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Hydrothiolysis of Carbofunctional α,β-Unsaturated Sulfides as an Approach to the Synthesis of 1,7-Dithiocarbonyl Compounds

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Abstract—Bis(1-*N,N*-dimethylimmonio-3-phenylprop-2-en-3-yl) sulfide diperchlorate and (1-*N,N*-dimethylimmonio-3-phenylprop-2-en-3-yl) (5,5-dimethyl-1-morpholiniocyclohex-2-en-3-yl) sulfide diperchlorate react with hydrogen sulfide giving rise to the corresponding 1,7-thioxoimmonio sulfides. Treating with the hydrogen sulfide (1-*N,N*-dimethylimmonio-3-phenylprop-2-en-3-yl) (1-oxo-2-phenyl-inden-3-yl) sulfide perchlorate led to preparation of (1-oxo-2-phenylinden-3-yl) (1-thioxo-3-phenylprop-2-en-3-yl) sulfide. The hydrothiolysis of (5,5-dimethyl-1-morpholiniocyclohex-2-en-3-yl) (1-*N,N*-dimethylimmonio-2-phenylinden-3-yl) sulfide diperchlorate and (5,5-dimethyl-1-morpholiniocyclohex-2-en-3-yl) (1-oxo-2-phenylinden-3-yl) sulfidea perchlorate resulted in products of the sulfide bond cleavage in the initial immonium salts.

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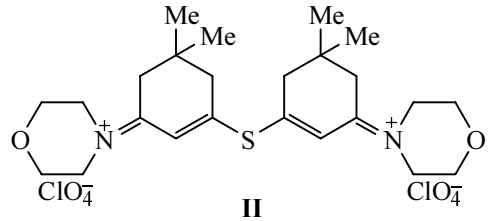
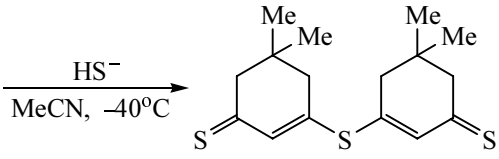
The most efficient among the preparation methods we tested to synthesize the first unsaturated 1,7-dithione, bis(5,5-di-methyl-3-thioxocyclohex-1-enyl) sulfide (**I**), proved to be the hydrothiolysis at low temperature of the corresponding bisimmonium salt **II** [1, 2].



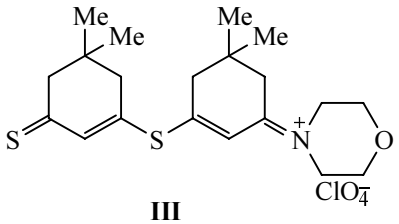
II



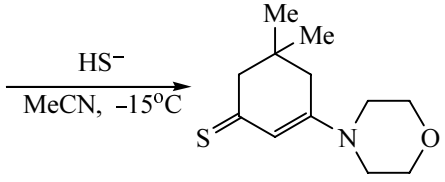
I

In the present study aiming at preparation of new representatives of 1,7-dithioxo-substituted systems and also of their monooxygen analogs we investigated the hydrothiolysis of bisimmonio- and immoniooxo-substituted symmetric and unsymmetrical α,β-unsaturated sulfides containing propenyl, cyclohexenyl, and indenyl substituents.

The hydrothiolysis of immoniothioxo-substituted (5,5-dimethyl-1-morpholiniocyclohex-2-en-3-yl) (5,5-dimethyl-1-thioxocyclohex-2-en-3-yl) sulfide perchlorate (**III**) occurring with a rupture of the C–S bond in the initial compound and resulting in the formation of enaminothioketone **IV** was described in [2].

