Russian Journal of Organic Chemistry, Vol. 37, No. 9, 2001, pp. 1335–1337. Translated from Zhurnal Organicheskoi Khimii, Vol. 37, No. 9, 2001, pp. 1400–1402.
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Hydrolysis of Bis[5,5-dimethyl-3-(4-oxa-1-azoniacyclohexylidene)-1-cyclohexenyl] Sulfide Diperchlorate*

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Received December 20, 2000

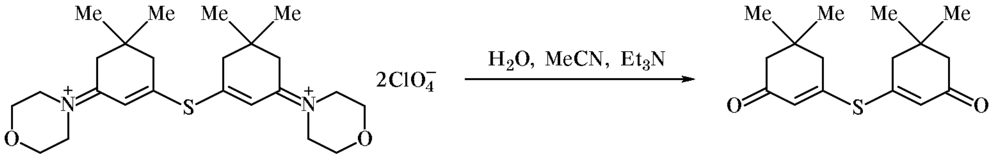
Abstract—Hydrolysis of bis[5,5-dimethyl-3-(4-oxa-1-azoniacyclohexylidene)-1-cyclohexenyl] sulfide diperchlorate, as well as of bis(5,5-dimethyl-3-thioxo-1-cyclohexenyl) sulfide, in the system MeCN–Et_3N yields a mixture of bis(5,5-dimethyl-3-oxo-1-cyclohexenyl) sulfide and isomeric 5,5-dimethyl-3-oxo-1-cyclohexenyl 3,3-dimethyl-5-oxo-1-cyclohexenyl sulfide. The structure of the products and their ratio were established by ^1H and ^{13}C NMR and IR spectroscopy.

We previously [1] synthesized bis(5,5-dimethyl-3-thioxo-1-cyclohexenyl) sulfide (**II**) by the action of hydrogen sulfide on bis[5,5-dimethyl-3-(4-oxa-1-azoniacyclohexylidene)-1-cyclohexenyl] sulfide (**I**). With the goal of synthesizing its oxygen-containing analog, bis(5,5-dimethyl-3-oxo-1-cyclohexenyl) sulfide (**III**), we have studied hydrolysis of diperchlorate **I**. The formation of dioxo sulfide **III** in the reaction of 3-chloro-5,5-dimethyl-2-cyclohexenone with Na_2S was reported in [2], but its yield was as low as 5%. The structure of **III** was confirmed by the IR and UV spectra.

The hydrolysis of diperchlorate **I** was carried out in acetonitrile at 50–60°C in the presence of a catalytic amount of triethylamine. As a result, we isolated dioxo sulfide **III** in 45% yield (Scheme 1). The structure of **III** was proved by the ^1H NMR, IR, and UV spectra. However, its melting point (mp 80–81°C) was considerably different from that given in [2] (mp 176–177°C). Therefore, we have reproduced the procedure described in [2]. The resulting dioxo sulfide **III** also had mp 80°C. When the hydrolysis was carried out with a threefold amount of triethylamine, we obtained a mixture of sulfide **III** and its isomer with a different location of the double bond in one of the cyclohexene rings, namely 5,5-dimethyl-3-oxo-1-cyclohexenyl 3,3-dimethyl-5-oxo-1-cyclohexenyl sulfide (**IV**); the isomer ratio was 8:2 (Scheme 2).

The structure of products **III** and **IV** and their ratio were established by the ^1H and ^{13}C NMR spectra using APT multipulse sequence and two-dimensional techniques (HETCOR and NOESY), as well as quantitative approaches to analysis of mixtures of organic compounds [3]. The spectral parameters of dioxo sulfides **III** and **IV** are given in table. An independent proof for the structure of **IV** was obtained by the IR spectrum of its mixture with isomer **III**; three carbonyl absorption bands were present at 1717, 1649, and 1668 cm^{-1}. The first of these belongs to the unconjugated carbonyl group in **IV**, and the two latter,

Scheme 1.



