

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

R. M. Makaeva, V. V. Zorin, R. R. Musavirov, L. S. Brod'ko, S. V. Gvozdik, and R. S. Musavirov

Ufa State Petroleum Technical University, ul. Kosmonavtov 1, Ufa, 450062 Bashkortostan, Russia

Research Institute of Fine Chemicals, Ufa, Bashkortostan, Russia

Received July 5, 1999

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.

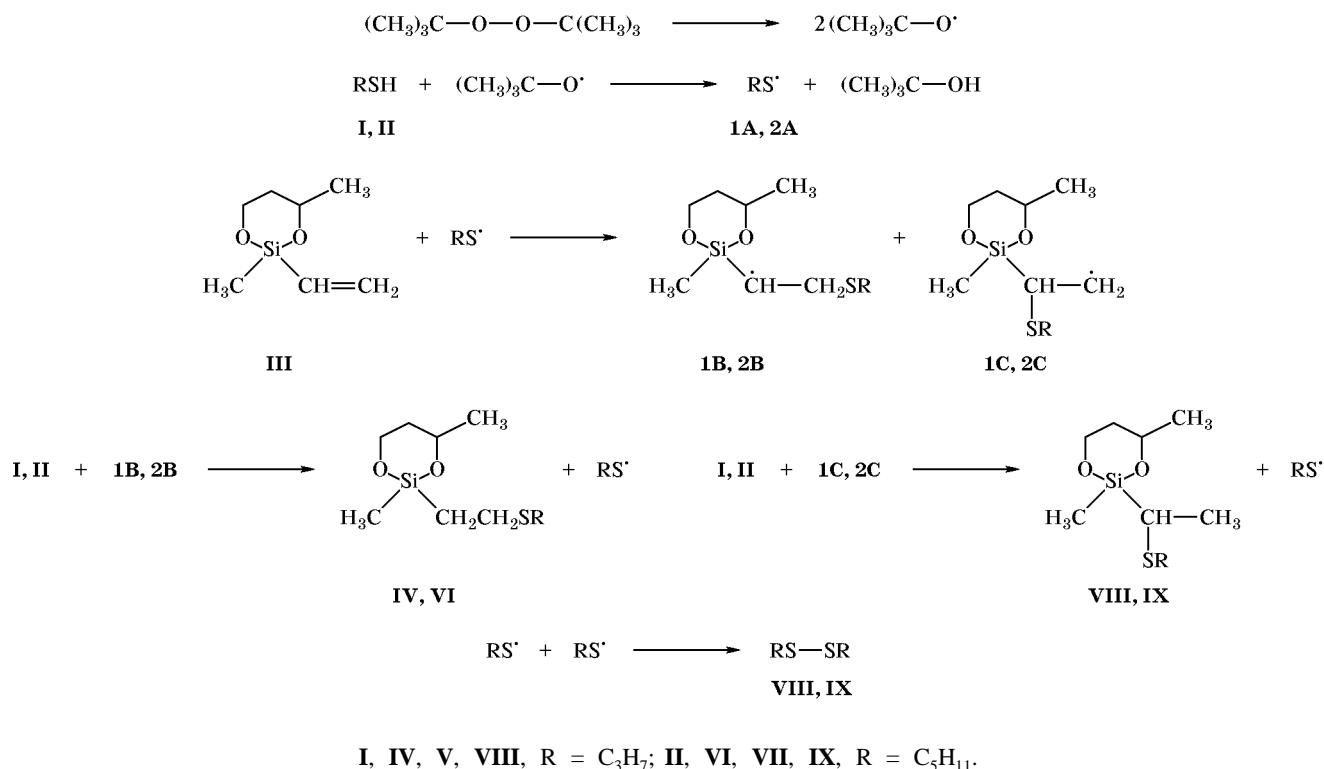
The double bond in molecule **III** is conjugated with the silicon atom, which provides the possibility for Michael addition [3, 4]. In fact, by reaction of **III** with alkanethiols **I** and **II** in the presence of the corresponding sodium thiolates at 100°C in DMF we obtained mixtures of α - and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

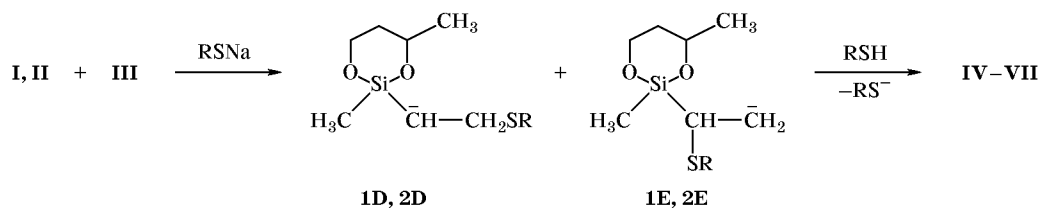
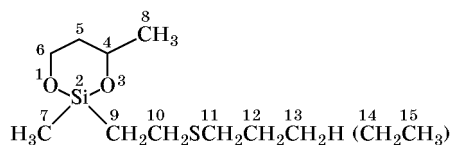


Table 2. ^{13}C NMR spectra (δ_{C} , ppm) of 2,4-dimethyl-1,3-dioxo-2-silacyclohexanes **IIIa**, **IIIb**, **IVa**, **IVb**, **VIa**, and **VIb**

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 alkanethiols 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.

REFERENCES

- Freidlina, R.Kh., Velichko, F.K., Zlotskii, S.S., Rakhmankulov, D.L., and Terent'ev, A.B., *Radikal'naya telomerizatsiya* (Radical Telomerization), Moscow: Khimiya, 1988, p. 183.
- Safarova, G.M., Makaeva, R.M., Zorin, V.V., and Rakhmankulov, D.L., *Russ. J. Gen. Chem.*, 1998, vol. 68, no. 8, pp. 1235–1239; *Zh. Org. Khim.*, 1992, vol. 28, no. 3, pp. 545–548.
- Sason, J.F. and Brooks, H.G., *J. Am. Chem. Soc.*, 1952, vol. 74, no. 15, pp. 4582–4585.
- Rakhmankulov, D.L., Karakhanov, R.A., Zlotskii, S.S., Kantor, E.A., Imashev, U.B., and Syrkin, A.M., *Khimiya i tekhnologiya 1,3-dioksatsikloalkanov. Tekhnologiya organicheskikh veshchestv (Itogi nauki i tekhniki)* [Chemistry and Technology of 1,3-Dioxacycloalkanes. Technology of Organic Substances (Advances in Science and Technology)], Moscow: VINITI, 1975, vol. 5.
- Rakhmankulov, D.L., Zlotskii, S.S., Kantor, E.A., Karakhanov, R.A., and Zorin, V.V., *Mekhanizmy reaktsii atsetalei* (Mechanisms of Acetal Reactions), Moscow: Khimiya, 1987.
- Benkeser, W.R., Bennet, E.W., and Hickner, R.A., *J. Am. Chem. Soc.*, 1957, vol. 79, no. 23, pp. 6253–6256.
- Voronkov, M.G., Davydova, V.P., and Dolgov, B.N., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1958, no. 6, pp. 698–701.
- Zorin, V.V., Kukovitskii, D.M., Zlotskii, S.S., Todres, Z.V., and Rakhmankulov, D.L., *Zh. Obshch. Khim.*, 1983, vol. 53, no. 4, pp. 906–910.