

Intramolecular $[2_\pi + 2_\pi]$ Photocycloaddition of Group 14 Organometallic Compounds Bearing a Styrene Chromophore: A Route to Sila- and Germa-cyclophanes and Spiro Compounds

Kazuhisa Nakanishi, Kazuhiko Mizuno,* and Yoshio Otsuji*

Department of Applied Chemistry, College of Engineering, University of Osaka Prefecture, Sakai, Osaka 591, Japan

Irradiation of bis- and tetrakis-(4-vinylbenzyl)silanes and their germane analogue caused efficient intramolecular $[2_\pi + 2_\pi]$ cycloaddition, to give $[2.3]$ sila- and germa-cyclophanes and also sila- and germa-spiro compounds.

Intramolecular photocycloaddition of styrene derivatives has been widely investigated for mechanistic and synthetic purposes.¹ However, little is known about the intramolecular photocycloaddition of organometallic compounds, although the synthesis of metallacyclophanes and metallaspiro compounds might well be possible by such a route. We now report an efficient intramolecular $[2_\pi + 2_\pi]$ photocycloaddition of bis- and tetrakis-(4-vinylbenzyl)silanes and of a germane analogue.

The starting group 14 organometallic compounds, **1a-d**, **3a-c**, **6**, and **7**, were prepared by Grignard coupling of 4-chloromethylstyrene with appropriate Si-, Ge-, and Sn-compounds.

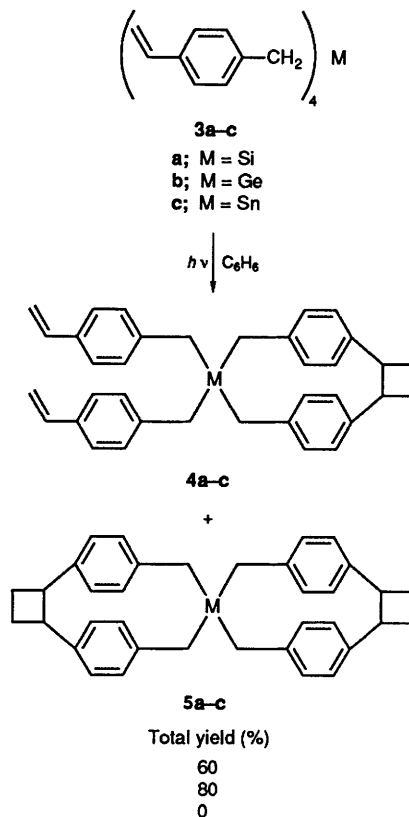
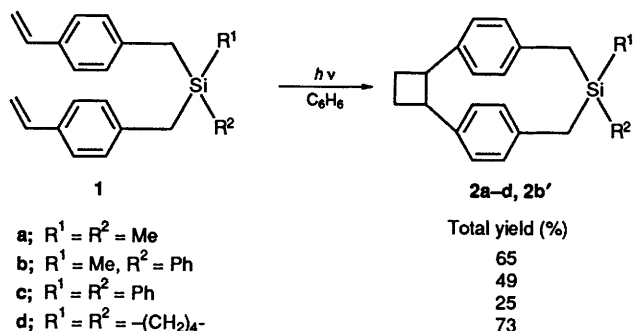
Irradiation of **1a** with a 300 W high-pressure mercury lamp through a Pyrex filter under a nitrogen atmosphere for 14 h gave the $[2_\pi + 2_\pi]$ cycloadduct **2a**, m.p. 100–102 °C, as the sole isolable product in 65% isolated yield. Similarly, the photoreaction of other bis(4-vinylbenzyl)silanes, **1b-d**, afforded the corresponding cycloadducts, **2b-d**. In the case of **1b**, the stereoisomer **2b'** was also obtained. These products were isolated by column chromatography on silica gel and their structures were established on the basis of their spectral properties (mainly by ¹H NMR) and elemental analyses.

The ¹H NMR spectrum of **2a** exhibited two kinds of AB quartet due to aromatic protons at δ 6.33 and 6.58. These signals were unchanged in the temperature range of –60 to 80 °C. The *cis*-configuration of substituents on the cyclobutane ring was confirmed by the characteristic methine proton signals at δ 4.06.^{2,†}

The photoreactions proceeded efficiently in both benzene and acetonitrile. They were sensitised by triplet sensitisers such as acetophenone ($E_T = 308$ kJ mol⁻¹) and benzophenone ($E_T = 287$ kJ mol⁻¹), but were not sensitised by Michler's ketone ($E_T = 259$ kJ mol⁻¹).³ The formation of **2a** was not quenched by the addition of a triplet quencher such as 2-methylbuta-1,3-diene and O₂.