I **III**

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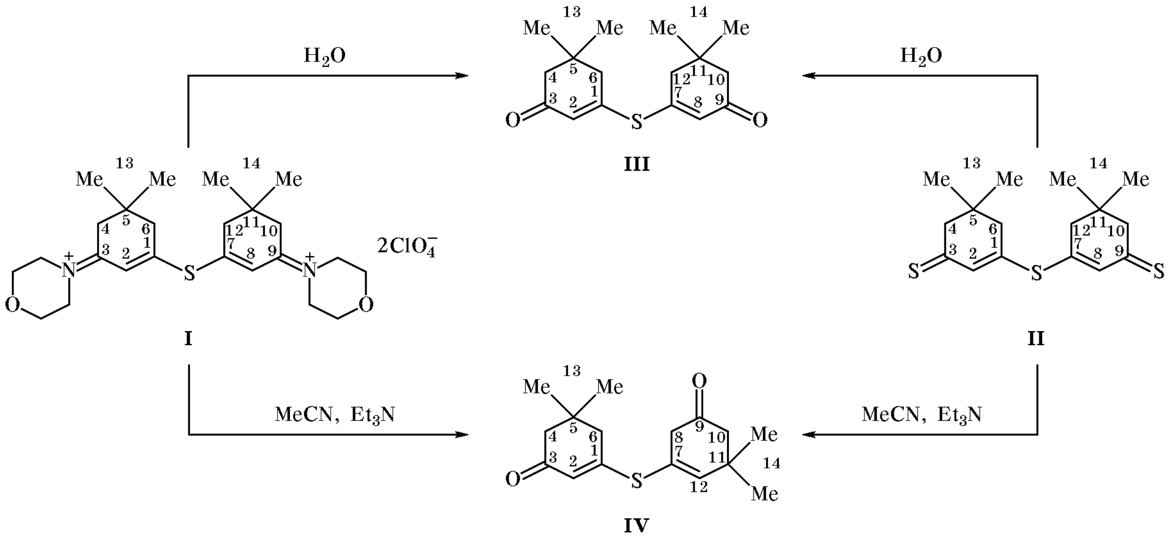
[*] This study was financially supported by the Russian Foundation for Basic Research (project no. 98-03-32863a).

Scheme 2.



to the conjugated carbonyl groups in **III** and **IV**. The hydrolysis of dithioxo sulfide **II** in the system acetonitrile–triethylamine at 0–5°C gave a mixture of the same isomers **III** and **IV** at a ratio of 8.7 : 1.3.

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra of mixtures of compounds **III** and **IV** were recorded on a Varian VXR-500S spectrometer at 500.1 (^{1}H) and 125.5 MHz (^{13}C) using CDCl$_3$ as solvent. Quantitative ^{13}C NMR data were obtained with a pulse delay of 2.5 s (90° pulse); Chromium tris(acetylacetonate), c = 0.02 M, was used as relaxant. The relative error in determination of the components was 4.6%. The two-dimensional NMR spectra (HETCOR and NOESY) were obtained on a Bruker DPX-400 spectrometer at 400.13 (^{1}H) and 100.6 MHz (^{13}C). The IR spectra were measured on an IFS 25 instrument in KBr. The UV spectra were recorded on a Specord UV-Vis spectrophotometer. The progress of reactions was monitored, and the purity of products was checked, by TLC on Silufol UV-254 plates using chloroform–ethyl acetate (3 : 1) as eluent.

Reaction of bis[5,5-dimethyl-3-(4-oxa-1-azoniacyclohexylidene)-1-cyclohexenyl] sulfide diperchlorate (I) with H$_2$O. *a.* To a solution of 1.5 g (2.4 mmol) of diperchlorate **I** in 36 ml of acetonitrile, heated to 40°C, we added dropwise while stirring 18 ml of water and then 0.02 ml of triethylamine. The mixture was stirred for 6 h at 50–60°C, cooled, and poured into 120 ml of ice water. The product was extracted into benzene, and the extract was washed with ice water, dried over Na$_2$SO$_4$, and evaporated. The yellow oily residue was kept for 5 days at 5°C, and the crystals thus formed were washed with hexane and dried under reduced pressure. We isolated 0.3 g (45%) of bis(5,5-dimethyl-3-oxo-1-cyclohexenyl) sulfide (**III**) as colorless crystals with mp 80–81°C (published data [2]: mp 176–177°C). ^{1}H NMR spectrum (CDCl$_3$), δ, ppm: 1.08 s (12H, CH$_3$), 2.28 s (4H, C^{4}H$_2$), 2.42 d (4H, C^{6}H$_2$, ^4J = 1.3 Hz), 6.16 t (2H, HC=C, ^4J = 1.3 Hz). IR spectrum, ν, cm^{-1}: 1582 (C=C−S), 1658 (C=O); published data [2]: IR spectrum (CHCl$_3$), ν, cm^{-1}: 1580 (C=C−S), 1660 (C=O). UV spectrum (MeCN), λ_{max}, nm (log ε): 214 (4.18), 275 (4.16), 309 (4.12). Published data [2]: UV spectrum (EtOH), λ_{max}, nm (log ε): 232 (3.96), 278 (3.97), 313 (3.90). Found, %: C 69.20; H 8.06; S 11.15. $C_{16}H_{22}O_2S$. Calculated, %: C 69.06; H 7.91; S 11.51.

