ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2020, Vol. 46, No. 1, pp. 28–36. © Pleiades Publishing, Ltd., 2020.
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Synthesis of Sulfur-Containing Cymantrene Derivatives Having Potential Photo- and Electrochemical Properties

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Received July 3, 2019; revised August 5, 2019; accepted August 15, 2019

Abstract—With the aim of preparing of sulfur-containing derivatives of cymantrene, the hydrolysis of isothiouronium salts of alkylcymantrenes was studied under various conditions as well as subsequent chemical transformations of hydrolysis products. It was found that alkylcymantrenylthiols can be prepared either by hydrolysis of isothiouronium salts under the action of NaOH in a EtOH-acetone (4 : 1) mixture for 2 h or by the reduction of the corresponding disulfides by $LiAlH_4$ formed in the course of this reaction in good yield for 6 h. Electrochemical properties of disulfides $Cym(CHCH_3)SS(CHCH_3)Cym$ ($Cym = C_5H_4Mn(CO)_3$) in solution before and after irradiation with a Hg lamp at λ365 nm were studied. The structures of the compounds were established by the X-ray analysis ($CymCH(CH_3)SSCH(CH_3)Cym$ (**I**) (CIF file CCDC no. 1921952) and $CymCH_2SCH_2Cym$ (**II**) (CIF file CCDC no. 1921953)).

Keywords: cymantrene, isothiouronium salts of manganese complexes, disulfides, electrochemical properties, irradiation, X-ray diffraction analysis

DOI: 10.1134/S1070328420010030

INTRODUCTION

The studies of the properties of various organometallic compounds, in particular, those based on cyclopentadienyl manganese tricarbonyl (cymantrene $Cym = C_5H_4Mn(CO)_3$) showed their efficiency when using in the catalytic [1], photochemical [2], photochromic [3], biological [4], chemosensor [5], and other systems [6]. Thus, the development of methods for the introduction of diverse functional groups into the cymantrene molecule is an urgent task. Thiols and sulfides are active groups readily undergoing alkylation [7] and transalkylation reactions [8] and oxidation and reduction processes [9]. These groups participating in the photoreactions [10] are important for maintaining the oxidation–reduction balance in proteins [11] and are used for the development of fluorescent bioprobes [12, 13] and traps of heavy metal ions [14].

In this work, in order to synthesize the sulfur-containing cymantrene derivatives, namely, thiols, disulfides, and sulfides, $CymCH(CH_3)SSCH(CH_3)Cym$ (**I**) and $CymCH_2SCH_2Cym$ (**II**), we studied the hydrolysis (under various conditions) of the corresponding isothiouronium salts of alkylcymantrenes, which is the key step in the preparation of the cymantrenethio derivatives. The chemical transformations of the hydrolysis products and their derivatives were also carried out.

EXPERIMENTAL

Anhydrous tetrahydrofuran (THF) obtained by distillation over sodium benzophenone ketyl or sodium in an argon atmosphere was used. Commercially available and applied in synthetic procedures isoamyl bromide (Aldrich) and hydrazine hydrate (Aldrich) were used as received. Bromomethylcymantrene ($CymCH_2Br$) (**III**) and bromoethylcymantrene ($CymCH(CH_3)Br$) (**IV**) were synthesized according to the described procedure [15].

^1H and ^{13}C NMR spectra were recorded on a Bruker Avance 400 spectrometer (400.13 and 100.61 MHz, respectively) using the following solvents as internal standards: acetone, 2.05; chloroform, 7.26; and DMSO, 2.50 ppm (δ relative to Me_4Si). The signals in the ^1H and ^{13}C NMR spectra were determined by JMODECHO and 2D correlation analysis experiments, including COSY and NOESY. IR spectra were recorded on a Bruker IR Fourier spectrometer with a resolution of 2 cm^{-1} in KBr cells. Mass spectra (electron impact ionization) were detected on Kratos MS 890 and Finnigan POLARIS Q spectrometers at 70 eV. The course of the reactions and purity of the products were monitored by analytical thin layer chromatography (TLC) on the Silufol UV-245 plates (Kavalier). Silica gel 60 (Merck, grain size 0.040–0.063 mm) was used for column chromatography.

Synthesis of 2-cymantrenylmethyl-2-thiopseudoureas hydrobromide (V · HBr). Thiourea (0.9 g, 11.1 mmol) was added with stirring to a solution of compound **III** (3.1 g, 10.4 mmol) in acetone (25 mL) under an argon atmosphere. The reaction mixture was stirred at 40°C for 3 days. The solvent was removed in vacuo, and the residue was washed with EtOAc. The yield 3.7 g (96%).

For $C_{10}H_{10}N_2O_3SBrMn$

Anal. calcd., %	C, 32.19	H, 2.70	N, 7.52	S, 8.59	Br, 21.41	Mn, 14.7
Found, %	C, 32.21	H, 3.00	N, 7.89	S, 8.78	Br, 21.41	Mn, 14.4

^{1}H NMR (25°C, DMSO-d$_6$, δ, ppm (*J*, Hz)): 4.16 (s, 2H, CH$_2$), 5.00 (m, 2H, H–Cp), 5.20 (m, 2H, H–Cp), 9.05 (s, 1.5H, NH), 9.21 (s, 1.5H, NH).

Synthesis of 2-cymantrenyl-1-ethyl-2-thiopseudourea hydrobromide (VI · HBr). Thiourea (1.5 g, 20.0 mmol) was added with stirring to a solution of compound **IV** (5.0 g, 16.2 mmol) in acetone (25 mL) in argon. The reaction mixture was stirred at 40°C for 3 days. The solvent was removed in vacuo, and the residue was washed with EtOAc. The yield 5.9 g (95%).

