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Thermal and Photochemical Reactions of Benzosilacyclobutenes with Alcohols. Intermediacy of o-Silaquinone Methide in the Photochemical Reactions

Kyung-Tae Kang*, Ung Chan Yoon⁺, Hee Chan Seo, Kwang Nam Kim, Hwan Young Song, and Jae Chul Lee

*Department of Chemical Education,

Department of Chemistry, Pusan National University, Pusan 609-735. Received August 23, 1990

Benzosilacyclobutenes were prepared from the reactions of 1,1-dichlorobenzosilacyclobutene with Grignard reagents or t-butyllithium. In the thermal reactions with alcohols, benzosilacyclobutenes underwent both benzyl-silicon and aryl-silicon bond rupture to yield (dialkyl)alkoxy-o-tolylsilanes and (dialkyl)alkoxybenzylsilanes, respectively. The photochemical reactions, however, produced only the former products *via* o-silaquinone methides.

Introduction

Benzo-condensed four-membered ring systems are of special theoretical and synthetic interest because of their valence isomerization between the strained benzenoid form (1) and the o-quinoidal form (2).



Benzocyclobutenes (1, Z=CR₂)¹, benzazetines (1, Z=NR)², and benzothiete (1, Z=S)³ are well documented.

A benzosilacyclobutene (1, R=SiPh₂) has been prepared in 1964⁴ as the first example of metallabenzocyclobutenes.⁵ However, reports on benzosilacyclobutenes are quite rare.⁶ This may be due to the lack of general synthetic routes to benzosilacyclobutenes. When we began our work, only three benzosilacyclobutenes had been prepared.^{4,6a,8}

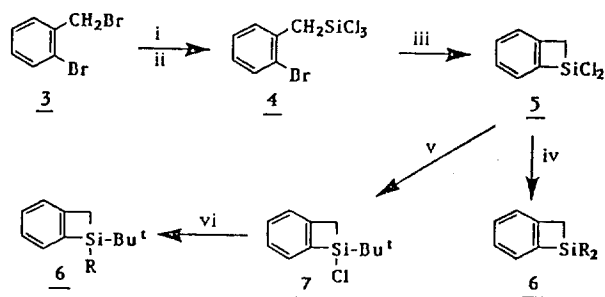
We have succeeded in the development of rather general route to various 1,1-disubstituted benzosilacyclobutenes *via*

the reaction of 1,1-dichlorobenzosilacyclobutene (5) with Grignard reagents or t-BuLi. This easy access renewed the interest to continue our studies on the chemistry of benzosilacyclobutenes.

Here we report the synthesis of benzosilacyclobutenes and their thermal and photochemical reactions with alcohols.⁷ We wish to find that these reactions proceed *via* the intermediate formation of o-silaquinone methide (2, Z=SiR₂) by the opening of the four-membered ring.⁸

Results and Discussion

Synthesis of Benzosilacyclobutenes. 1,1-Dimethyl- and 1,1-diphenyl-2,3-benzo-1-silacyclo-2-butenes (6a and 6b) have been prepared previously from the reaction of o-bromobenzylbromide with magnesium and subsequently with dichlorodimethylsilane or dichlorodiphenylsilane. The yields were moderate (27-36%).^{4,6a} Recently, 6a was also synthesized from the reaction of 1-magnesabenzocyclobutene with dichlorodimethylsilane in THF.⁵ However, these methods have limitations for the general synthetic routes of benzosilacyclobutenes because dialkyldichlorosilanes (except dichlorodimeth-



g, R=Me, 85%

h, R=Et, 80%

77%

a, R=Me, 90%

b, R=Ph, 88%

c, R=Et, 86%

d, R=Vinyl, 57%

e, R=i-Pr, 83%

f, R=t-Bu, 55%

i) Mg/ether ii) SiCl₄ iii) excess Mg

iv) 2 eq. of RMgX or t-BuLi

v) 1 eq. of t-BuLi vi) RMgX

Scheme 1.

ylsilane or dichlorodiphenylsilane) are not so easily available, and the yields are expected to be poor for the bulkier dichlorodialkylsilanes.