b. The reaction was carried out with 1.5 g (2.4 mmol) of salt **I** in 36 ml of acetonitrile, 9 ml of H$_2$O, and 0.06 ml of triethylamine as described above in *a*. The product was extracted into diethyl ether, and the extract was washed with ice water, dried over Na$_2$SO$_4$, and evaporated. The residue, an orange thick oil, was treated with hexane and dried under reduced pressure. We isolated 0.58 g (87%) of a mixture of bis(5,5-dimethyl-3-oxo-1-cyclohexenyl) sulfide (**III**) and 5,5-dimethyl-3-oxo-1-cyclohexenyl 3,3-dimethyl-5-oxo-1-cyclohexenyl sulfide (**IV**) as a light yellow powder with mp 68–70°C. IR spectrum, ν, cm^{-1}: 1582 (C=C−S); 1649, 1668, 1717 (C=O). Found, %: C 69.01; H 7.81; S 11.69. $C_{16}H_{22}O_2S$. Calculated, %: C 69.06; H 7.91; S 11.51.

^1H and ^{13}C NMR spectra of compounds **II**, **III**, and **IV**

Atom no.	**II**		**III**		**IV**	
	δ_C, ppm	δ, ppm (*J*, Hz)	δ_C, ppm	δ, ppm (*J*, Hz)	δ_C, ppm	δ, ppm (*J*, Hz)
C^1	148.53		155.11		161.53	
C^2	138.56	6.92 t ($^4J_{2,6}$ = 1.2)	129.00	6.10 t ($^4J_{2,6}$ = 1.3)	119.58	5.70 t ($^4J_{2,6}$ = 1.2)
C^3	232.61		196.21		195.59	
C^4	59.70	2.77 s	50.69	2.28 s	50.83	2.18 s
C^5	34.58		34.01		33.94	
C^6	45.12	2.34 d ($^4J_{2,6}$ = 1.2)	44.56	2.39 d ($^4J_{2,6}$ = 1.3)	43.72	2.25 br.s
C^7	148.53		155.11		122.05	
C^8	138.56		129.00		43.27	2.95 d ($^4J_{8,12}$ = 1.7)
C^9	232.61		196.21		206.34	
C^{10}	59.70		50.69		52.15	2.35 s
C^{11}	34.58		34.01		37.49	
C^{12}	45.12		44.56		151.09	6.30 t ($^4J_{12,8}$ = 1.7)
C^{13}	27.10	1.07 s	27.77	1.06 s	27.78[a]	1.08 s
C^{14}	27.10		27.77		28.74[a]	0.99 s

[a] Alternative assignment is possible.

Hydrolysis of bis(5,5-dimethyl-3-thioxo-1-cyclohexenyl) sulfide (II). To a suspension of 0.1 g (0.3 mmol) of dithioxo sulfide **II** in 10 ml of acetonitrile, cooled to 0–5°C, we added dropwise with stirring 2 ml of water and then a solution of 0.01 ml of triethylamine in 1 ml of acetonitrile. The mixture was stirred for 8 h at 0–5°C, left overnight at 5°C, filtered, and poured into 30 ml of ice water. The product was extracted into diethyl ether, and the extract was washed with ice water, dried over Na_2SO_4, and evaporated. The residue, a yellow thick oil, was treated with hexane and dried under reduced pressure. We obtained 0.05 g (60%) of a mixture of bis(5,5-dimethyl-3-oxo-1-cyclohexenyl) sulfide (**III**) and 5,5-dimethyl-3-oxo-1-cyclohexenyl 3,3-dimethyl-5-oxo-1-cyclohexenyl sulfide (**IV**) as a light yellow powder with mp 71–73°C. IR spectrum, ν, cm^{-1}: 1582 (C=C–S); 1656, 1670, 1718 (C=O).

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