For $C_{11}H_{12}N_2O_3SBrMn$

Anal. calcd., %	C, 34.13	H, 3.12	N, 7.24	S, 8.24	Br, 20.64	Mn, 14.2
Found, %	C, 33.97	H, 3.03	N, 7.19	S, 8.04	Br, 21.54	Mn, 14.0

^{1}H NMR (25°C, acetone-d$_6$, δ, ppm (*J*, Hz)): 1.76 (d, 3H, CH$_3$, *J* = 6.6), 4.89 (m, 1H, H–Cp), 5.03 (m, 1H, H–Cp), 5.12 (q, 1H, CH, *J* = 6.6), 5.35 (m, 1H, H–Cp), 5.40 (m, 1H, H–Cp), 8.99 (s, 1.5H, NH), 10.02 (s, 1.5H, NH).

General procedure for the hydrolysis of isothioureas (A). A solution of NaOH (2 equiv) in H$_2$O (10 mL) was added to a solution of the corresponding isothiourea **V** · HBr or **V** · HBr (1 equiv) dissolved in 40 mL of the corresponding solvent (EtOH–acetone mixture in various ratios). The reaction mixture was stirred on reflux for 2–6 h. Then H$_2$O (100 mL) was added, and the aqueous solution was extracted with EtOAc (3 × 100 mL). The organic layers were washed with water and a saturated solution of NaCl and dried over Na$_2$SO$_4$.

Synthesis of cymantrenylmethylthiol (VII) was carried out according to the general procedure of hydrolysis of isothioureas (A) starting from compound **V** · HBr (3.0 g, 8.0 mmol) and NaOH (0.6 g, 15.7 mmol) in a mixture of solvents EtOH–acetone (4 : 1,) and the reaction mixture was refluxed for 2 h. The yield was 1.2 g (60%).

For $C_9H_7O_3SMn$

Anal. calcd., %	C, 43.46	H, 2.56	S, 12.61
Found, %	C, 43.21	H, 2.82	S, 12.82

^{1}H NMR (25°C, acetone-d$_6$, δ, ppm (*J*, Hz)): 3.61 (s, 2H, CH$_2$), 4.94 (m, 2H, H–Cp), 5.13 (m, 2H, H–Cp).

Synthesis of cymantrenyl-1-ethylthiol (VIII) was carried out according to the general procedure of hydrolysis of isothioureas (A) starting from compound **VI** · HBr (6.0 g, 15.7 mmol) and NaOH (1.2 g, 31.4 mmol) in a mixture of solvents EtOH–acetone (4 : 1,) and the reaction mixture was refluxed for 2 h. The yield 0.8 g (20%).

For $C_{10}H_9O_3SMn$

Anal. calcd., %	C, 45.61	H, 3.58	S, 11.94
Found, %	C, 45.50	H, 3.41	S, 12.12

^{1}H NMR (25°C, acetone-d$_6$, δ, ppm (*J*, Hz)): 3.61 (s, 2H, CH$_2$), 4.94 (m, 2H, H–Cp), 5.13 (m, 2H, H–Cp).

Synthesis of di(cymantrenylmethyl) disulfide (IX) was carried out according to the general procedure of hydrolysis of isothioureas (A) starting from compound **V** · HBr (1.0 g, 2.7 mmol) and NaOH (0.2 g, 5.3 mmol) in a mixture of solvents EtOH–acetone (1 : 1,) and the reaction mixture was refluxed for 6 h. The yield 0.5 g (36%), mp 78–79°C (hexane–EtOAc).

For $C_{18}H_{12}O_6S_2Mn_2$

Anal. calcd., %	C, 43.37	H, 2.41	S, 12.85	Mn, 22.1
Found, %	C, 43.40	H, 2.31	S, 12.93	Mn, 21.9

^{1}H NMR (25°C, CDCl$_3$, δ, ppm (*J*, Hz)): 3.42 (s, 2H, CH$_2$ 4.75 (m, 2H, H–Cp), 4.85 (m, 2H, H–Cp). ^{13}C NMR (25°C, CDCl$_3$, δ, ppm (*J*, Hz)): 30.17 (CH$_2$), 82.14 (2C–Cp), 83.28 (2C–Cp), 101.29 (C*i*–Cp), 224.83 (3CO).

Synthesis of di(cymantrenyl-1-ethyl) disulfide (I) was carried out according to the general procedure of hydrolysis of isothioureas (A) starting from compound **VI** · HBr (2.0 g, 8.4 mmol) and NaOH (0.4 g, 15.7 mmol) in a mixture of solvents EtOH–acetone (1 : 1), and the reaction mixture was refluxed for 6 h.

Isomer 1: yield 1.6 g (38%), mp 67–68°C (hexane–EtOAc).

For $C_{20}H_{16}O_6S_2Mn_2$

Anal. calcd., %	C, 45.64	H, 3.06	S, 12.18	Mn, 20.9
Found, %	C, 45.58	H, 3.21	S, 11.98	Mn, 20.8

^{1}H NMR (25°C; $CDCl_3$; δ, ppm (*J*, Hz)): 1.53 (d, 6H, CH_3, *J* = 7.0), 3.46 (q, 2H, CH, *J* = 7.0), 4.63 (m, 2H, H–Cp), 4.80 (m, 2H, H–Cp), 4.86 (m, 2H, H–Cp), 4.93 (m, 2H, H–Cp). ^{13}C NMR (25°C; $CDCl_3$; δ, ppm (*J*, Hz)): 20.07 (2C–CH_3), 43.06 (2CH), 79.47 (C–Cp), 83.13 (C–Cp), 83.45 (C–Cp), 83.52 (C–Cp), 105.12 (C*i*–Cp), 224.58 (3C–CO).

