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PROTON-INITIATED CONVERSION OF DITHIOCARBAMATES OF 9,10-ANTHRACENEDIONE

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Abstract. Proton-initiated conversion of dithiocarbamate derivatives of the 9,10-anthracenedione under conditions of acid-catalyzed cyclodehydration using the action of a mixture of H_2SO_4-AcOH and further treatment with perchloric acid was investigated. Based on the data of the spectral methods (^{1}H, ^{13}C NMR, IR, UV spectroscopy), it is established that the reaction stops at the stage of protonation of the sulfur atom of the thiocarbonyl group with the formation of perchlorates. The UV spectra of the obtained perchlorates are characterized by a hypochromic shift with a clearly pronounced absorption maximum.

Keywords: 9,10-anthracenedione, dithiocarbamates, acid-catalyzed cyclodehydration, perchlorates, spectroscopic studies.

1. Introduction

During the last 150 years, derivatives of the 9,10-anthracenediones have been attracted a considerable attention due to their wide application as natural and synthetic dyes, biologically active substances, antitumor drugs, analytical reagents, indicators, luminophores, catalysts for important industrial processes, *etc*. [1].

The possibility of obtaining such valuable substances in practical terms on the basis of 9,10-anthracenedione derivatives provides a close link between the research in the field of chemistry of these compounds and the most important direction of synthetic organic chemistry – the target synthesis of new systems with a given set of chemical, physical and biological properties. An increase in the number of publications devoted to the synthesis and use of 9,10-anthracenedione derivatives indicates a growing interest of researchers in these compounds [2].

In the theoretical aspect, the chemistry of 9,10-anthracenediones is important for studying the patterns of organic reactions, the relationship between the structure and properties of organic compounds. Particularly valuable for the formation of ideas about the relationship between structure and properties is the fact that many reactions in the series of 9,10-anthracenedions occur in a peculiar way [3].

However, despite the widely studied chemistry of 9,10-anthracenediones, many types of compounds based on it remain little studied or unknown. Therefore, it seems relevant to obtain and investigate the chemical properties of the new derivatives of 9,10-anthraquinone, and also to find among them compounds useful for practical use.

Organic dithiocarbamates are important products and have found wide application in fine organic synthesis and in many areas, particularly in agriculture as insecticides, herbicides, pesticides and fungicides, in the industry as slimicides in water-cooled systems and in paper production, in analytical chemistry for the determination of cations, in the chemistry of polymers as RAFT agents, vulcanization accelerators, *etc*. [4].

Taking into account the practical value of dithiocarbamates both in theoretical and practical significance, in previous works [5, 6] we obtained mono- and bisdithiocarbamate derivatives of 9,10-anthracenediones. Some of the obtained compounds have a powerful biological potential [5, 7, 8].

It is known the structural modification of the dithiocarbamate fragment opens up wide possibilities for the obtaining of a number of heterocyclic derivatives [4]. The interaction of organic dithiocarbamates with a mixture of H_2SO_4-AcOH under acid-catalyzed cyclodehydration leads to the formation of mesoionic salts of dithiolium [9]. In recent years, this direction was developed by a group of Romanian researchers [10]. On the other side, one or both of the oxygen atoms of the carbonyl groups of 9,10-anthracenedione and some of its derivatives are capable of mono- and diprotonation in H_2SO_4 or in a mixture of H_2SO_4-AcOH, and a significant influence on this process has a substituent in the 9,10-antatsendione ring [11].

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2. Experimental

The ^{1}H and ^{13}C NMR spectra of the synthesized compounds were obtained on a Varian Mercury–400 spectrometer (400 and 100 MHz, respectively) in solutions of DMSO-d_6, the internal standard of TMS. IR spectra are recorded on the Specord M-80 spectrophotometer in tablets with KBr. The electronic absorption spectra obtained with the Specord M-40 spectrophotometer in methanol solutions in a concentration of $(1{\cdot}10^{-4})$–$(1{\cdot}10^{-5})$ mmol/l. The individuality of the compounds obtained was monitored by TLC on Silufol UV-254 plates in solvents system benzene:acetonitrile (6:1).

Dithiocarbamates **1-5** were obtained using the procedure given in [5].

General procedure for the preparation of perchlorates 6-10. 0.2 g (0.563 mmol) of (9,10-dioxo-9,10-dihydroanthracen-1-yl) diethylcarbamodithioate **1** was added to 20 ml of a H_2SO_4-AcOH (1: 3) mixture, heated to 353 K and kept at this temperature for 30 min. Thereafter, 0.5 ml of $HClO_4$ was added to the mixture, kept with stirring and 353 K for an additional 20 min. It was cooled, diluted with a 5-fold amount of water, and the precipitate of perchlorate **6** was filtered off. Perchlorates **7-10** were prepared analogously.

