

Homolytic and Conjugate Addition of Thiols to 2,4-Dimethyl-2-vinyl-1,3-dioxo-2-silacyclohexane

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Abstract—Homolytic reaction of 1-propane- and 1-pentanethiols to 2,4-dimethyl-2-vinyl-1,3-dioxo-2-silacyclohexane, initiated by di-*tert*-butyl peroxide at 130°C, yields a mixture of isomeric sulfides (95%) as a result of addition at the α - and β -positions of the vinyl group. Conjugate addition of alkanethiols in the presence of the corresponding sodium thiolate at 100°C gives 10% of the same α - and β -regioisomeric sulfides at a ratio of 1:20.

Thiols are known to react with olefins in the presence of radical initiators to form sulfides via addition at the double bond [1]. Base-catalyzed addition of thiols to compounds having a conjugated double bond also yields the corresponding sulfides (Michael reaction) [2]. Likewise, vinylsilanes can also be involved in nucleophilic addition reactions [3]. As a rule, cyclic acetals and their heteroanalogs are stable toward bases and are very reactive in liquid-phase homolytic processes. Therefore, their functionalization at the unsaturated side chain via radical reactions may be impossible [4, 5].

Taking the above into account, in the present work we studied the addition of 1-propanethiol (**I**) and 1-pentanethiol (**II**) to 2,4-dimethyl-2-vinyl-1,3-dioxo-2-silacyclohexane (**III**) in the presence of radical initiators and bases. The reaction of thiols **I** and **II** with olefin **III** in the presence of di-*tert*-butyl peroxide at 130°C in an inert atmosphere (reaction time 2 h) gave 95% of sulfides **IV–VII**. The products were mixtures of isomers formed by thiol addition at the α - and β -positions of the vinyl group. The isomer ratio α : β was 1:20. Also, small amounts of the corresponding dialkyl disulfides were formed as chain termination products (Table 1).

Presumably, the predominant formation of the β -addition products is determined by the greater stability of intermediate radical species **1B** and **1B** with unpaired electron on the α -carbon atom, as compared to isomeric structures **1C** and **2C** (Scheme 1).

The effect of the reactant ratio and temperature was examined in the reaction of **III** with 1-pentanethiol (**II**) (Table 1). Both decrease and increase of the olefin **III** concentration resulted in reduced yield of sulfides **IV** and **V**. The reaction direction and the yield of products almost did not change on lowering the temperature to 70°C, azobis(isobutyronitrile) (AIBN) being used as initiator.

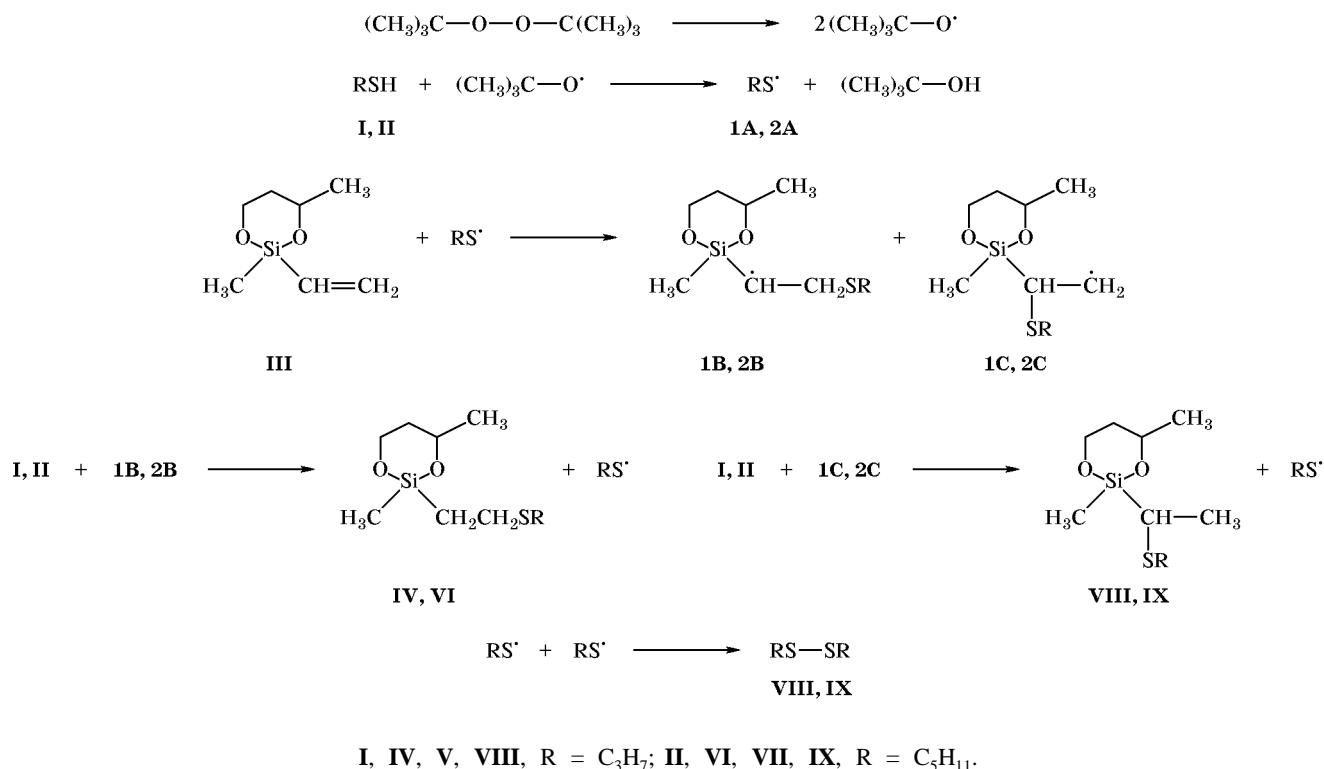
The double bond in molecule **III** is conjugated with the silicon atom, which provides the possibility for Michael addition [3, 4]. In fact, by reaction of **III** with alkanethiols **I** and **II** in the presence of the corresponding sodium thiolates at 100°C in DMF we obtained mixtures of α - and β -isomers **IV–VII** at