Isomer 2: yield 1.5 g (35%), mp 82–83°C (hexane–EtOAc).

For $C_{20}H_{16}O_6S_2Mn_2$

Anal. calcd., %	C, 45.64	H, 3.06	S, 12.18	Mn, 20.9
Found, %	C, 45.41	H, 3.01	S, 11.80	Mn, 20.6

^{1}H NMR (25°C; $CDCl_3$; δ, ppm (*J*, Hz)): 1.52 (d, 6H, CH_3, *J* = 7.0), 3.45 (q, 2H, CH, *J* = 7.0), 4.62 (m, 2H, H–Cp), 4.81 (m, 2H, H–Cp), 4.89 (m, 2H, H–Cp), 4.92 (m, 2H, H–Cp). ^{13}C NMR (25°C; $CDCl_3$; δ, ppm (*J*, Hz)): 20.10 (2C–CH_3), 43.02 (2C–CH), 79.43 (C–Cp), 83.14 (C–Cp), 83.43 (2C–Cp), 105.25 (C*i*–Cp), 224.59 (3C–CO).

Synthesis of (dicymantrenylmethyl) sulfide (II) was carried out according to the general procedure of hydrolysis of isothioureas (A) starting from compound **V** (1.0 g, 2.7 mmol) and NaOH (0.2 g, 5.3 mmol) in a mixture of solvents EtOH–acetone (1 : 1), and the reaction mixture was refluxed for 6 h. The yield 0.25 g (20%), mp 81–82°C (hexane–EtOAc).

For $C_{18}H_{12}O_6SMn_2$

Anal. calcd., %	C, 46.37	H, 2.59	S, 6.88	Mn, 23.6
Found, %	C, 46.36	H, 2.51	S, 6.84	Mn, 23.4

^{1}H NMR (25°C; $CDCl_3$; δ, ppm (*J*, Hz)): 3.38 (s, 2H, CH_2), 4.69 (m, 2H, H–Cp), 4.77 (m, 2H, H–Cp). ^{13}C NMR (25°C; $CDCl_3$; δ, ppm (*J*, Hz)): 36.65 (C–CH_2), 82.39 (2C–Cp), 83.81 (2C–Cp), 99.79 (C*i*–Cp), 224.52 (3C–CO).

Synthesis of cymantrenylmethyl isoamyl sulfide (X). Compound **VII** (2.0 g, 8.0 mmol) in dimethylformamide (DMF) (10 mL) was added with stirring to a suspension of K_2CO_3 (5.5 g, 40 mmol) in DMF (20 mL) in argon, and the mixture was kept for 30 min. Then isoamyl bromide (1.5 mL, 12 mmol) was added dropwise to the reaction mixture, and the mixture was heated at 60°C for 6 h. The resulting reaction mixture was poured to ice water (100 mL), the product was extracted with EtOAc (3 × 75 mL), and the organic layer was dried over $MgSO_4$. The solvent was removed in vacuo, and compound **X** was isolated using column chromatography (hexane–EtOAc (4 : 1) as an eluent). The yield 1.5 g (60%).

For $C_{14}H_{17}O_3SMn$

Anal. calcd., %	C, 52.50	H, 5.35	S, 10.01	Mn, 17.2
Found, %	C, 52.38	H, 5.52	S, 9.86	Mn, 17.0

^{1}H NMR (25°C; acetone-d$_6$, δ, ppm (*J*, Hz)): 0.80 (d, 6H, CH_3, *J* = 6.5), 1.48 (q, 2H, CH_2, *J* = 7.8), 1.68 (m, 1H, CH), 2.61 (t, 2H, CH_2, *J* = 7.6), 3.41 (s, 2H, CH_2–S), 4.88 (m, 2H, H–Cp), 5.01 (m, 2H, H–Cp). ^{13}C NMR (25°C; $CDCl_3$; δ, ppm (*J*, Hz)): 22.29 (2C–CH_3), 27.47 (C–CH), 28.50 (C–CH_2), 30.29 (C–CH_2S), 38.19 (C–CH_2S), 82.06 (2C–Cp), 83.01 (2C–Cp), 102.67 (C*i*–Cp), 224.25 (3C–CO).

Synthesis of cymantrenylethyl isoamyl sulfide (XI) was carried out similarly to that of compound **X** starting from compound **VIII** (2.0 g, 8.0 mmol), K_2CO_3 (5.5 g, 40 mmol), and isoamyl bromide (1.5 mL, 12 mmol). The yield 1.2 g (44%).