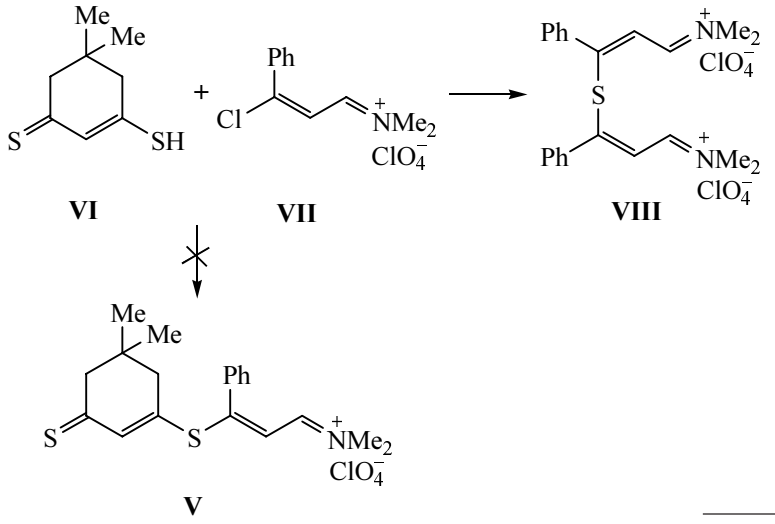


III



IV

We failed to obtain another such sulfide, namely (1-*N,N*-dimethylimmonio-3-phenylprop-2-en-3-yl) (5,5-dimethyl-1-thioxocyclohex-2-en-3-yl) sulfide perchlorate



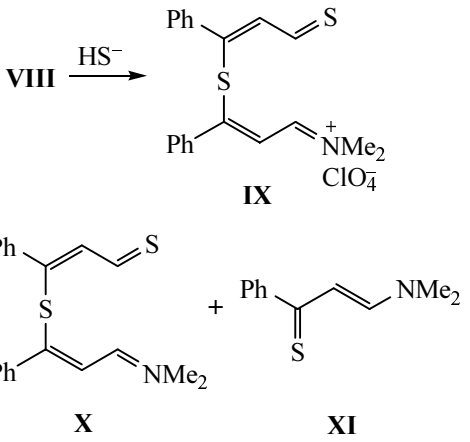
VI **VII** **VIII**

V

(**V**), by reaction of 5,5-dimethyl-3-mercaptocyclohex-2-ene-1-thione (**VI**) with *N*-(3-phenyl-3-chloroprop-2-en-1-ylidene)-*N,N*-dimethylimmonium perchlorate (**VII**). Instead of the expected compound **V** we isolated bis(1-*N,N*-dimethylimmonio-3-phenylprop-2-en-3-yl) sulfide diperchlorate (**VIII**).

The purposeful synthesis of bisimmonio-substituted sulfides was performed applying the reaction of enaminothioketones with immonium haloderivatives perchlorates [3], and immoniooxo-substituted derivatives were prepared by treating the enaminothioketones with 3-bromo-2-phenylinden-1-one [4].

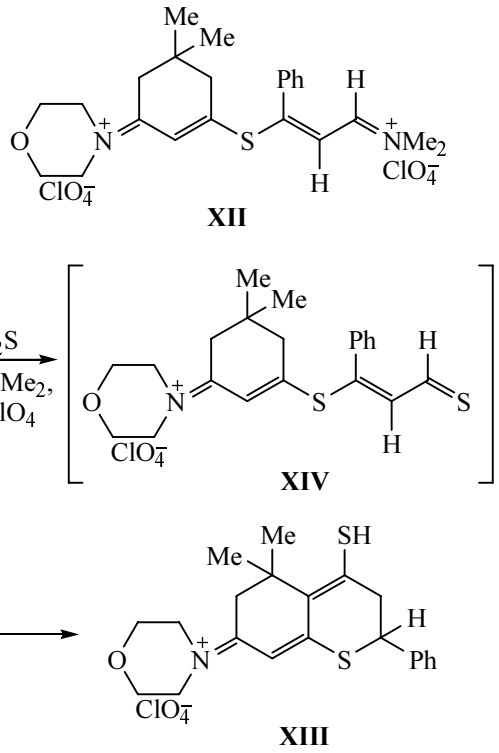
The reaction of symmetric diperchlorate **VIII** [3] with hydrogen sulfide in DMF at –60°C led to the formation of (1-thioxo-3-phenylprop-2-en-3-yl) (1-*N,N*-dimethylimmonio-3-phenylprop-2-en-3-yl) sulfide perchlorate (**IX**), a product of hydrothiolysis of one immonium group in salt **VIII**, and also to the formation of (1-thioxo-3-phenylprop-2-en-3-yl) (1-*N,N*-dimethyamino-3-phenylprop-1-en-3-yl) sulfide (**X**) and of the known 3-*N,N*-dimethylamino-1-phenylprop-2-en-1-thione (**XI**) [5].