The reaction of the Grignard reagent from o-bromobenzyl bromide (3) with tetrachlorosilane in ether gave 4, which was then cyclized to 1,1-dichlorobenzosilacyclobutene (5) by excess magnesium. The overall yield of 5 from 3 was 36%.

Benzosilacyclobutenes 6a-6f were prepared from the reaction of 5 with two equivalents of the corresponding Grignard reagents or t-BuLi, respectively (Scheme 1).

This method allowed us to prepare benzosilacyclobutenes with the different alkyl substituents on silicon. The reaction of 1-t-butyl-1-chlorobenzosilacyclobutene (7) obtained from 5 and one equivalent of t-BuLi, with methylmagnesium iodide or ethylmagnesium bromide afforded 6g or 6h, respectively in good yields.

Thermal Reactions of Benzosilacyclobutenes with Alcohols. The yields, reaction conditions and the relative ratio of the two products (8 and 9) in the thermal reactions of benzosilacyclobutenes 6 and alcohols are listed in Table 1. Eaborn *et al.* reported (dimethyl)methoxy-o-tolylsilane (8a) as the only product in the pyrolytic reaction of 1,1-dimethylbenzosilacyclobutene (6a) in neutral methanol.^{6a} In contrast we find that the thermal reaction of 6a in methanol produced not only (dimethyl)methoxy-o-tolylsilane (8a), resulting from benzyl-silicon bond cleavage, but also (dimethyl)methoxybenzylsilane (9a), from aryl-silicon bond cleavage (entry 1 in Table 1).

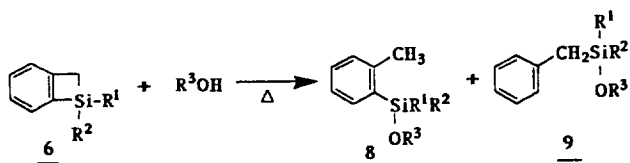
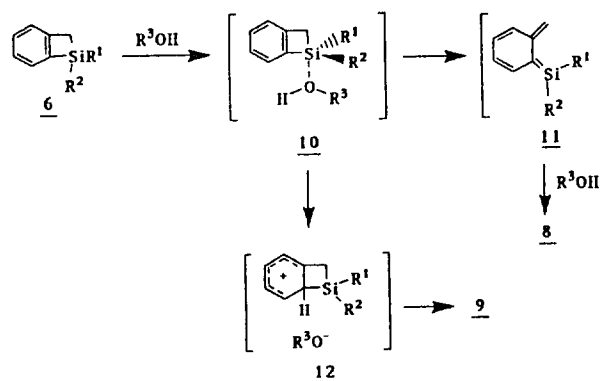


Table 1. Thermal Reactions of Benzosilacyclobutenes in Alcohols

| Entry | R ¹ | R ² | R ³ | Ratio of product 8:9 | Reaction condition | Total yield (%) |
|-------|----------------|----------------|----------------|----------------------|--------------------|-----------------|
| a | Me | Me | Me | 70 30 | 0°, 6 h | 100 |
| b | Ph | Ph | Me | 85 15 | 0°, 6 h | 100 |
| c | Et | Et | Me | 70 30 | rt, 8 h | 100 |
| d | i-Pr | i-Pr | Me | 70 30 | reflux, 15 h | 98 |
| e | t-Bu | Et | Me | 70 30 | reflux, 5 h | 79 |
| f | vinyl | vinyl | Me | 70 30 | rt, 10 h | 100 |
| g | t-Bu | t-Bu | Me* | 70 30 | reflux, 1.5 h | 95 |
| h | Me | Me | Et | 20 80 | reflux, 5 h | 89 |
| i | Ph | Ph | Et | 15 85 | reflux, 5 h | 93 |
| j | Et | Et | Et | 0 100 | reflux, 7 h | 81 |
| k | Me | Me | i-Pr | 0 100 | reflux, 7 h | 68 |
| l | Et | Et | i-Pr | 0 100 | reflux, 15 h | 68 |

*Methanolic sodium methoxide was used instead of methanol



Scheme 2.