(9,10-Dioxo-9,10-dihydroanthracen-1-yl) diethylcarbamodithioate perchlorate 6. Yield: 61 %. mp 601–603 K. ^{1}H NMR, δ, ppm: 1.46 (3H, t, J = 6.8 Hz, CH_3), 1.48 (3H, t, J = 7.2 Hz, CH_3), 4.01-4.13 m (4H, CH_2), 8.01 m (3H, CH_{ar}), 8.24 m (2H, CH_{ar}), 8.39-8.41 d (1H, CH_{ar}), 8.65-8.68 d (1H, CH_{ap}). ^{13}C NMR, δ, ppm: 11.08, 11.38 (CH_3) 54.40, 55.38 (CH_2) 127.67, 127.72, 129.35, 130.76, 132.16, 132.76, 133.06, 133.47, 135.08, 135.68, 136.27, 141.41 (C_{ar}) 181.48, 182.58 (C=O) 188.81 (C=S). IR spectrum, cm^{-1}: 1672, 1623 (C=O quinoid ring), 1292 (-S-C(S)-), 1088 (ClO_4). UV spectrum, nm: 252, 273, 370. Found: C, 50.17; H, 3.89; Cl, 7.83; N, 3.02; S, 14.11. $C_{19}H_{18}ClNO_6S_2$. Calcd.: C, 50.05; H, 3.98; Cl, 7.78; N, 3.07; S 14.06.

(9,10-Dioxo-9,10-dihydroanthracen-1-yl) morpholine-4-carbodithioate perchlorate 7. Yield: 62 %. mp. 581–583 K. ^{1}H NMR, δ, ppm: 3.81-3.88 (m, 8H, CH_2), 7.88-7.96 (m, 3H, CH_{Ar}), 8.13-8.25 (m, 4H, CH_{Ar}). ^{13}C NMR, δ, ppm: 68.61, 69.37 (CH_2), 126.13, 126.34, 126.75, 126.93, 127.21, 128.39, 133.81, 134.69, 134.93, 136.83 137.11, 140.31, (C_{Ar}), 182.13, 182.69 (C=O), 189.41 (C=S). IR spectrum, cm^{-1}: 1668, 1642 (C=O), 1272 (-S-C(S)-), 1093 (ClO_4). UV spectrum, nm: 254, 281, 374. Found: C, 48.62; H 3.43; Cl, 7.47; N, 3.02; S, 13.71. $C_{19}H_{16}ClNO_7S_2$. Calcd.: C, 48.56; H 3.43; Cl, 7.54; N 2.98; S, 13.65.

(9,10-Dioxo-9,10-dihydroanthracen-1-yl) piperidine-1-carbodithioate perchlorate 8. Yield: 58 %. mp 588–590 K. ^{1}H NMR, δ, ppm: 1.75 (m, 6H, CH_2) 4.11-4.31 (m, 4H, CH_2) 7.93-8.09 (m, 4H, CH_{Ar}) 8.19-8.29 (m, 3H, CHAr). ^{13}C NMR δ (ppm): 26.13, 27.32, 29.41, 55.43, 56.81 (CH_2), 127.43, 127.69, 127.84, 128.91, 133.11, 133.45, 135.16, 135.29, 135.81, 136.17, 137.61, 140.38 (C_{Ar}) , 181.76, 182.21 (C=O), 188.89 (C=S). IR spectrum, cm^{-1}: 1668, 1635 (C=O), 1273 (-S-C(S)-), 1090 (ClO_4). UV spectrum, nm: 258, 278, 376. Found: C, 51.28; H, 3.93; Cl, 7.63; N, 3.03; S, 13.66. $C_{20}H_{18}ClNO_6S_2$. Calcd.: C, 51.34; H, 3.88; Cl, 7.58; N 2.99; S, 13.70.

