Photochemical Generation of an Intermediate Containing a Silicon-Carbon Double Bond or Its Equivalent from 1,1-Diphenylsilacylobutane

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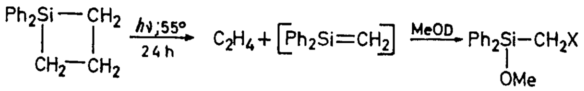
Summary Photolysis of 1,1-diphenylsilacyclobutane at 2537 Å and 55° produces a high yield of the novel intermediate $Ph_2Si{=}CH_2$ which adds MeOD.

ALTHOUGH silacyclobutanes have been studied extensively,[1] their photochemistry has been overlooked. We have found that irradiation of 1,1-diphenylsilacyclobutane (**1**) at 2537 Å produces the unstable intermediate $Ph_2Si{=}CH_2$ (**2**) in very high yield.[2] Intermediate (**2**) could be trapped as $Ph_2(CH_2D)SiOMe$ (**3a**) by carrying out the photolysis in cyclohexane-methan[^{2}H]ol solution.

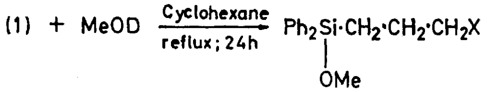
The reaction is 80% complete after 24 h and (**3**) was obtained (*ca.* 95% yield) in high isotopic purity (*ca.* 90%).



(1) (2) (3)

a; X = D (*ca.* 90%)
b; X = H (*ca.* 10%)

It was isolated by preparative g.l.c. and identified by comparison with a known sample of $Ph_2(Me)SiOMe$. The presence of deuterium in (**3a**) was shown by an exact mass measurement on the parent peak (Found: *m/e* 229·1024) and the isotopic purity was estimated by measuring the relative



$$(1) + \text{MeOD} \xrightarrow[\text{reflux; 24h}]{\text{Cyclohexane}} \underset{\text{OMe}}{\text{Ph}_2\text{Si}}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\text{X}$$

(4)

a; X = D (*ca*. 90%)
b; X = H (*ca*. 10%)

areas of the OMe (s, τ 6·51, 3·0 H) and Si–CH_2 (m, τ 9·5, 2·1 H) peaks in the ^{1}H n.m.r. spectrum.

That generation of (**2**) from (**1**) is photo-induced is shown by the different 'dark' reaction in which methan[^{2}H]ol opens the silacyclobutane ring to give (**4**) in a silicon–carbon cleavage reaction expected for an angle-strained Si atom in a small ring.[1] No trace of (**3**) was detected by g.l.c.

The structure of (**4**) was deduced from its ^{1}H n.m.r. spectrum {τ 2·5 (10H, m, Si–Ph), 6·52 (3H, s, Me), and 8·3—9·3 (6·3H, m, $[CH_2]_3$)}, and its parent peak (*m/e* 257). The isotopic purity of (**4**) was measured from the relative peak heights.

We recently reported[3] that pentaphenylmethyldisilane undergoes photochemical dehydrosilylation to give (**2**), triphenylsilane, and some minor products. The reaction described here, however, not only gives higher yields of (**2**) but also is essentially free of side products since ethylene is evolved as a gas. Photolysis of (**1**) is the most convenient low temperature method of generating intermediates like (**2**) yet to be reported.[4] We are currently investigating other silacyclobutanes as sources for different Si=C species as part of our study of the properties of these unusual intermediates.[5]

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[1] For a recent review of the chemistry of silacyclobutanes see R. Damrauer, *Organometallic Chem. Rev.* (*A*), 1972, **8**, 67.

[2] It has been observed that 1,1-dimethylsilacyclobutane yields $Me_2Si{=}CH_2$ when heated to 550° in the vapour phase: M. C. Flowers and L. E. Gusel'nikov, *J. Chem. Soc.* (*B*), 1968, 419. These authors have also reported a vapour-phase addition of water to $Me_2Si{=}CH_2$ to give Me_3SiOH.

[3] P. Boudjouk, J. R. Roberts, C. M. Golino, and L. H. Sommer, *J. Amer. Chem. Soc.*, 1972, **94**, 7926.

[4] For a recent report that the photolysis of a sila-alkene precursor (neat) at 77 or 28 K affords some $Me_2Si{=}CH_2$, and for the finding that only *traces* of 1,1,3,3-tetramethyldisilacyclobutane derived from $Me_2Si{=}CH_2$ were formed by solution photochemistry (cyclohexane; 2537 Å), see T. J. Barton and E. Kline, *J. Organometallic Chem.*, 1972, **42**, C21.

[5] It has been observed that $Me_2Si{=}CH_2$ reacts with heptanal to give oct-1-ene and the cyclic trimer $(Me_2SiO)_3$. This reaction apparently goes through an intermediate containing a silicon–oxygen double bond. D. Roark and L. H. Sommer, submitted for publication.