IX

X **XI**

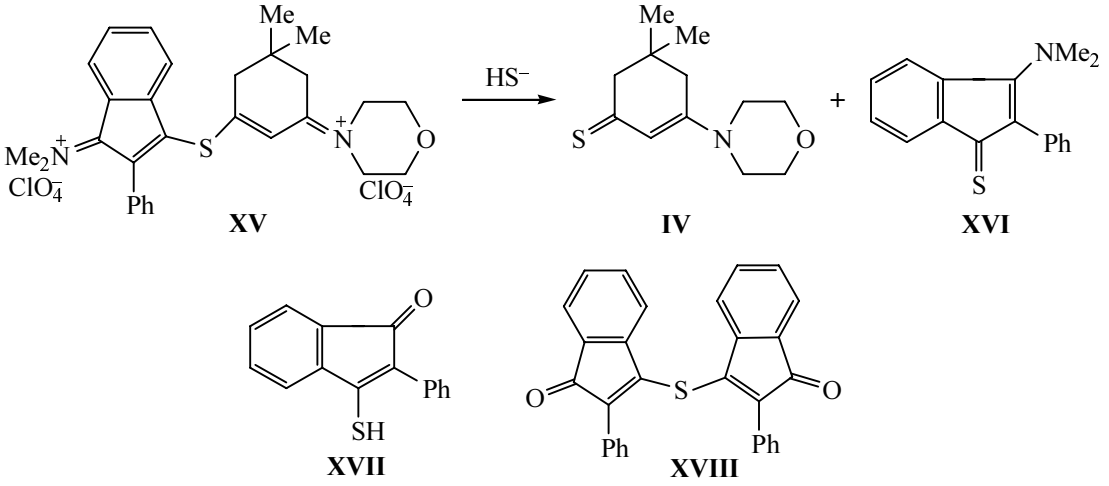
By reaction of (1-*N,N*-dimethylimmonio-3-phenylprop-2-en-3-yl) (5,5-dimethyl-1-morpholinio-cyclohex-2-en-3-yl) sulfid diperchlorate (**XII**) [3] with hydrogen sulfide in DMF we obtained 5,5-dimethyl-4-mercapto-7-morpholinio-2-phenyl-2,3,5,6-tetrahydro-7*H*-thiochromen perchlorate (**XIII**). Its formation may be attributed to the heterocyclization of the primarily arising (1-thioxo-3-phenylprop-2-en-3-yl) (5,5-dimethyl-1-morpholiniocyclohex-2-en-3-yl) sulfide perchlorate (**XIV**). We formerly observed a similar formation of thiochromen derivatives [6].



XII

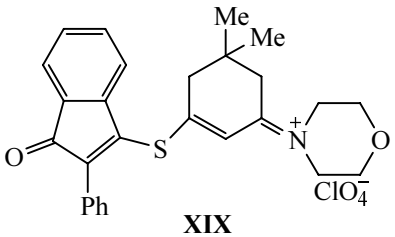
XIV

XIII



The hydrothiolysis of (5,5-dimethyl-1-morpholiniocyclohex-2-en-3-yl) (1-*N,N*-dimethylimmonio-2-phenylindene-3-yl) sulfide diperchlorate (**XV**) in DMF or acetonitrile in the presence of triethylamine at low temperature (–40...–60°C) caused the cleavage of the C–S bond in initial salt **XV** to produce compounds containing cyclohexene or indene fragments. We identified among the reaction products 5,5-dimethyl-3-morpholinocyclohex-2-ene-1-thione (**IV**) [7], 3-*N,N*-dimethylamino-2-phenylindene-1-thione (**XVI**) [8], and also 3-oxo-2-phenyl-1-indenethiol (**XVII**), and bis(1-oxo-2-phenylinden-3-yl) sulfide (**XVIII**) [9].