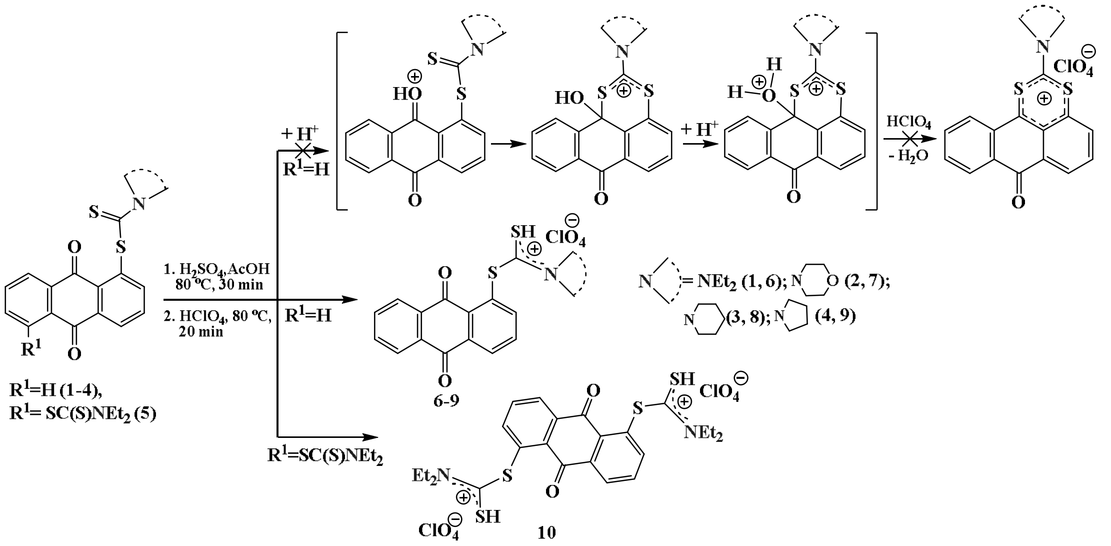
(9,10-Dioxo-9,10-dihydroanthracen-1-yl) pyrrolidine-1-carbodithioate perchlorate 9. Yield: 63 %. mp 604–606 K. ^{1}H NMR, δ, ppm: 2.14-2.21 (m, 4H, CH_2) 3.87-4.05 (m, 4H, CH_2) 7.98-8.09 (m, 3H, CH_{Ar}) 8.11- 8.36 (m, 4H, CH_{Ar}). ^{13}C NMR δ (ppm): 26.47, 28.15, 53.16, 58.89 (CH_2), 127.13, 127.43, 127.93, 128.21, 133.38, 134.19, 134.33, 134.72, 135.81, 136.26, 136.54, 141.91 (C_{Ar}), 181.18 , 182.31 (C=O), 189.56 (C=S). IR spectrum, cm^{-1}: 1670, 1648 (C=O), 1258 (-S-C(S)-), 1097 (ClO_4). UV spectrum, nm: 255, 271, 372. Found: C, 50.28; H, 3.55; Cl, 7.81; N, 3.09; S 14.13. $C_{19}H_{16}ClNO_6S_2$. Calcd.: C, 50.28; H, 3.55; Cl, 7.81; N, 3.09; S 14.13.

(9,10-Dioxo-9,10-dihydroanthracene-1,5-diyl) bis(diethylcarbamodithioate) diperchlorate 10. Yield: 63 %. mp > 603 K. ^{1}H NMR, δ, ppm: 1.41-1.49 (m, 12H, CH_3), 4.09-4.18 (m, 8H, CH_2), 7.91-8.06 (m, 4H, CH_{Ar}), 8.17 -8.21 (m, 2H, $CH2_{Ar}$). ^{13}C NMR, δ, ppm: 11.17, 11.49 (CH_3) 54.51, 55.34 (CH_2), 128.69, 132.18, 134.38, 135.93, 137.86, 141.42 (C_{Ar}), 181.98, 182.09 (C=O), 188.61 (C=S). IR spectrum, cm^{-1}: 1674, 1632 (C=O), 1266 (-S-C(S)), 1100 (ClO_4). UV spectrum, nm: 252, 273, 371. Found: C, 41.05; H, 3.97; Cl, 10.13; N, 3.91; S, 18.29. $C_{24}H_{28}Cl_2N_2O_{10}S_4$. Calcd.: C, 40.97; H 4.01; Cl 10.08; N, 3.98; S 18.23.

3. Results and Discussion

Taking into account the foregoing and the absence of information on the reactions of the derivatives of 9,10-anthracenedione with the formation of mesoionic salts in the literature, we carried out a protonation of dithiocarbamate derivatives **1-5** obtained earlier [5], in a mixture of H_2SO_4-AcOH (1:3) and further treatment of the mixture with 70% $HClO_4$ using the procedure of [12] (Scheme 1).

According to the data of the spectra of ^{1}H, ^{13}C NMR, IR, UV and elemental analysis, it can be argued that the reaction stops at the stage of protonation of the sulfur atom of the thiocarbonyl group to form compounds **6-10**. This agrees with the data on the greater propensity to protonate the thiocarbonyl group in strong acids compared to the nitrogen atom in the dithiocarbamate fragment [13].