For $C_{15}H_{19}O_3SMn$

Anal. calcd., %	C, 53.89	H, 5.73	S, 9.59	Mn, 16.4
Found, %	C, 53.78	H, 5.48	S, 9.09	Mn, 16.5

^{1}H NMR (25°C; $CDCl_3$; δ, ppm (*J*, Hz)): 0.92 (d, 6H, CH_3, *J* = 6.5), 1.45 (m, 2H, CH_2, *J* = 7.8), 1.52 (d, 3H, CH_3), 1.68 (m, 1H, CH), 2.55 (m, 2H, CH_2), 3.41 (m, 1H, CH–S), 4.59 (m, 1H, H–Cp), 4.75 (m, 1H, H–Cp), 4.79 (m, 1H, H–Cp), 4.90 (m, 1H, H–Cp). ^{13}C NMR (25°C; $CDCl_3$; δ, ppm (*J*, Hz)): 21.65 (C–CH_3), 22.28 (2C–CH_3), 27.57 (CH), 29.17 (C–CH_2), 36.81 (C–CH), 38.34 C–CH_2S), 79.27 (C–Cp), 82.78 (C–Cp), 82.83 (C–Cp), 82.99 (C–Cp), 107.91 (C*i*–Cp), 225.14 (3C–CO).

General procedure for the reduction of sulfides and disulfides with $LiAlH_4$ (B). The corresponding sulfide or disulfide (1.0 equiv) in 40 mL THF was added dropwise in argon to a suspension of $LiAlH_4$ (1.0 equiv) in THF (100 mL) when the temperature of the reaction mixture was 30°C. The mixture was stirred at room temperature for 3 h. Ether (300 mL) cooled to 0°C was added to the reaction mixture. The mixture was neutralized with a saturated solution of NH_4Cl (25 mL) and acidified with a 15% solution of HCl to pH 5.5. The precipitate was decanted and dissolved in 15% HCl, and the solution was extracted with EtOAc (3 × 200 mL). The organic layers were joined, washed with H_2O (2 × 200 mL), dried over Na_2SO_4, and evaporated. The residue was purified by column chromatography using a hexane–EtOAc (2 : 1) system as a solvent.

General procedure for the preparation of asymmetric sulfides from isothiouronium salts in the presence of KOH and hydrazine hydrate (C). The corresponding

Table 1. Crystallographic data and structure refinement parameters for compounds **I** and **II**

Parameter	Value	
	I	**II**
FW	526.33	466.22
T, K	120	120
Crystal system	Orthorhombic	Monoclinic
Space group	$P2_12_12_1$	$P2_1/c$
Z	4	4
a, Å	6.9630(4)	7.1315(6)
b, Å	13.6145(7)	10.7852(8)
c, Å	22.8148(12)	23.2587(18)
β, deg	90	96.5250(10)
V, Å^3	2162.8(2)	1777.3(2)
ρ_{calc}, g cm^{-3}	1.616	1.742
μ, cm^{-1}	13.94	15.71
F(000)	1064	936
$2\theta_{max}$, deg	50	50
Number of measured reflections	26421	22972
Number of independent reflections	5758	5515
Number of reflections with $I > 2\sigma(I)$	5363	4903
Number of refined parameters	274	244
R_1, wR_2 ($I > 2\sigma(I)$)	0.0361, 0.0826	0.0324, 0.0799
R_1, wR_2 (for all reflections)	0.0397, 0.0849	0.0378, 0.0837
GOOF	0.999	1.032
Residual electron density (max/min), e Å^{-3}	1.428/–0.732	0.628/–0.658

bromide (1 equiv) was added to isothiouronium salt (1 equiv), and a solution of KOH (2 equiv) in hydrazine hydrate (6 mL) was slowly added with stirring. The mixture was stirred at 20–25°C for 11 h and extracted with dichloromethane. The extract was dried over $MgSO_4$. The product was purified by column chromatography using a hexane–EtOAc (3 : 1) system as an eluent. The spectral characteristics and elemental analysis data were completely identical to those of the described above asymmetric sulfides.

General procedure for the preparation of symmetric sulfides from cymantrenylalkyl bromides in the presence of ethanolamine and sulfur (D). Powdered sulfur (3 equiv) was added to a mixture of monoethanolamine (1 equiv) and hydrazine hydrate (10 equiv). The mixture was stirred at 80–85°C for 2 h and cooled down to room temperature. The corresponding cymantrenylalkyl bromide (3 equiv) was added by portions with stirring. The reaction mixture was stirred at room temperature for 6 h. The products were extracted with CH_2Cl_2, dried over $MgSO_4$, and purified by column chromatography using a hexane–EtOAc (3 : 1) system as an eluent followed by crystallization.

X-ray diffraction analysis. Experimental data sets were obtained on a SMART APEX II diffractometer [16] (graphite monochromator, $\lambda(\text{Mo}K_\alpha)$ = 0.71073 Å, ω scan mode). The structures were solved by a direct method and refined in the full-matrix anisotropic approximation for F^2 for non-hydrogen atoms. The positions of the hydrogen atoms were calculated from geometric concepts and refined isotropically by imposing restraints on the C–H bond lengths and their equivalent thermal parameters (U_{eq}(H)). For the methyl groups, the C–H distances were fixed to be 0.96 Å and $U_{eq}(\text{H}) = 1.5\ U_{eq}(\text{C})$, where U_{eq}(C) is the carbon atom of the methyl group. In the case of other hydrogen atoms, these values were 0.92 Å and 1.2 U_{eq}(C). All calculations were performed using the SHELTL PLUS 5.1 and SHELX-2014 program packages [17, 18]. The main crystallographic data and parameters of X-ray diffraction experiments for compounds **I** and **II** are presented in Table 1.