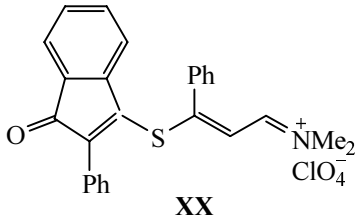
The treating with the hydrogen sulfide of (5,5-dimethyl-1-morpholiniocyclohex-2-en-3-yl) (1-oxo-2-phenylinden-3-yl) sulfide perchlorate (**XIX**) [4] (acetonitrile, triethylamine, –40°C) also resulted in the rupture of the sulfide bond in initial salt **XIX** and in formation of enaminothioketone **IV** [7], oxothiol **XVII**, and dioxosulfide **XVIII** [9].



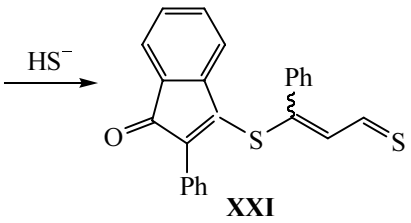
XIX

$\xrightarrow{HS^-}$ **IV** + **XVII** + **XVIII**

(1-*N,N*-Dimethylimmonio-3-phenylprop-2-en-3-yl) (1-oxo-2-phenylinden-3-yl) sulfide perchlorate (**XX**) [4] reacted with the hydrogen sulfide (DMF, –60°C) at the carboiminium group with the retention of the divinyl sulfide fragment giving rise to (1-oxo-2-phenylinden-3-yl (1-thioxo-3-phenylprop-2-en-3-yl) sulfide (**XXI**) as a mixture of two geometric isomers.



XX



XXI

Thus the study of the hydrothiolysis of carbofunctional α,β-unsaturated sulfides demonstrated that the course of the reaction depended on the character of the substituents attached to the fragment C=C–S–C=C. The target 1,7-dithiocarbonyl compound we succeeded to synthesize only from bis-(5,5-dimethyl-1-morpholiniocyclohex-2-en-3-yl) sulfide diperchlorate (**II**) [1]. By the hydrothiolysis of immoniooxo-substituted salt **XX** a monooxygen analog of the dithioxosulfide was obtained. In all other cases formed either 1,7-thioxoimmonio-substituted derivatives or the products of the initial sulfide fragmentation due to the cleavage of the C–S bond.

EXPERIMENTAL

IR spectra were recorded on a spectrophotometer IFS-25 from samples in KBr pellets. ^{1}H NMR spectra were registered on spectrometers Jeol FX-90Q and Bruker

DPX-400, extenal reference HMDS. The reaction progress was monitored and the purity of products obtained was checked by TLC on Silufol UV-254 plates using as eluent a mixture chloroform–ethyl acetate, 3:1.

Reaction of 5,5-dimethyl-3-mercaptocyclohex-2-ene-1-thione (VI) with *N*-(3-phenyl-3-chloroprop-2-en-1-ylidene)-*N,N*-dimethylimmonium perchlorate (VII). To a solution of 0.52 g (3 mmol) of enthiolthione **VI** in 20 ml of anhydrous methanol at 10°C under argon atmosphere was added while stirring 0.88 g (3 mmol) of perchlorate **VII**. The reaction mixture was stirred for 4 h and was left overnight at 5°C. The precipitate formed was filtered off and washed with methanol. We obtained 0.63 g (38%) of bis(1-*N,N*-dimethylimmonio-3-phenylprop-2-en-3-yl) sulfide diperchlorate (**VIII**) as a yellow powder, t.decomp. 178–195°C. The decomposition temperature, IR and ^{1}H NMR spectra of compound **VIII** were identical to those published in [3]. Found, %: C 48.16; H 4.73; N 5.18; S 5.81. $C_{22}H_{26}Cl_2N_2O_8S$. Calculated, %: C 48.09; H 4.74; N 5.10; S 5.83.

