

RING EXPANSION OF SILACYCLOPENTADIENYL CARBENE TO SILABENZENE

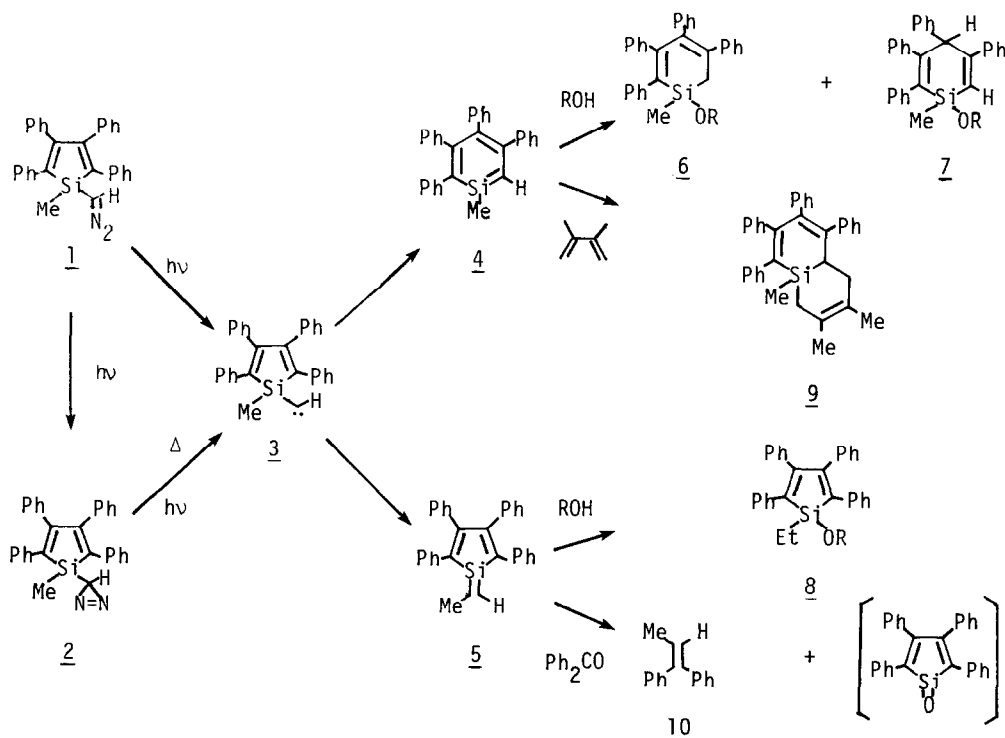
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**Abstract:** Silacyclopentadienylmethylene generated from thermolysis and photolysis of 1-methyl-2,3,4,5-tetraphenylsilacyclopentadienyl-diazomethane and -diazirine rearranges to silabenzene by ring expansion and to 5-silafulvene by 1,2-migration of a methyl group. These intermediates were successfully trapped by alcohols, diene, and ketone.

Intramolecular reactions of  $\alpha$ -silylcarbenes are attractive as potential sources of silenes in particular.<sup>1)</sup> Recently, we reported that intramolecular reaction of 2-silacyclohexadienylidene afforded 6-silafulvene by ring contraction,<sup>2)</sup> and one might expect silacyclopentadienylcarbene to behave similarly to give silabenzene by ring expansion and 5-silafulvene by 1,2-migration of substituent. Several examples of silabenzene intermediates have recently been described.<sup>3)</sup>

We report here strong evidence for the existence of silabenzene obtained by photochemical or thermal fragmentation of 1-methyl-2,3,4,5-tetraphenylsilacyclopentadienyl-diazomethane 1 and -diazirine 2.

Synthesis of 1 was by a modification of the original method of Shioiri.<sup>4)</sup> To the Grignard reagent prepared from 1-chloromethyl-1-methyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene in THF, a slight excess of diphenylphosphorylazide was added at 0°C. Upon usual work up, 1 was obtained in 78% yield as yellow crystals and recrystallized from ether, m.p. 154-156°C (decomp.).<sup>5)</sup>



Photolysis of a benzene solution of 1 with excess methanol gave 1-methyl-1-methoxy-2,3,4,5-tetraphenyl-1-silacyclohexa-2,4,-diene 6 (R=Me) (7%), 1-methyl-1-methoxy-2,3,4,5-tetraphenyl-1-silacyclohexa-2,5-diene 7 (R=Me) (8%), 1-ethyl-1-methoxy-2,3,4,5-tetraphenyl-1-silacyclopentadiene 8 (R=Me) (19%), and the diazirine 2 (48%). Diazirine 2 is relatively stable toward light of wavelength greater than 350 nm. Thus, photolysis of a benzene solution of 1 with filtered light from a high pressure mercury lamp<sup>6)</sup> gave a 64% yield of 2 as greenish yellow crystals which decomposed above 78°C. The products 6 and 7 appear to be derived from methanolysis of 2,3,4,5-tetraphenyl-1-silatoluene 4 which could arise by ring expansion in 1-methyl-2,3,4,5-tetraphenylsila-cyclopentadienylmethylene 3. Compound 8 is the evident product of methanolysis of 6-methyl-1,2,3,4-tetraphenyl-5-silafulvene 5 formed by methyl shift of 3. Similarly, photochemical generation of silabenzene 4 and 5-silafulvene 5 followed by trapping with tert-butanol could lead to 1-methyl-1-tert-butoxy-2,3,4,5-tetraphenyl-1-silacyclohexa-2,4-diene 6 (R=t-Bu) (14%),

1-ethyl-1-tert-butoxy-2,3,4,5-tetraphenyl-1-silacyclopentadiene 8 (R=t-Bu) (15%), and the diazirine 2 (38%). Compound 1 was stable thermally in refluxing benzene, but heating in the presence of anhydrous cupric sulfate resulted in polymeric products.

