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Preliminary communication

Concerning the reactivity of the silacyclopropane ring: comparison with ring-opening reactions of 1,1-dimethyl-1-silacyclobutane

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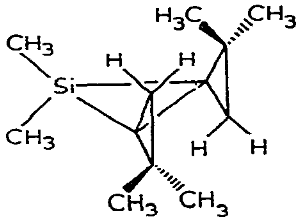
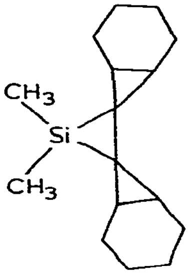
In an earlier communication[1], we reported the isolation and characterization of the first stable compounds containing the silacyclopropane system. The reactivity of the next higher silacycloalkane system, the silacyclobutanes, has been studied in some detail*, and so it seemed appropriate to include in our initial survey of the chemistry of silacyclopropanes those reagents whose action on silacyclobutanes had been examined by previous workers. The results we report here confirm that the SiC_2 ring contains one of the most, if not the most, reactive of silicon–carbon bonds known.

In order to facilitate the isolation and characterization of the reaction products, we carried out our experiments with 1,1-dimethyl-*trans*-bis-2,3-[2′,2′-dimethylcyclopropylidene]-1-silacyclopropane, I, although some reactions of II were studied as well.



(I)



(II)

Our initial preparative studies[1] had shown that I and II react exothermally with the oxygen in the air at room temperature; I, a liquid at room temperature, fumes in dry air, and II, a crystalline solid, rapidly is converted to a polymeric oil when exposed to oxygen. Consequently, all reactions of I and II must be studied in an atmosphere of dry nitrogen. Our further work has shown that both I and II are hydrolytically unstable. When a 100% excess of distilled water was added to their THF solutions at room temperature, an exothermic reaction gave the respective silanols, IIIa and IV, in high yield. IIIa was isolated by distillation as a liquid; IV, a solid with m.p. 43.5–46.5°, was isolated by column chromatography.

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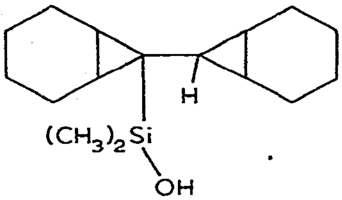
* For a detailed review of the chemistry of silacyclobutanes, *cf.* ref. 2.



(IV)

The exothermic reactions of I and II with methanol already have been noted[1]. That such reactivity is general with respect to alcohols was demonstrated by the reaction of I with t-butanol, which also was quite exothermic and gave the t-butoxysilane IIIb in 80% yield. GLC analysis of IIIb, as well as its NMR spectrum, suggested the presence of only one isomer. An exothermic reaction between I and phenol in benzene solution at room temperature resulted in formation of the phenoxysilane IIIc in 83% yield.

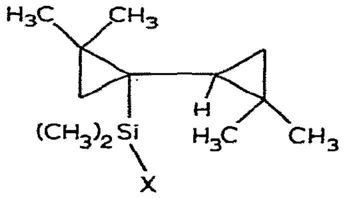
Two secondary amines, diethyl- and diisopropyl-amine, in contrast, did not react with I at room temperature, but a reaction time of 6 h at 65° served to give IIId in 57% yield when I was treated with Et_2NH in benzene. Diisopropylamine, however, did not react with I under these conditions. Cleavage of I with isopropylamine in benzene gave IIIe in 62% yield after 3 h at 55° and ammonia reacted with I in THF at room temperature to produce IIIf in 56% yield. Ring cleavage of I to give silylamines also could be effected with lithium dialkylamides. Thus, the addition of I to Et_2NLi in THF at −78°, followed by slow warming to 25°, gave an orange solution. This color was discharged by addition of solid NH_4Cl and subsequently IIId was isolated in 67% yield. A similar procedure carried out using i-Pr_2NLi resulted in formation of an orange solution, but its treatment with solid ammonium chloride produced the disilazane IIIg in 60% yield, rather than the expected diisopropylaminosilane. Presumably a transamination sequence involving the NH_4Cl used to quench the reaction mixture was responsible for this product.