Hydrothiolysis of bis(1-*N,N*-dimethylimmonio-3-phenylprop-2-en-3-yl) sulfide diperchlorate (VIII). Into a solution of 0.38 g (0.7 mmol) of salt **VIII** in 4 ml of DMF at –60°C was passed for 4 h a flow of dry hydrogen sulfide. The reaction mixture was poured into 50 g of ice-water mixture. The separated precipitate was filtered off, repeatedly washed with water, and dried in a vacuum desiccator over P_2O_5. We obtained 18 g of a mixture containing (1-thioxo-3-phenylprop-2-en-3-yl) (1-*N,N*-dimethylimmonio-3-phenylprop-2-en-3-yl) sulfide perchlorate (**IX**) and (1-thioxo-3-phenylprop-2-en-3-yl)(1-*N,N*-dimethyl-amino-3-phenylprop-1-en-3-yl)sulfide (**X**) as an orange powder. IR spectrum, ν, cm^{-1}: 623 and 1092 (ClO_4), 1545, 1601 (C=C–S, C=C), 1644 (C=N$^+$). ^{1}H NMR spectrum (CD_3CN), δ, ppm: 3.50 and 3.70 s [6H, =N$^+$(CH_3)$_2$], 6.60 d (1H, =C<u>H</u>CH=N$^+$), 7.01 d (1H, =C<u>H</u>CH=S), 8.50 d (1H, CH=S), 8.90 d (1H, HC=N$^+$) (for compound **IX**); 2.64 s (1H, CH), 3.04 and 3.24 s [6H, N(CH_3)$_2$], 6.88 d (1H, C<u>H</u>=CHN), 6.99 d (1H, =C<u>H</u>CH=S), 8.32 d (1H, CH=S), 8.80 d (1H, =CHN) (for compound **X**); 7.37 m (10H, H_{arom}). The coupling constant $^3J_{\nu-\nu}$ for groups =CHCH= in compounds **IX** and **X** has the same value equal to 6.8 Hz. The filtrate from compounds **IX** and **X** was treated with chloroform, the chloroform solution was washed with water and dried over Na_2SO_4. On evaporation of the solvent the residue (0.07 g) was investigated by TLC (eluent ethyl acetate) and IR spectroscopy [ν(C=S) 1117 cm^{-1}]; by comparison with an authentic substance [5] the presence of 3-*N,N*-dimethyl-amino-1-phenylprop-2-ene-1-thione (**XI**) was detected.

Hydrothiolysis of (1-*N,N*-dimethylimmonio-3-phenylprop-2-en-3-yl) (5,5-dimethyl-1-morpholiniocyclohex-2-en-3-yl) sulfide diperchlorate (XII). Into a solution of 0.24 g (0.4 mmol) of salt **XII** in 5 ml of DMF at 20°C was passed for 30 min a flow of dry hydrogen sulfide. The reaction mixture was poured into 30 g of ice-water mixture. The separated precipitate was filtered off, washed with water, and dried in a vacuum desiccator over $CaCl_2$. We obtained 0.15 g (80%) of 5,5-dimethyl-4-mercapto-7-morpholinio-2-phenyl-2,3,5,6-tetrahydro-7*H*-thiochromen perchlorate (**XIII**) as a powder of mustard color, mp 123–125°C. IR spectrum, ν, cm^{-1}: 623 and 1096 (ClO_4), 1556, 1576 (C=C), 1651 (C=N$^+$), 2484 (SH). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 0.82 and 0.87 s (6H, CH_3), 2.44 m (2H, 6-CH_2), 2.64 m (2H, 3-CH_2), 3.55 s (1H, SH), 3.66 m (1H, 2-CH), 3.67 and 3.83 m (8H, morpholine), 6.30 s (1H, HC=), 7.35–7.57 m (5H, C_6H_5). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 27.4, 27.6 (CH_3), 34.5 (C^5), 43.0 [=N$^+$(CH_2)$_2$], 50.3 (C^6), 50.9 (C^3), 63.4 [O(CH_2)$_2$], 66.1 (C^2), 110.0 (C=N$^+$), 122.1 (=C–H), 127–140 (C_{Ph}, C^4, C^9, C^{10}). Found, %: C 54.20; H 5.45; Cl 6.84; N 2.17; S 13.82. $C_{21}H_{26}ClNO_5S_2$. Calculated, %: C 53.45; H 5.51; Cl 7.53; N 2.97; S 13.57.