Table 1. Homolytic addition of 1-pentanethiol (**II**) to 2,4-dimethyl-2-vinyl-1,3-dioxo-2-silacyclohexane (**III**) in the presence of 5 wt % of di-*tert*-butyl peroxide (reaction time 2 h, temperature 130°C)

Molar ratio III : II	Conversion, %		Product fraction, %		
	II	III	IV	V	VIII
1:1	100	95	90	5	5
1:2	50	100	79	4.8	13.6
3:2	96	72	43	3	8.2
1:1 ^a	90	100	85	4	4

^a Temperature 70°C, 5 wt % of azobis(isobutyronitrile).

Scheme 1.



a ratio of 1:20. However, the yield was poor (10%) because of considerable tarring. As in the radical process, the predominant formation of β -isomers **IV** and **VI** is explained [6] by the greater stability of intermediate anionoid adducts **1D** and **2D** compared to **1E** and **2E** (Scheme 2).

Compounds **III** and **IV–IX** were identified by the ^1H and ^{13}C NMR and mass spectra; their structure was confirmed by elemental analysis. We failed to isolate sulfides **V** and **VII**, and they were identified by the GC–MS data. According to the ^1H and ^{13}C NMR spectra, initial olefin **III** is a mixture of diastereoisomers **IIIa** and **IIIb**. The six-membered ring has a *chair* conformation with equatorial orientation of the methyl group on C^4 for both diastereoisomers. The equatorial orientation of the C^4 -methyl group follows from the direct ^1H – ^{13}C coupling constants

which are equal to 143.5 and 143.8 Hz for **IIIa** and **IIIb**, respectively. Sulfides **IV** and **VI**, like initial vinylsilane **III**, are also diastereoisomeric mixtures (60:40, Table 2). The ^{13}C NMR spectra of **IVa**, **IVb**, **VIa**, and **VIb** contain signals from the SiCH_3 ($\delta_{\text{C}} -1.88$ to -3.26 ppm), CH_2Si ($\delta_{\text{C}} 15.42$ – 16.92 ppm), CH_2O ($\delta_{\text{C}} 62.75$ – 63.11 ppm), and CHO groups ($\delta_{\text{C}} 69.43$ – 69.86 ppm).

Unlike **IIIa** and **IIIb**, isomers **IVa/IVb** and **VIa/VIb** show only one signal from the 4- CH_3 group at $\delta_{\text{C}} 24.11$ and 24.20 ppm, respectively. This fact may be explained by strong conformational lability of their molecules; fast exchange between the axial and equatorial conformers leads to averaging of the chemical shifts. The alkylthio group in **IV** and **VI** is also characterized by averaged chemical shifts of the C^{11} – C^{15} atoms, for these atoms are remote from

Scheme 2.