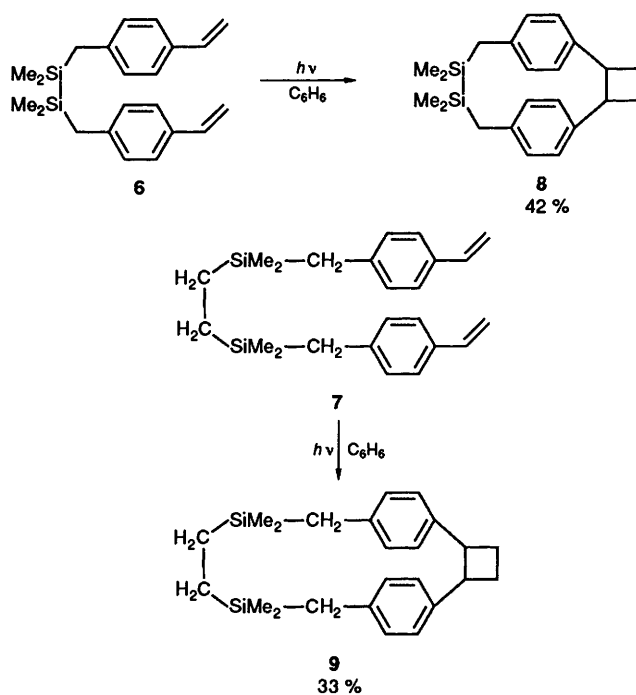
Irradiation of tetrakis(4-vinylbenzyl)silane (**3a**) and its germane analogue **3b** in benzene afforded respectively a mixture of **4a** and **5a** and a mixture of **4b** and **5b** in good yields. Irradiation of isolated **4a** and **4b** gave the spiro compounds **5a** and **5b**, respectively. In contrast, the photoreaction of the organotin compound **3c** failed to give **4c** and **5c**, only insoluble polymeric material being obtained.

The photoreactions of **6** and **7** in benzene gave **8** and **9**, respectively, along with small amounts of polymeric materials.



† Spectral properties of *cis*- and *trans*-1,2-bis(4-trimethylsilylmethylphenyl)cyclobutanes: *cis* isomer δ (270 MHz $CDCl_3$) –0.09 (s, 18 H), 1.91 (s, 4 H), 2.38–2.41 (m, 4 H), 3.88–3.93 (m, 2 H) and 6.72 (ABq, 8 H, J Hz: 8.2); *trans* isomer δ (270 MHz, $CDCl_3$) –0.11 (s, 18 H), 1.94 (m, 4 H), 1.98–2.34 (m, 4 H), 3.42–3.54 (m, 2 H) and 7.01 (ABq, 8 H, J Hz: 8.1).

The fluorescent light intensities of **1a** and **3a** were considerably weaker than the intensity of fluorescence of 4-trimethylsilylmethylstyrene. This is due to intramolecular quenching in the former compounds. However, in these compounds no



excimer emission between two styrene chromophores was observed.

The intramolecular $[2_\pi + 2_\pi]$ photocycloaddition of group 14 organometallic compounds can occur *via* both singlet and triplet states of their alkene moieties, depending on the reaction environment. In the direct photoreaction, the reaction proceeds

via a nonemissive, intramolecular singlet excimer. In contrast, in the triplet-sensitised photoreaction, the reaction proceeds *via* an excited triplet state.

Experimental

Typical Procedure for $[2_\pi + 2_\pi]$ Photocycloaddition of Dimethylbis(4-vinylbenzyl)silane (1a**).—**A solution of **1a** (250 mg, 0.86 mmol) in anhydrous benzene (76 ml) was irradiated for 14 h with a 300 W high-pressure mercury lamp through a Pyrex filter under a nitrogen atmosphere. The solvent was removed and the residue was chromatographed on silica gel. Elution with hexane gave **2a** (162 mg, 65%). Recrystallisation of this from ethanol gave an analytical pure sample: m.p. 100–102 °C (Found: C, 82.3; H, 8.4%; M^+ , 292. $C_{20}H_{24}Si$ requires C, 82.12; H, 8.27%; M^+ , 292); $\delta_H(CDCl_3)$ 0.26 (3 H, s, CH_3), 0.28 (3 H, s, CH_3), 2.44–2.52 (4 H, m, CH_2), 4.04–4.08 (2 H, m, CH), 6.33 (4 H, ABq, $\Delta\nu$ 62 Hz, J 8 Hz, ArH) and 6.58 (4 H, ABq, $\Delta\nu$ 14 Hz, J 8 Hz, ArH); $\delta_C(CDCl_3)$ –0.33, 25.8, 29.7, 47.1, 128.1, 131.1, 136.6 and 137.5.

References

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