(5,5-Dimethyl-1-morpholiniocyclohex-2-en-3-yl) (1-N,N-dimethylimmonio-2-phenylinden-3-yl) sulfide diperchlorate (XV). To a solution of 0.33 g (1 mmol) of 5,5-dimethyl-3-chlorocyclohex-2-ene-1-morpholinium perchlorate (**XXII**) [10] in 15 ml of anhydrous methanol was added 0.15 g (1.2 mmol) of $NaClO_4$, and while stirring and heating to 40–45°C was added by portions 0.27 g (1 mmol) of 3-*N,N*-dimethylamino-2-phenylindene-1-thione (**XVI**) [8]. The reaction mixture was stirred for 3 h, then cooled, the separated dark-red precipitate was filtered off, washed with anhydrous methanol, and dried in a vacuum desiccator over P_2O_5. Yield 0.42 g (64%), mp 190–193°C. IR spectrum, ν, cm^{-1}: 623 and 1091 (ClO_4), 1586 (C=C–S), 1566, 1647 (C=N$^+$). ^{1}H NMR spectrum (DMF-d_6), δ, ppm: 1.06 s (6H, CH_3), 2.72 m (2H, 4-CH_2), 2.88 m (2H, 6-CH_2), 3.50 s [6H, =N$^+$(CH_3)$_2$], 3.70 and 3.94 m ($CH_2N^+CH_2$ and CH_2OCH_2), 6.94 s (1H, HC=), 7.55 m (9H, H_{arom}). Found, %: C 52.07; H 5.61; Cl 11.51; N 4.16; S 4.77. $C_{29}H_{34}Cl_2N_2O_9S$. Calculated, %: C 52.97; H 5.17; Cl 10.81; N 4.26; S 4.87.

Hydrothiolysis of compound XV. *a.* Into a solution of 1.0 g (1.5 mmol) of salt **XV** in 18 ml of DMF was passed at –60°C for 7 h a flow of dry hydrogen sulfide. The reaction mixture was poured into 100 g of ice-water mixture. The separated bright-brown precipitate was filtered off, repeatedly washed with ice water, and dried in a vacuum desiccator over P_2O_5 at 5°C. We obtained

a mixture of compounds (0.4 g) containing according to TLC and IR spectrum 3-*N,N*-dimethylamino-2-phenylindene-1-thione (**XVI**) [8], 3-oxo-2-phenylindene-1-thiol (**XVII**) [9], bis(1-oxo-2-phenylinden-3-yl) sulfide (**XVIII**) [9], and also unidentified substances. IR spectrum, ν, cm^{-1}: 1253 (C=S) (compound **XVI**), 1689 (C=O), 2537 (SH) (compound **XVII**), 1597 (C=C–S), 1707 (C=O) (compound **XVIII**).