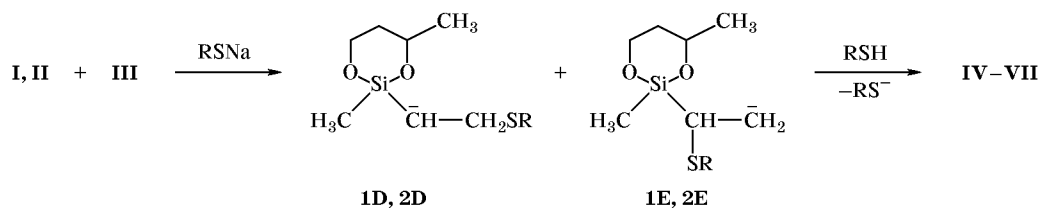
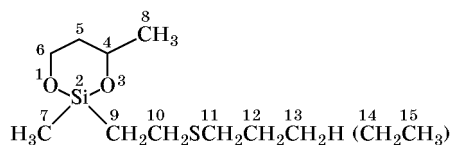


Table 2. ^{13}C NMR spectra (δ_{C} , ppm) of 2,4-dimethyl-1,3-dioxo-2-silacyclohexanes **IIIa**, **IIIb**, **IVa**, **IVb**, **VIa**, and **VIb**

Comp. no.	C ⁴	C ⁵	C ⁶	C ⁷	C ⁸	C ⁹	C ¹⁰	C ¹¹	C ¹²	C ¹³	C ¹⁴	C ¹⁵
IIIa	69.74	38.02	63.12	-2.41	24.21	133.83	134.96					
IIIb	69.74	38.37	62.71	-4.88	24.09	134.72	135.21					
IVa	69.43	38.0	62.64	-2.87	24.11	16.89	25.92	33.59	22.64	13.34		
IVb	69.78	38.17	62.99	-1.88	24.11	15.47	25.44	33.76	22.64	13.34		
VIa	69.86	38.18	63.11	-3.26	24.20	16.92	26.07	31.76	31.01	29.11	22.18	13.88
VIb	69.53	38.24	62.75	-1.84	24.20	15.42	25.59	31.59	31.01	29.11	22.18	13.88

Table 3. ^1H NMR spectra (δ , ppm) of 2,4-dimethyl-1,3-dioxo-2-silacyclohexanes **III**, **IV**, and **VI**

Comp. no.	4-H	5-H ₂	6-H ₂	7-H ₃	8-H ₃	9-H ₂	10-H ₂	11-H ₂	12-H ₂	13-H ₂	14-H ₂	15-H ₂
III	4.07 m	1.63 m	3.93 m	0.15 s	1.18 d	5.99 m	5.59 m					
IV	4.11 m	1.52 m	3.98 t	0.11 s	1.16 d	0.90 t	2.54 t	2.42 t	1.62 m	0.91 t		
VI	4.19 m	1.34 m	4.05 m	0.20 s	1.25 d	1.10 t	2.63 t	2.52 t	1.53–1.83 m			0.90 t

Table 4. Mass spectra, m/z (I_{rel} , %) of 2,4-dimethyl-1,3-dioxo-2-silacyclohexanes **IV–VII** and disulfides **VIII** and **IX**

Comp. no.	R	$M^{+\cdot}$	$[M-C_2H_4]^+$	$[M-R]^+$	$[M-CH_2CH_2SR]^+$	$[CH_2CH_2SR]^{+\cdot}$	$[SR]^{+\cdot}$	$[C_3H_7]^+$
IV	C ₃ H ₇	234 (3.4)	206 (8.3)	191 (4.6)	131 (100)	103 (21.6)		
V	C ₃ H ₇	234 (4.4)	206 (1.2)	191 (30.7)	131 (100)	103 (23.9)		
VI	C ₅ H ₁₁	262 (3.5)	234 (9.0)	191 (1.8)	131 (100)			
VII	C ₅ H ₁₁	262 (3.1)	233 (3.4) ^a	191 (38.9)	131 (100)			
VIII	C ₃ H ₇	150 (21.5)		107 (19.5)			75 (3)	43 (100)
IX	C ₅ H ₁₁	206 (30)		136 (26.1) ^b			103 (12.6)	43 (100)