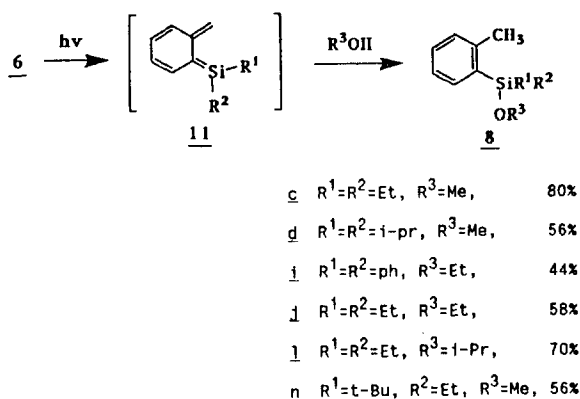
The other 1,1-dialkyl-, diphenyl- or divinyl-benzosilacyclobutenes also reacted thermally with methanol to give a mixture of 8 and 9 (entries b-g).

The ratio of isomeric products of 8 and 9 was determined by the peak integrations of aryl-methyl protons in 8 and benzyl protons in 9 at their ¹H-NMR spectra.

Benzosilacyclobutenes 6a, 6b, and 6c underwent similar displacement reactions in ethanol yielding isomeric mixture of 8 and 9 (entries h-j). In these reactions, however, the aryl-silicon bond cleavage was predominant yielding more 9 than 8. The relative proportion of 9 was even greater, when bulkier isopropyl alcohol was employed (entries k and l).

The thermal reaction of benzosilacyclobutene with alcohols is thought to proceed initially *via* pentavalent coordinate silicon intermediates (10). The formation of 8 may involve an o-silaquinone methide intermediate which is efficiently trapped by alcohol⁹ while the formation of 9 must result a protodesilylation pathway (Scheme 2).

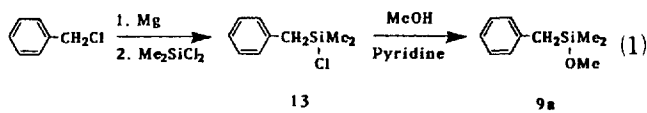
Photochemical Reactions of Benzosilacyclobutenes with Alcohols. The photochemical reactions of benzosilacyclobutenes were carried out by irradiating alcoholic solutions of benzosilacyclobutene with high pressure mercury arc lamp (Vycor filter) at 5°. In the photoreactions, only (dial-



Scheme 3.

kyl)alkoxy-o-tolylsilanes (**8**) were obtained in 40-80% yield (Scheme 3). Yields were calculated based on consumed benzosilacyclobutenes. (Dialkyl)alkoxyl-benzylsilanes (**9**) could not be detected even on the examination by NMR spectra. Without irradiation the reactions were extremely sluggish under otherwise the same reaction conditions.

When we irradiated (dimethyl)methoxybenzylsilane (**9a**) or (diethyl)ethoxybenzylsilane (**9j**) in methanol, no photodecomposition of **9a** or **9j** was observed. The starting **9a** or **9j** was almost completely recovered. (Dimethyl)methoxybenzylsilane **9a** was prepared from (chloro)dimethylbenzylsilane as in Eq. (1).



The photolysis of benzosilacyclobutene in alcohol was not affected by oxygen. Irradiation of methanol solution of **6c** with continued bubbling of oxygen also gave **8d** in 53% yield. The result suggests that the singlet excited state of benzosilacyclobutene is responsible for the ring opening to o-silaquinone methide (**11**) which is trapped by alcohols to afford **8**.

