

THERMAL REACTIONS OF BENZOSILACYCLOBUTENES WITH ALCOHOLS

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ABSTRACT

In the thermal reaction with alcohols, benzosilacyclobutenes underwent both benzyl-silicon and aryl-silicon bond rupture to yield (dialkyl)alkoxy-*o*-tolylsilanes and (dialkyl)-alkoxybenzylsilanes, respectively.

Benzocyclobutenes undergo thermal and photochemical ring opening to highly reactive *o*-quinonoid intermediates.¹ The analogous ring opening of benzosilacyclobutenes (1) to *o*-silaquinone methides (2), however, has not been reported.²

Eaborn *et al.* found (dimethyl)methoxy-*o*-tolylsilane 4a as the only product in the pyrolytic reaction of 1,1-dimethyl-2,3-benzo-1-silacyclo-2-butene (3a, R=Me) in neutral methanol.³

In contrast we find that benzosilacyclobutenes (1)⁴ react thermally with methanol and other alcohols to produce, not only (dialkyl)alkoxy-*o*-tolylsilanes (3a-j) but also (dialkyl)-alkoxybenzylsilane (4a-j). These latter products result from aryl-silicon bond cleavage. Both the substituents on silicon and the particular alcohol affect the ratio of 3 to 4.⁵ Ethanol and *i*-propanol favor formation of aryl-Si cleavage products 4.

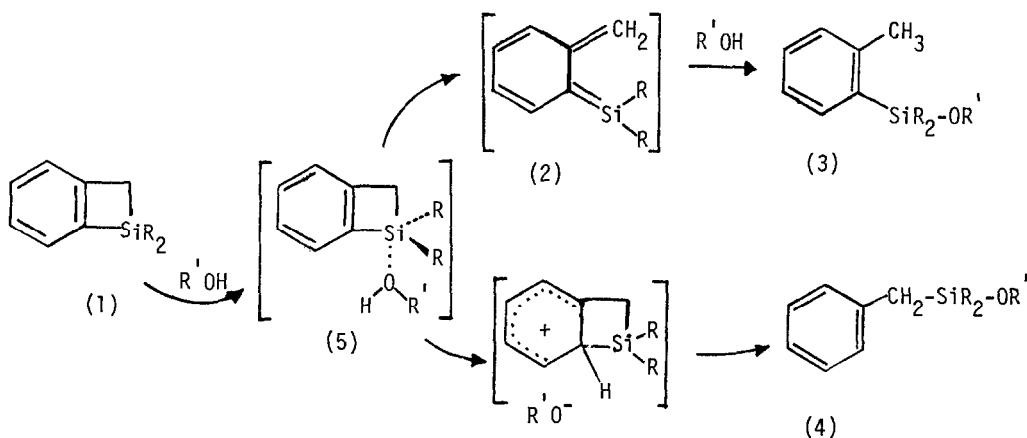
Table: Thermal reaction of benzosilacyclobutenes in alcohols.

Entry	R	R'	Ratio of Products*		Total Yield (%)
			<u>3</u>	<u>4</u>	
a	Me	Me	70	30	100
b	Ph	Me	85	15	100
c	Et	Me	70	30	100
d	<i>i</i> -Pr	Me	70	30	98
e	<i>t</i> -Bu	Me**	70	30	57
f	Me	Et	20	80	89
g	Ph	Et	15	85	93
h	Et	Et	0	100	81
i	Me	<i>i</i> -Pr	0	100	68
j	Et	<i>i</i> -Pr	0	100	68

* See note 5.

** Methanolic sodium methoxide was used instead of methanol.

The thermal reaction of benzosilacyclobutenes with alcohols is thought to proceed initially via pentavalent coordinate silicon intermediates (5). The formation of **3** may involve an *o*-silaquinone methide intermediate which is efficiently trapped by alcohol⁶ while the formation of **4** must result from a protodesilation pathway. The factors affecting the ratio of **3** to **4** are under further study.



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References and Notes

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- The ratio of isomeric products was determined from the integration of aryl-methyl protons in **3** and benzyl protons in **4**: for example, **3c**, NMR (CCl₄, δ) 0.8-1.1 (10H, m), 2.40 (3H, s), 3.39 (3H, s), and 6.8-7.4 (4H, m); **4c**, NMR (CCl₄, δ) 0.8-1.1 (10H, m), 2.10 (2H, s), 3.33 (3H, s), and 6.8-7.4 (6H, m). MS: **3c**: m/e 208 (M⁺, 9%), 179 (100), 151 (65), 121 (25), 105 (30); **4c**, m/e 208 (M⁺, 11%), 151 (10), 117 (100), 89 (82).
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