The filtrate was treated with chloroform, the chloroform solution was washed with water and dried with Na_2SO_4. On evaporating the solvent the residue was dissolved in ethyl acetate and passed through a column packed with silica gel (70/230 mesh), eluent chloroform–ethyl acetate, 3:1. We obtained 0.26 g (77%) of orange crystals of 5,5-dimethyl-3-morpholinocyclohex-2-ene-1-thione (**IV**), mp 159–162°C (publ.: mp 161–162°C [7]). IR spectrum, ν, cm^{-1}: 1116 (C=S), 1522 (C=C).

b. Into a solution of 0.3 g (0.45 mmol) of diperchlorate **XV** in 10 ml of anhydrous acetonitrile was passed at –40°C for 20 min a flow of dry hydrogen sulfide, then 0.01 ml of triethylamine was added, and a flow of dry hydrogen sulfide was passed at the same temperature for 2 h. The reaction mixture was poured into 50 g of a mixture ice-chloroform. The chloroform layer was separated, washed with water, and dried with Na_2SO_4. The solvent was partly evaporated in a vacuum, and the residue was subjected to column chromatography on silica gel (70/230 mesh), eluent chloroform–ethyl acetate, 2:1. We obtained 0.08 g (40%) of red crystals of bis(oxoindenyl) sulfide **XVIII**. IR spectrum, ν, cm^{-1}: 1600 (C=C–S), 1709 (C=O) and 0.04 g (40%) of orang crystals of thioketone **IV**. IR spectrum, ν, cm^{-1}: 1117 (C=S), 1523 (C=C) (cf with method *a*).

Hydrothiolysis of (5,5-dimethyl-1-morpholiniocyclohex-2-en-3-yl) (1-oxo-2-phenylinden-3-yl) sulfide perchlorate (XIX). Into a solution of 0.25 g (0.5 mmol) of perchlorate **XIX** in 20 ml of anhydrous acetonitrile was passed at –40°C for 15 min a flow of dry hydrogen sulfide, then 0.01 ml of triethylamine was added, and a flow of dry hydrogen sulfide was passed at the same temperature for 10 h. The reaction mixture was flushed with argon at –40°C till complete removal of the hydrogen sulfidea. The solution over the precipitate was removed with a pipette, the precipitate was washed with cooled acetonitrile and dried in a vacuum at low temperature. We obtained 0.05 g of a red powder containing a mixture of oxoindenethiol **XVII** and dioxosulfide **XVIII**. IR spectrum, ν, cm^{-1}: 1684 (C=O), 2536 (SH) (oxothiol **XVII**); 1595 (C=C–S), 1705 (C=O) (dioxosulfide **XVIII**) (cf. [9]).

In the reaction mixture separated from the precipitate of compounds **XVII** and **XVIII** we detected by means of TLC and IR spectroscopy [ν, cm^{-1}: 1116 (C=S), 1522 (C=C)] the presence of enaminothioketone **IV** [7].

Hydrothiolysis of (1-*N,N*-dimethylimmonio-3-phenylprop-2-en-3-yl) (1-oxo-2-phenylinden-3-yl) sulfide perchlorate (XX). Into a solution of 0.25 g (0.5 mmol) of salt **XX** in 18 ml of DMF a flow of dry hydrogen sulfide was passed at –60°C for 6 h. The reaction mixture was poured into 50 g of ice-water mixture. The separated precipitate was filtered off, washed with ice water, dried in a vacuum desiccator over P_2O_5, and then subjected to chromatography on silica gel (40/100 mesh, solvent and eluent chloroform–ethyl acetate, 3:1). We obtained 0.1 g (55%) of (1-oxo-2-phenylinden-3-yl) (1-thioxo-3-phenylprop-2-en-3-yl) sulfide (**XXI**) as orange crystals, mp 77–80°C. IR spectrum, ν, cm^{-1}: 1595 (C=C–S), 1662 (C=C), 1707 (C=O). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 6.20 and 6.37 d (1H, HC=), 6.8–7.6 m (14H, H_{arom}), 9.26 and 10.40 d (1H, CH=S). Found, %: C 74.12; H 4.20; S 16.78. $C_{24}H_{16}OS_2$. Calculated, %: C 75.00; H 4.17; S 16.67.

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