The coordinates of atoms and other parameters for the structures of compounds **I** and **II** were deposited with the Cambridge Crystallographic Data Centre (CIF files CCDC nos. 1921952 and 1921953 for compounds **I**

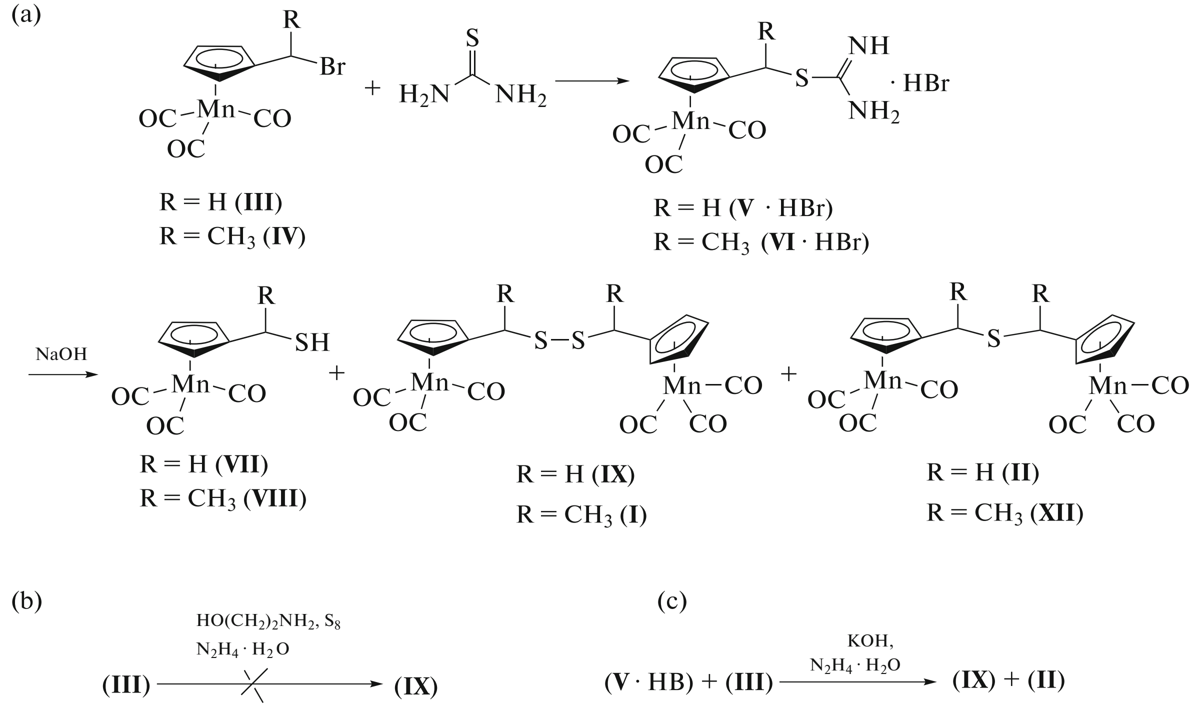
Table 2. Ratio of products **IX** to **II** in the alkaline hydrolysis of isothiouronium salt **V**

Reaction time, h	Ratio EtOH : acetone		
	4 : 1	1 : 1	1 : 4
2	5 : 1	2 : 1	3 : 1
4	6 : 1	2 : 1	4 : 1
6	6 : 1	2 : 1	4 : 1

and **II**, respectively); deposit@ccdc.cam. ac.uk or http://www.ccdc.cam.ac.uk/data_request/ cif).

RESULTS AND DISCUSSION

Cymantrenylalkylthiols were synthesized by a standard method used for the preparation of benzylthiols [19] and hydrolysis of the corresponding isothiouronium salts of alkylcymantrenes. Isothiouronium salts $CymCH_2SC(NH)NH_2 \cdot HBr$ (**V** · HBr) and $CymCH(CH_3)SC(NH)NH_2 \cdot HBr$ (**VI** · HBr) were synthesized in the quantitative yield from compounds **III** and **IV** and thiourea (Scheme 1a). Their subsequent hydrolysis in the presence of NaOH on reflux was carried out, unlike the earlier described procedure [19], in organic solvents, because the cymantrenyl salts are absolutely insoluble in water. The hydrolysis of compounds **V** · HBr and **VI** · HBr in an EtOH–acetone (4 : 1) mixture for 2 h affords cymantrenylalkylthiols $CymCH_2SH$ (**VII**) and $CymCH(CH_3)SH$ (**VIII**) in 60 and 20% yields, respectively (Scheme 1a). However, by-products were formed together with thiols **VII** and **VIII**.



Scheme 1.

A change in the hydrolysis conditions (reaction time and ratio of solvents) made it possible to shift the reaction direction to these or other products (Table 2). For example, the hydrolysis of compound **V** · HBr in an EtOH–acetone (1 : 1) mixture of solvents for 2 h predominantly affords thiol **VII** (54% yield), and the yield of by-products $CymCH_2SSCH_2Cym$ (**IX**) and **II** is low (12% for compound **IX** and 7% for compound **II**), whereas their ratio is 2 : 1 (Table 2). The elongation of the reaction time to 6 h results in the formation of products **IX** and **II** only (36% yield for compound **IX** and 20% for compound **II**) (Table 2). In the case of hydrolysis of racemic isothiouronium salt **VI** · HBr, only thiol **VIII** and by-product **I** were formed. Reaction product **I** was separated into two fractions, being the *meso* form and a mixture of enantiomers, by reprecipitation from 96% EtOH. A change in the reaction time and ratio of solvents does not lead to the formation of the second product **XII** but changes the ratio of compounds **VIII** : **I** from 1 : 1 on reflux for 2 h to 0 : 1 when the reaction is carried out for 6 h. Thus, in both cases, the elongation of the hydrolysis time to 6 h results in the formation of by-products only.