Experimental

All reactions involving t-butyllithium or Grignard reagents were carried out under an atmosphere of argon, in glassware which had been dried at 110° for at least 2 h. NMR spectra were recorded in carbon tetrachloride with Varian EM 360A spectrometer. Mass spectra were determined on a Hitachi RMU-6L mass spectrometer (70 eV). High resolution mass spectra were taken with a JEOL JMS-D300 spectrometer.

(o-Bromobenzyl)trichlorosilane(4). The Grignard reagent, o-bromobenzylmagnesium bromide prepared from o-bromobenzyl bromide (**3**, 25 g, 0.1 M) and magnesium (2.6 g, 0.11 M) in ether (100 ml) was added slowly to an ethereal (80 ml) solution of tetrachlorosilane (34 g, 0.2 M) at 0°C. The mixture was stirred for 1 h at room temperature and then refluxed for 12 h. The resulting inorganic salts were filtered, and washed with a total of 50 ml anhydrous ether under nitrogen atmosphere. After removal of ether by simple distillation and vacuum distillation (2 mmHg, 107-110°) gave

18.3 g(60%) of **4**. NMR: δ 3.10(2H, s), 6.8-7.5(4H, m).

1,1-Dichlorobenzosilacyclobutene(5). To a warm ether (20 ml) containing magnesium (5.8 g, 0.24 M) an ethereal (60 ml) solution of **4** (18.3 g, 0.06 M) and 1,2-dibromoethane (3 ml) was added slowly (4 h). The mixture was refluxed for 3 days. The inorganic salts were filtered and washed with ether under nitrogen. Distillation (10 mmHg, 85-90°) gave 6.8 g (60%) of **5**. NMR: δ 2.90(2H, s), 7.0-7.5(4H, m).

Typical Procedure for The Reaction of 5 with Grignard Reagents. To an ethereal (35 ml) solution of methyl magnesium iodide [prepared from methyl iodide (4.5 g, 0.032 M) and magnesium (0.85 g, 0.035 M)] **5** (2 g, 0.011 M) in ether (25 ml) was added slowly (1 h) at 0°, and then stirred at room temperature for 1 h. The reaction was quenched with a cold sat. NH_4Cl solution, and extracted with ether (30 ml \times 2). The crude product was purified by column chromatography on acidic alumina (hexane) to afford 1.4 g (90%) of **6a**. NMR: δ 0.47(6H, s), 2.09(2H, s), 6.8-7.4(4H, m).

Other 1,1-dialkyl-1,1-divinyl- or 1,1-diphenylsilabenzocyclobutenes **6b-6e** were prepared similarly.

6b: NMR δ 2.46(2H, s), 7.0-7.7(14H, m).

6c: NMR δ 0.8-1.3(10H, m), 2.05(2H, s), 6.9-7.3(4H, m).

6d: NMR δ 2.22(2H, s), 5.5-6.6(6H, m), 6.8-7.3(4H, m).

6e: NMR δ 0.9-1.4(14H, m), 2.05(2H, s), 7.0-7.3(4H, m).

1-t-Butyl-1-methylbenzosilacyclobutene (**6g**) and 1-t-butyl-1-ethylbenzosilacyclobutene (**6h**) were also prepared similarly from 1-t-butyl-1-chlorobenzosilacyclobutene (**7**).

6g: NMR δ 0.49(3H, s), 0.93(9H, s), 2.05(2H, br.s), 6.8-7.3(4H, m).

6h: NMR δ 0.8-1.1(14H, m), 2.05(2H, br.s), 6.9-7.4(4H, m).