^a $[M-C_2H_5]^{+\cdot}$.^b $[M-C_3H_{10}]^{+\cdot}$.**Table 5.** Yields, constants, and elemental analyses of compounds **III**, **IV**, and **VI**

Comp. no.	Yield, %	bp, °C (<i>p</i> , mm)	d_{20}^{20} , g/cm ³	n_D^{20}	Found, %			Formula	Calculated, %		
					C	S	Si		C	S	Si
III	95	150	0.9197	1.4243	52.89		17.14	C ₇ H ₁₄ O ₂ Si	53.12		17.75
IV	90	150 (1.5)	1.0056	1.4694	51.94	13.15	11.23	C ₁₀ H ₂₂ O ₂ SSi	51.23	13.68	11.98
VI	90	145 (1.5)	1.0784	1.4715	55.27	11.84	10.13	C ₁₂ H ₂₆ O ₂ SSi	54.91	12.22	10.70

the chiral center. Following the 1,3-*syn*-interaction rule, isomers **IVb** and **VIb** characterized by more upfield SiCH₃ signal were assigned the structure with *syn*-arrangement of the methyl groups on the silicon atom and C⁴. Correspondingly, the 2- and 4-methyl groups in isomers **IVa** and **VIa** are arranged *anti*.

We can conclude that homolytic addition of alkane-thiols to 2,4-dimethyl-2-vinyl-1,3-dioxo-2-silacyclohexane is much more efficient (from the viewpoint of reaction conditions and product yield) than the corresponding nucleophilic reaction.

EXPERIMENTAL

The ¹H and ¹³C NMR spectra were recorded on a Bruker AM-300 spectrometer (300 and 75 MHz, respectively) from 5–20 vol % solutions in CDCl₃ containing HMDS as internal reference. The signals were assigned using proton decoupling technique and also multipulse DEPT and JMODECHO sequences. The ¹³C NMR spectra were obtained with complete decoupling from protons, and the direct carbon–proton coupling constants were determined from the NOE spectra. The mass spectra were run on an HP-5972A mass-selective detector coupled with an HP-5890 gas chromatograph (HP-5 30-m glass capillary column, 5% of phenylmethylsilicone, oven temperature programming from 100 to 250°C). Gas–liquid chromatography was performed on a Chrom-5 instrument (thermal conductivity detector, 3-m column packed with SE-30 on Chromaton N-AW, oven temperature programming from 50 to 250°C).

Initial olefin **III** was synthesized by the procedure reported in [7]. The spectral parameters and analytical data of the products are given in Tables 2–5.

Homolytic addition of 1-propanethiol (I) to 2,4-dimethyl-2-vinyl-1,3-dioxo-2-silacyclohexane (III). A 10-ml glass ampule (preliminarily evacuated and filled with argon) was charged with 1.58 g (0.01 mol) of olefin **III**, 0.76 g (0.01 mol) of thiol **I**, and 0.073 g (0.0005 mol) of di-*tert*-butyl peroxide. The ampule was cooled, sealed, and placed in a metal bomb. The bomb was mounted in a holder and immersed in a silicone bath heated to 130°C. The bomb was agitated at a rate of ~60 min⁻¹ for 2 h. Fractional distillation of the mixture gave 2,4-dimethyl-2-(2-propylthioethyl)-1,3-dioxo-2-silacyclohexane (**IV**) and dipropyl disulfide (**VIII**).

The reaction of 1-pentanethiol (**II**) with 2,4-dimethyl-2-vinyl-1,3-dioxo-2-silacyclohexane (**III**) was

performed in a similar way. The isolated product was 2,4-dimethyl-2-(2-pentylthioethyl)-1,3-dioxo-2-silacyclohexane (**VI**).

Nucleophilic addition of 1-propanethiol (I) to 2,4-dimethyl-2-vinyl-1,3-dioxo-2-silacyclohexane (III). Sodium 1-propanethiolate was synthesized by the procedure described in [8]. A mixture of 7.9 g (0.05 mol) of olefin **III**, 3.42 g (0.045 mol) of thiol **I**, and 0.49 g (0.005 mol) of sodium 1-propanethiolate in 20 ml of DMF was stirred for 5 h at 100°C. The mixture was analyzed by GC–MS. The overall yield of sulfides **IV** and **V** was 10%.

The reaction of 1-pentanethiol (**II**) with olefin **III** in the presence of sodium 1-pentanethiolate was performed in a similar way. According to the GC–MS data, 10% of sulfides **VI** and **VII** was obtained.

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