The structures of all synthesized compounds were proved by ^1H and ^{13}C NMR spectroscopy, mass spectrometry, IR spectroscopy, and elemental analysis.

Table 3. ^{1}H and ^{13}C NMR data for benzyl sulfide, benzyl disulfide, **IX**, and **II**

Compound	^{1}H NMR, ppm CH_2	^{13}C NMR, ppm CH_2
$PhCH_2SCH_2Ph$ [20]	3.58	35.50
$CymCH_2SCH_2Cym$ (**IX**)	3.38	30.17
$PhCH_2SSCH_2Ph$ [21]	3.61	43.38
$CymCH_2SSCH_2Cym$ (**II**)	3.42	36.65

Compounds **I** and **II** were additionally studied by X-ray diffraction analysis. An analysis of compounds **IX** and **II** by the ^{1}H NMR method showed that the signals from the protons of the SCH_2 group and Cp ring almost coincided (Table 3). A substantial difference in the positions of the signals from carbon of the SCH_2 group is observed in the ^{13}C NMR spectra for compounds **IX** and **II**, and the signals are observed at 30.17 and 36.65 ppm, respectively. It is known [20, 21] that the presence of two sulfur atoms in the molecule shifts the signals from carbon of the CH_2 group to a weak field compared to that of the monosulfide. In our case, a similar situation is observed (Table 3). The ^{1}H and ^{13}C NMR spectra for two enantiomeric forms of compound **I** are nearly identical with the maximal difference in chemical shifts equal to 0.02 ppm for all protons in the ^{1}H NMR spectra and 0.13 ppm for the chemical shift for the C_i–Cp carbon atom.

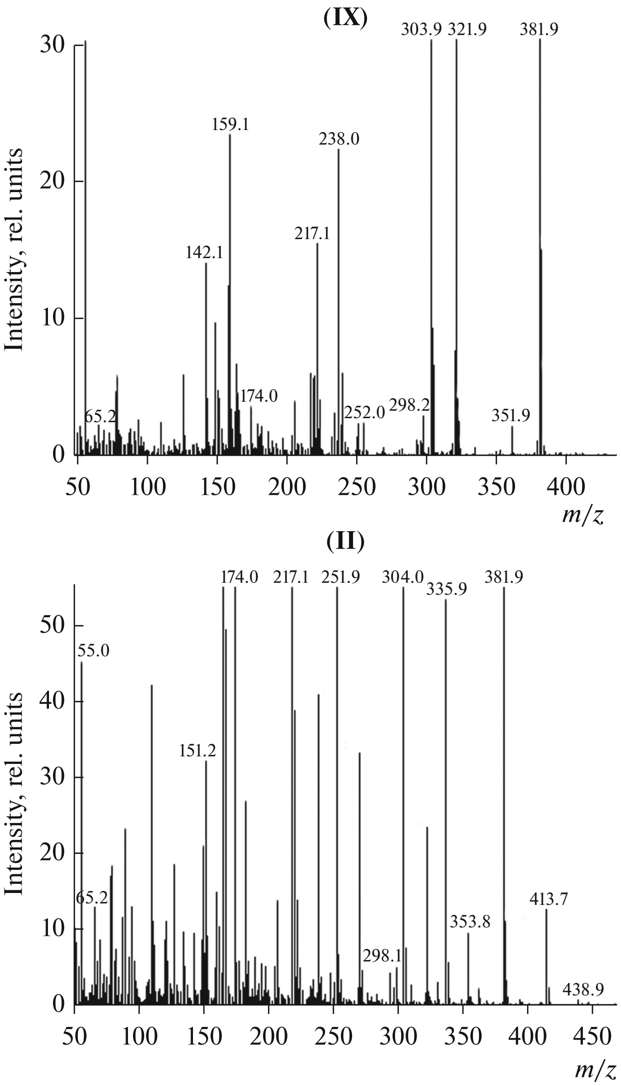
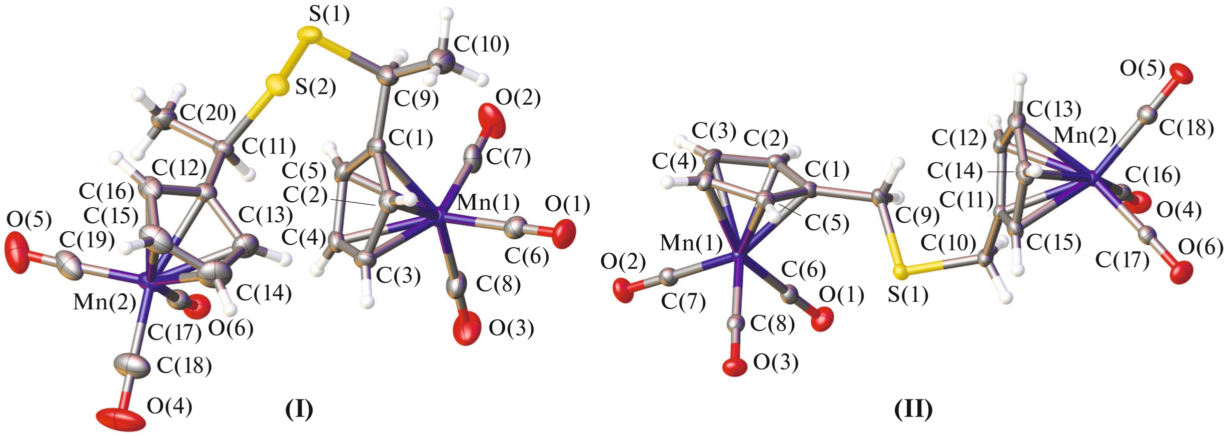


Fig. 1. Mass spectra of compounds **IX** and **II**.