1,1-Di-t-Butylbenzosilacyclobutene(6f). A hexane (60 ml) solution of **5** (4.36 g, 23.1 mmol) was cooled to -10°C (ice/salt bath). t-BuLi-pentane solution (2.0 M, 25 ml, 50 mmol) was added slowly, and the mixture was stirred at room temperature for 2 h and then refluxed for 2 h. The reaction mixture was poured into a cold 0.1 N aq. HCl, the organic layer was washed with water, dried (over MgSO_4) and rotary evaporated. After flash column chromatography (acidic alumina, hexane), and subsequent Kugelrohr distillation (2 mmHg, 115-120°) gave 2.97 g (55%) of **6f**. NMR: δ 1.05(18H, s), 2.02(2H, s), 6.8-7.3(4H, m). Exact mass calcd. for $\text{C}_{15}\text{H}_{24}\text{Si}$ m/e 232.1646; found 232.1656.

1-t-Butyl-1-Chlorobenzosilacyclobutene(7). To a cold (-78°C), stirred solution of **5** (10 g, 0.053 M) in hexane (40 ml), t-BuLi (2.0 M, 13 ml, 0.026 M) was added slowly. After 30 min, the mixture was allowed to warm to room temperature and stirred for 18 h. The inorganic salts were filtered and washed with ether under nitrogen. Distillation (1.2 mmHg, 121-123°) afforded 8.5 g (77%) of **7**. NMR: δ 1.10(9H, s), 2.43(2H, s), 6.8-7.3(4H, m).

General Procedures of the Thermal Reactions of Benzosilacyclobutenes 6 with Alcohols. An alcoholic (2 ml) solution of benzosilacyclobutenes **6** (1 mmol) was stirred under reaction conditions shown in Table 1. The solution was evaporated and chromatographed on silica gel (hexane) to give **9** and/or **8**.

8a: NMR δ 0.35(6H, s), 2.39(3H, s), 3.30(3H, s), 6.7-7.4(4H, m).

9a: NMR δ 0.03(6H, s), 2.15(2H, s), 3.36(3H, s), 6.7-7.4(5H, m).

8b: NMR δ 2.23(3H, s), 3.54(3H, s), 6.8-7.7(14H, m).

9b: NMR δ 2.59(2H, s), 3.40(3H, s), 6.8-7.7(15H, m).

8c: NMR δ 0.8-1.1 (10H, m), 2.40(3H, s), 3.39(3H, s), 6.8-7.4(4H, m); MS m/e 208(M^+ , 9%), 179(100), 151(65), 121(25), 105(30).

9c: NMR δ 0.8-1.1(10H, m), 2.10(2H, s), 3.33(3H, s), 6.8-7.4(5H, m); MS m/e 208(M^+ , 11%), 151(10), 117(100), 89(82).

8d: NMR δ 0.7-1.3(5H, m), 0.96(9H, s), 2.42(3H, s), 3.55(3H, s), 6.8-7.5(4H, m).

9d: NMR δ 0.7-1.3(5H, m), 0.88(9H, s), 2.17(2H, s), 3.42(3H, s), 6.8-7.2(5H, m).

8e: NMR δ 0.5-1.1(14H, m), 2.45(3H, s), 3.55(3H, s), 6.9-7.5(4H, m).

9e: NMR δ 0.5-1.1(14H, m), 2.15(2H, s), 3.38(3H, s), 6.9-7.5(4H, m).

8f: NMR δ 2.37(3H, s), 3.46(3H, s), 5.6-6.4(6H, m), 6.5-7.5(4H, m).

9f: NMR δ 2.20(2H, s), 3.35(3H, s), 5.6-6.4(6H, m), 6.5-7.5(5H, m).

8g: NMR δ 1.02(18H, s), 2.49(3H, s), 3.64(3H, s), 6.8-7.5(4H, m).

9g: NMR δ 0.94(18H, s), 2.22(2H, s), 3.50(3H, s), 6.8-7.5(5H, m).

8h: NMR δ 0.37(6H, s), 1.15(3H, t, $J=6.6$ Hz), 2.45(3H, s), 3.58(2H, q, $J=6.6$ Hz), 6.8-7.5(4H, m).