Diazirine 2 itself was also found to produce the silylcarbene 3 under photochemical condition and led to the products 6 (R=t-Bu) (19%), 8 (R=t-Bu) (28%), and 32% of unreacted 2 in tert-butanol. The reaction was general, as photolysis of 2 with methanol gave similar products.

Alternatively, the diazirine 2 could be decomposed with tert-butanol in a sealed Pyrex tube at ca. 150°C with vigorous reaction and afforded products 6 (R=t-Bu) (31%) and 8 (R=t-Bu) (49%). Similarly, thermolysis with methanol gave 6 (R=Me) (22%), 7 (R=Me) (22%), and 8 (R=Me) (42%).

Further evidences for generation of silabenzene 4 and 5-silafulvene 5 as intermediates come from their reactions with diene and ketone. When 2 was thermally decomposed in 2,3-dimethyl-1,3-butadiene in the Pyrex tube, Diels-Alder adduct 9 was formed in 14% yield. When 2 was heated in the presence of benzophenone, 1,1-diphenylpropene 10 was isolated in 14% yield. This compound can be explained as arising from labile silaoxetane produced by [2+2] reaction of the 5-silafulvene 5 and ketone.<sup>7)</sup>

It is clear from our results that silabenzene and 5-silafulvene are generated from the photolysis and thermolysis of silacyclopentadienyl-diazomethane and -diazirine. Higher yields of these intermediates are obtained from the thermolysis of the diazirine.

#### References and Notes

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- 5) All new compounds were characterized by NMR, IR, mass spectral data, and elemental analysis. Some representative data are as follows.  
 Compound 1 :  $^1\text{H}$  NMR ( $\delta$ ,  $\text{CCl}_4$ ) 0.58 (s, 3H, SiMe), 2.88 (s, 1H,  $\text{CHN}_2$ ), 6.72-7.28 (m, 20H, ArH); IR ( $\text{cm}^{-1}$ , KBr) 2070 ( $=\text{N}_2$ ); Mass m/e 440 ( $\text{M}^+$ ), 412 ( $\text{M}^+-28$ ); Anal. Calcd for  $\text{C}_{30}\text{H}_{24}\text{N}_2\text{Si}$ : C 81.77, H 5.49, N 6.35, Found: C 81.51, H 5.66, N 6.03.  
 Compound 2 :  $^1\text{H}$  NMR ( $\delta$ ,  $\text{CCl}_4$ ) -0.18 (s, 1H,  $\text{CHN}_2$ ), 0.37 (s, 3H, SiMe), 6.76-7.24 (m, 20H, ArH); Mass m/e 440 ( $\text{M}^+$ ), 412 ( $\text{M}^+-28$ ); Anal. Calcd for  $\text{C}_{30}\text{H}_{24}\text{N}_2\text{Si}$ : C 81.77, H 5.49, N 6.35, Found: C 81.89, H 5.58, N 6.13.  
 Compound 6 (R=t-Bu) : white crystals, m.p. 149-150°C;  $^1\text{H}$  NMR ( $\delta$ ,  $\text{CCl}_4$ ) 0.07 (s, 3H, SiMe), 1.31 (s, 9H, O-t-Bu), 2.33 (s, 2H, Si- $\text{CH}_2$ -CPh=), 6.70-7.08 (m, 20H, ArH); IR ( $\text{cm}^{-1}$ , KBr) 1050 (Si-O-C); Mass m/e 486 ( $\text{M}^+$ ); Anal. Calcd for  $\text{C}_{34}\text{H}_{34}\text{OSi}$ : C 83.90, H 7.04, Found: C 83.59, H 7.14.  
 Compound 7 (R=Me) : white crystals, m.p. 167-168°C;  $^1\text{H}$  NMR ( $\delta$ ,  $\text{CCl}_4$ ) 0.56 (s, 3H, SiMe), 3.32 (s, 3H, OMe), 5.10 (s, 1H, =CPh-CHPh-CPh=), 6.30 (s, 1H, Si-CH=CPh), 6.80-7.29 (m, 20H, ArH); IR ( $\text{cm}^{-1}$ , KBr) 1085 (Si-O-C); Mass m/e 444 ( $\text{M}^+$ ); Anal. Calcd for  $\text{C}_{31}\text{H}_{28}\text{OSi}$ : C 83.73, H 6.34, Found: C 83.76, H 6.41.  
 Compound 8 (R=t-Bu) : yellowish green crystals, m.p. 117-118°C;  $^1\text{H}$  NMR ( $\delta$ ,  $\text{CCl}_4$ ) 0.98-1.05 (m, 5H, SiEt), 1.24 (s, 9H, O-t-Bu), 6.75-7.11 (m, 20H, ArH); IR ( $\text{cm}^{-1}$ , KBr) 1045 (Si-O-C); Mass m/e 486 ( $\text{M}^+$ ); Anal. Calcd for  $\text{C}_{34}\text{H}_{34}\text{OSi}$ : C 83.90, H 7.04, Found: C 83.88, H 7.08.
- 6) A methanol solution of phenanthrene (10 g/l) is used as a filtered solution (path length 1 cm).
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