An analysis of the mass spectra of the mono- and disulfides showed a similar pattern. The sulfides are usually characterized by an intense peak of the molecular ion. However, in the case of the cyclopentadienyl manganese tricarbonyl derivatives, the molecular ion can rarely be detected by the electron impact ionization method because of the instant loss of CO groups (one or several) [22, 23]. The intense peak with *m/z* 382 [M–3CO] and low-intensity peaks with *m/z* 438 [M–CO], 354 [M–4CO], and 298 [M–6CO] were detected for compound **II** (Fig. 1). The intense molecular peaks with *m/z* 217 [M–SCH_2Cym] and 251 [M–$CH_2C_5H_4$ + 2] are observed. It is known that upon electron impact ionization the disulfides eject one or two sulfur atoms [24]. The mass spectrum of compound **IX** exhibits the intense ion peak with *m/z* 382. Thus, the ion peaks similar to those of compound **II** are observed in the mass spectrum of compound **IX** (Fig. 1). The peak with *m/z* 322 corresponds to doubling of two cymantrenylmethyl fragments with the loss of four CO groups. This fragmentation and many other intense peaks are characteristic of polyvariant processes that occur during the fragmentation of organic compounds of sulfur (sulfides and disulfides) under electron impact [24]. The mass spectra of two *meso* forms of compound **I** coincide in fragmentation. In this case, the S–S bond is primarily cleaved to form the [$SC_2H_5C_5H_4Mn(CO)_3$ + 2], [$SC_2H_5C_5H_4Mn$], and [$C_2H_5C_5H_4Mn$] ions with *m/z* 265, 180, and 162, respectively.

The structures of complexes **I** and **II** are confirmed by X-ray diffraction analysis (Fig. 2). In both complexes, the main bond lengths and bond angles lie in a narrow range and are close to those in the cymantrenyl type complexes [25]. It was established by the struc-



(I) **(II)**

Fig. 2. Structures of compounds **I** and **II** and their selected bond lengths and bond angles. For **I**: Mn(1)–C(1) 2.151, Mn(1)–C(6) 1.796, Mn(2)–C(12) 2.135, Mn(2)–C (17) 1.787, S(1)–S(2) 2.040, S(1)–C(9) 1.849, S(2)–C(11) 1.851, C(1)–C(9) 1.496, C(11)–C(12) 1.502 Å and C(1)Mn(1)C(6) 111.8°, C(12)Mn(2)C(17) 93.6°, Mn(1)C(1)C(9) 128.62°, Mn(2)C(12)C(11) 125.53°, S(2)S(1)C(9) 105.21°, S(1)S(2)C(11) 103.00°; for **II**: Mn(1)–C(1) 2.153 Mn(1)–C(6) 1.798, Mn(2)–C(11) 2.153, Mn(2)–C(16) 1.797, S(1)–C(9) 1.816, S(2)–C(10) 1.824, C(1)–C(9) 1.496, C(10)–C(11) 1.498 Å and C(1)Mn(1)C(6) 95.54°, C(11)Mn(2)C(16) 91.96°, Mn(1)C(1)C(9) 129.11°, Mn(2)C(11)C(10) 125.81°, C(9)S(1)C(10) 98.54°.

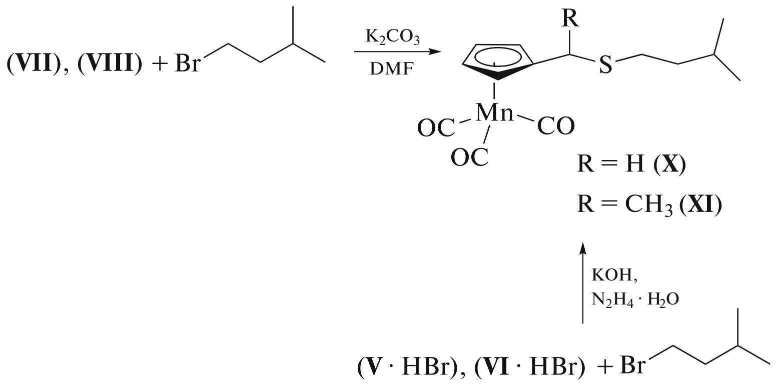
tural study that compound **I** was a racemic twin. In the crystal of compound **I**, the complex exists in the general position. Note that the C–C bond lengths in the cyclopentadienyl ring are alternated. The longest C–C bond (1.423(1) Å) is that with the carbonyl C=O group in the *cis* position (Fig. 2). This fact is characteristic of the manganese cyclopentadienyl compounds and was described earlier [26]. In the crystal of compound **I**, the molecules form zigzag chains along the crystallographic axis 2_1. Unlike the molecule of compound **I** bearing chiral centers, compound **II** has no chiral centers and crystallizes in the centrosymmetric space group. The molecule of compound **II**, as well as that of compound **I**, forms zigzag chains along the crystallographic axis *c*. The C–C bond lengths in the cyclopentadienyl ring are also (as in the previous case) alternated, which is consistent with the published results [26].

