{H}}$  0.82,  $a_m^{\text{H}}$  0.13 G. Above  $-20^{\circ}\text{C}$  a rapid and irreversible decay occurs giving compounds containing Si-H groups, polymeric material, and other products (detected by i.r. and  $^1\text{H}$  n.m.r. spectroscopy). Between  $-60$  and  $-35^{\circ}\text{C}$  the e.s.r. intensity depends on the temperature strongly and reversibly. The only reason we can see for this is the equilibrium in Scheme 2.<sup>†</sup>

<sup>†</sup> In co-operation with W. Dummer in this laboratory. Isolation of the disilane is in progress.

Mesomerism contributes to some extent to the stability of the radical as can be seen from the  $a$  values; however, mainly steric hindrance in the disilane is responsible for its spontaneous and reversible dissociation even at  $-60^{\circ}\text{C}$ .

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