Hydrogen sulfide opened the SiC_2 ring of I in THF at room temperature to give the thiol IIIh, and t-butyl mercaptan reacted with I in refluxing THF during 4.5 h. The product in this case, IIIi (64% yield), was obtained as a 4/1 mixture of isomers (by GLC and NMR analysis). Exothermic ring opening reactions also were observed when I was treated at room temperature with carboxylic acids in benzene solution. Prepared in this manner were IIIj (88% yield) and IIIk (87% yield).

In Table 2 we compare the reactivity of I toward various reagents with that of 1,1-dimethyl-1-silacyclobutane. The much higher reactivity of the silacyclopropane is readily apparent. Silacyclobutanes already are highly reactive (compared with the larger silacycloalkanes) because of increased ring strain[2]. Two factors may be considered as being primarily responsible for the extraordinarily high reactivity of the endocyclic Si—C bonds of I: still higher ring strain and the high degree of *s* character of the Si orbitals used in forming the Si—C(ring) bonds.

TABLE 1

RING-OPENING PRODUCTS DERIVED FROM 1,1-DIMETHYL-*trans*-BIS-2,3-[2′,2′-DIMETHYLCYCLOPROPYLIDENE]-1-SILACYCLOPROPANE[a]



(III)

Compound	*X*	*B.p. (°C/mmHg)*	n_D^{25}
IIIa	OH	41–44/0.02	1.4745
IIIb	$OCMe_3$	50/0.04	1.4538
IIIc	OPh	94–97/0.03	1.5070
IIId	NEt_2	62–64/0.03	1.4709
IIIe	NHPr-i	57–59/0.03	1.4643
IIIf	NH_2	43/0.05	1.4718
IIIg	½ NH	110/0.05	1.4890
IIIh	SH	45/0.02	
IIIi	$SCMe_3$	75/0.03	1.4838 (major isomer)
IIIj	OAc	60–62/0.05	1.4592
IIIk	O_2CCMe_3	77–79/0.04	1.4543

[a] The isolation of the OH, NH_2 and SH products, rather than their condensation products, no doubt is due to the steric bulk of the bicyclopropyl substituent.

All of the products listed in Table 1 are unstable with respect to hydrolysis (except, of course, the silanol). However, for all except thiol IIIh satisfactory analyses were obtained. Their mass spectra provided excellent evidence in favor of the structures given and further confirmation was provided by their IR and NMR spectra.

Full details of this and related work will be presented at a later date. Our studies of the chemistry of silacyclopropane systems are continuing.

ACKNOWLEDGMENTS

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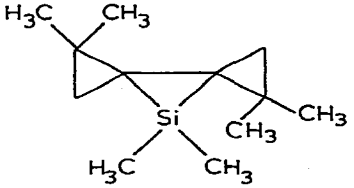
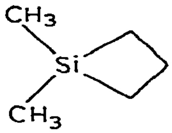
TABLE 2

COMPARISON OF THE REACTIVITY OF 1,1-DIMETHYL-*trans*-BIS-2,3-[2',2'-DIMETHYLCYCLOPROPYLIDENE]-1-SILACYCLOPROPANE AND 1,1-DIMETHYL-1-SILACYCLOBUTANE TOWARD RING OPENING REAGENTS

Reagent		
O_2	exothermic reaction at room temperature[1]	stable toward O_2
H_2O	reaction exothermic and complete at room temperature in homogeneous solution	10% yield of Me_2(n-Pr)SiOH after 8 h at reflux[3]
ROH	reaction exothermic and complete at room temperature (R = Me, Me_3C)	58% yield of Me_2(n-Pr)SiOR after 11 h at reflux (R = n-C_7H_{15}) [3]
HOAc	reaction exothermic and complete at room temperature	65% yield of Me_2(n-Pr)SiOAc after 8 h at 160–180° [3]
HCl(g)	rapid and complete reaction at −78° [1]	60% yield of Me_2(n-Pr)SiCl after 8 h at 20° [3]
Et_2NH	57% yield of IIId after 6 h at 65°	no reaction at reflux or at 150° in a sealed tube[3]
RLi (with subsequent hydrolysis)	rapid and complete reaction at −70° (R = Me) [1]	75% yield of Me_2(n-Pr)PhSi after 5 h at reflux[4] (R = Ph)

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