There were attempts to selectively isolate monosulfide **II** and disulfide **IX** using the earlier developed procedures for organic analogs [27]. The method for the synthesis of the disulfides was the reduction of elemental sulfur to disulfide anions using a hydrazine hydrate–monoethanolamine system [28]. However, in our case, no disulfide was isolated, under these conditions (Scheme 1b), because of the replacement of the bromide ion by the OH group and isolation of hydroxymethylcymantrene in 74% yield. In our case, the selective method for the preparation of symmetric and nonsymmetric monosulfides [27] was also inefficient. The reaction of isothiouroium salt **V** · HBr with compound **III** affords a mixture of disulfide **IX** and monosulfide **II** in a ratio of 1 : 1 in 18 and 19% yields, respectively (Scheme 1c). Compounds **IX** and **II** were crystallized from a hexane–EtOAc (5 : 1) mixture.

We assume that the formation of the sulfides and disulfides in all reactions is related to the fact that thiol is primarily formed during hydrolysis and then undergoes oxidative doubling due to the interaction of the sulfur atoms with the manganese atom. This assumption is confirmed by the fact that various cymantrene complexes can act as catalysts in the phototransformation of thiols into disulfides [1, 29]. The fact of the participation of manganese in the doubling reaction is also indirectly confirmed by the hydrolysis of the benzylisothiouronium salts that does not form any amount of the doubling products, under our conditions, but affords only benzylthiol in a yield higher than 94% regardless of the hydrolysis time. The hydrolysis of the benzylisothiouronium salt [30] with NaOH in a mixture of solvents EtOH–acetone (1 : 1) for 6 h in the presence of cymantrene (1 mol-equiv) affords symmetric dibenzyl disulfide in a yield of 24%.

Disulfides **IX** and **I**, unlike compound **II**, are easily reduced with lithium aluminum hydride to the corresponding thiols **VII** and **VIII** in almost quantitative yields, whereas the reduction of compound **II** with lithium aluminum hydride results in decomposition and the formation of methylcymantrene [31] in a yield of 62%, which confirms the assumed structure of the compounds.

Thiols **VII** and **VIII** were alkylated using a standard procedure in DMF in the presence of potassium dicarbonate (Scheme 2). The yields of isoamyl cymantrenylmethyl sulfide CymCH$_2$SC$_5$H$_{11}$ (**X**) and isoamyl cymantrenylethyl sulfide CymCH(CH$_3$)-SC$_5$H$_{11}$ (**XI**) were 60 and 44%, respectively.



Scheme 2.

The synthesis of nonsymmetric sulfide **X** from isothiouronium salt **V** turned out to be a more efficient method. Compound **V** was transformed into compound **X** in a hydrazine hydrate–alkali system according to the published procedure [27]. The yield of sulfide **X** in this procedure was 65%, whereas the total yield of compound **X** via the two-step procedure described above was halved (36%) (Scheme 2).

The data obtained by cyclic voltammetry show that compound **I** is reduced in two steps consecutively involving two electrons (Fig. 3). The potential at the cathodic peak on the curve (–1.49 V) is close to the potential of the cathodic peak of diphenyl disulfide [32]. This peak disappears completely after irradiation with the light of a Hg lamp at λ = 365 nm for 6 min, and only the peak at –0.9 V retains (Fig. 3). The shape of the cyclic voltammogram remains unchanged within 3 h after irradiation. The changes in the voltammogram during photolysis of compound **I** are related to the elimination of the CO ligand from the manganese atom. This results in the formation of the stable dicarbonyl complex, which is reduced in one step with the transfer of one electron.

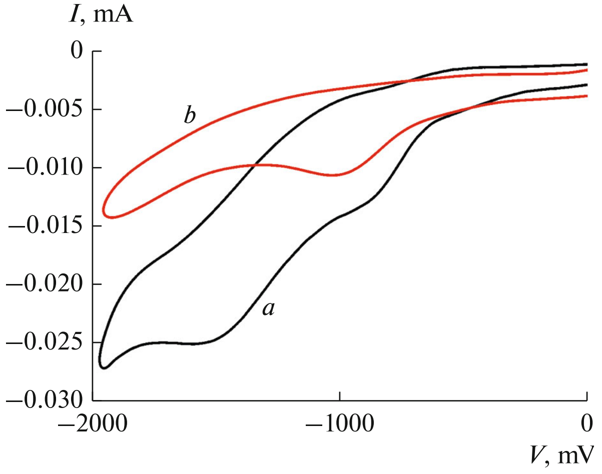


Fig. 3. Cyclic voltammetry in a 0.1 M solution of tetraethylammonium tetrafluoroborate: (*a*) in the presence of compound **I** (5.2×10^{-3} mol/L) and (*b*) after the irradiation of compound **I** for 6 min. The scan rate was 100 mV/s.

Thus, the methods for the preparation of a series of the sulfur-containing cymantrene derivatives with diverse functional groups, such as mercapto, sulfide, and disulfide groups, were developed, and the routes of hydrolysis of the corresponding isothiouronium salts were studied. The synthesized compounds can easily be modified with the purpose of developing the related photochromic systems. The electrochemical properties of compound **I** before and after irradiation were studied.

ACKNOWLEDGMENTS

The structures of the synthesized compounds were studied using the scientific equipment of the Center of Molecular Structure Investigation at the Nesmeyanov Institute of Organoelement Compounds (Russian Academy of Sciences).

FUNDING

The structural studies of the synthesized compounds were supported by the Ministry of Science and Higher Education of the Russian Federation. This work in part of the synthesis of the target products and studies of their properties was supported by the Russian Science Foundation, project no. 17-73-30036.

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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Translated by E. Yablonskaya