9h: NMR δ 0.09(6H, s), 1.13(3H, t, $J=6.6$ Hz), 2.12(2H, s), 3.56(2H, q, $J=6.6$ Hz), 6.8-7.2(5H, m).

8i: NMR δ 1.22(3H, t, $J=6.6$ Hz), 2.24(3H, s), 3.78(2H, q, $J=6.6$ Hz), 6.8-7.6(14H, m).

9i: NMR δ 1.12(3H, t, $J=6.6$ Hz), 2.59(2H, s), 3.66(2H, q, $J=6.6$ Hz), 6.7-7.6(15H, m).

9j: NMR δ 0.20-0.95(10H, m), 1.13(3H, t, $J=6.6$ Hz), 2.10(2H, s), 3.59(2H, q, $J=6.6$ Hz), 6.6-7.5(5H, m).

9k: NMR δ 0.03(6H, s), 1.08(6H, d, $J=6.6$ Hz), 2.10(2H, s), 3.90(1H, sept, $J=6.6$ Hz), 6.6-7.5(5H, m).

9l: NMR δ 0.30-1.10(10H, m), 1.08(6H, d, $J=6.6$ Hz), 2.10(2H, s), 3.90(1H, sept, $J=6.6$ Hz), 6.60-7.30(5H, m).

General Procedures for the Photochemical Reaction of Benzosilacyclobutenes 6 with Alcohols. In a quartz NMR tube placed a dichloromethane (0.3 ml)-methanol (1 ml) solution of a benzosilacyclobutene (1 mmol). A stream of dry argon was passed through the solution to displace the air, and the tube was sealed with a cap and paraffin film. The tube was placed in the ice-water bath (about 5°) and then irradiated externally with a high pressure mercury lamp (100 W) through a Vycor filter for 9-24 h. After removal of the solvent, the residue was subjected to preparative tlc (silica gel, hexane:ether=10:1), to give **8**.

8j: NMR δ 0.5-1.3(6H, m), 1.17(3H, t, $J=6.6$ Hz), 2.41(3H, s), 3.63(2H, q, $J=6.6$ Hz), 6.7-7.5(4H, m).

8l: NMR δ 0.50-1.30(6H, m), 1.13(6H, d, $J=6.6$ Hz), 2.46(3H, s), 3.95(1H, sept, $J=6.6$ Hz), 6.7-7.5(4H, m).

8n: NMR δ 0.40(3H, s), 0.92(9H, s), 2.44(3H, s), 3.43(3H, s), 6.9-7.5(4H, m).

Preparation of (Dimethyl)methoxybenzylsilane(9a).

An ethereal (50 ml) solution of methanol (2.86 g, 89 mmol) and pyridine (6.5 g, 91 mmol) was added to chloro(dimethyl)benzylsilane, **13**, (5.5 g, 30 mmol) in ether (50 ml) at 0°, and stirred at room temperature for 12 h. Distillation (5 mmHg, 92°) afforded 3.8 g (71%) of **9a**.

Chloro(dimethyl)benzylsilane (**13**) was prepared from the

reaction of benzylmagnesium chloride with dimethyldichlorosilane in ether. **13**:78% yield; bp. 98-100°/0.9 mmHg; NMR δ 0.40(6H, s), 2.35(2H, s), 6.9-7.4(5H, m).

Photoreaction of 6e with Methanol Under Oxygen Atmosphere. A dry dichloromethane (2 ml)-methanol (250 ml) solution of **6e** (495 mg, 2.42 mmol) in the photoreactor equipped with a dry-ice condenser was irradiated for 5 h at about 5°. Dry oxygen was bubbled into the solution throughout the irradiation. The reaction mixture was concentrated and then chromatographed on silica gel (hexane:ether=10:1) to give **8d** (217 mg, 38%) and unreacted **6e** (134 mg, 27%).

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