Scheme 1. Obtaining of the perchlorates **6-10**

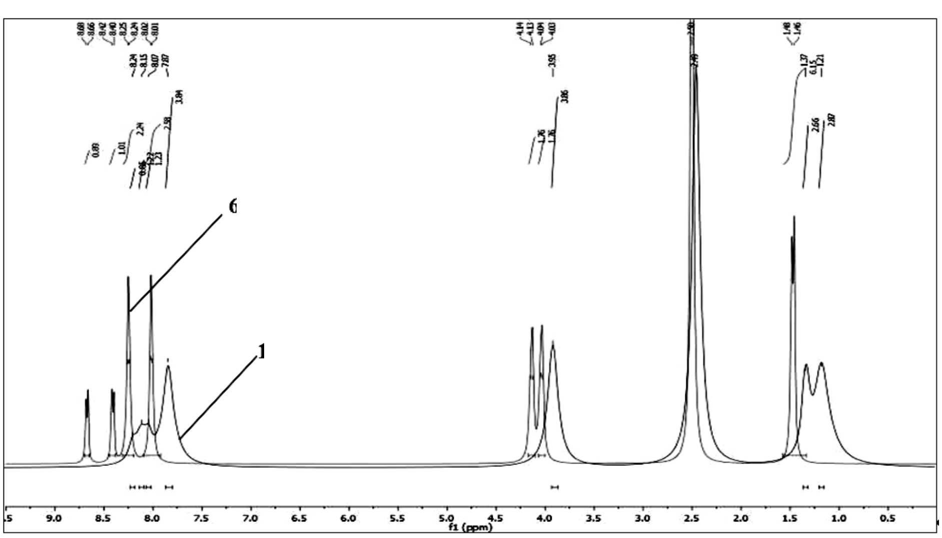


Fig. 1. ^{1}H NMR spectrum of (9,10-dioxo-9,10-dihydroanthracen-1-yl) diethylcarbamodithioate **1** and (9,10-dioxo-9,10-dihydroanthracen-1-yl) diethylcarbamodithioate perchlorate **6** in DMSO-d_6

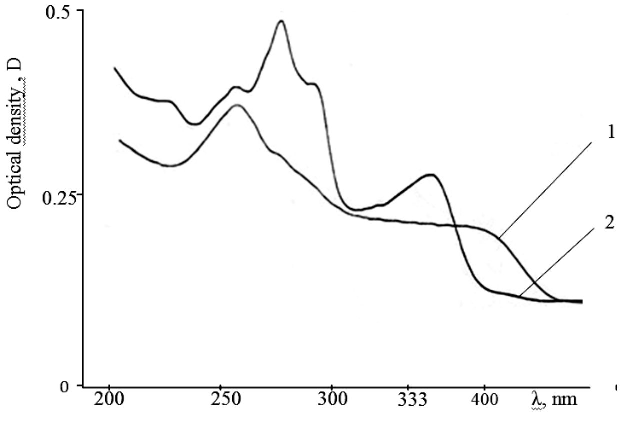


Fig. 2. Absorption spectra of compound **1** (1) and compound **6** (2)

The characteristic signals of the dithiocarbonyl substituent and the anthracenedione fragment are retained in the ^{1}H and ^{13}C NMR spectra of the obtained compounds, suggesting that there are no transformations of dithiocarbamates **1-5** in the mesoionic structure, as described in [9].

For all proton signals, shifts to a weak field are observed, and for signals of the carbon atom of the dithiocarbonyl moiety, small shifts toward the strong field to 189.56-188.61 ppm are presented. In particular, the ^{1}H NMR spectrum of compound **6** (Fig. 1) is characterized by a shift in the multiplet signal of four protons of two methylene groups of the diethyl substituent in a weak field at 4.01–4.13 ppm and signals of six protons of two methyl groups at 1.46–1.48 ppm as compared to the spectrum of the starting dithiocarbamate derivative **1** [5]. In the ^{13}C NMR spectrum of perchlorate **6**, the signals of the carbon atoms of the diethyl dithiocarbamate residue also shift in comparison with the ^{13}C NMR spectrum of the starting dithiocarbamate derivative **1** [5]: the carbonate signal of the thiocarbonyl group shifts from 192.4 ppm toward the strong field to 188.7 ppm, the carbon signals of the two methylene groups of the diethyl fragment shift to a weak field from 48.97, 49.61 ppm to 54.40, 55.38 ppm, respectively.

In the IR spectrum of the perchlorate **6**, in addition to the characteristic signals of the stretching vibrations of the dithiocarbamate and anthracenedione fragments, an intense wide absorption band appears at 1088 cm^{-1}, which corresponds to the asymmetric vibrations of the ClO_4^- anion.

It seemed also interesting to compare the electronic absorption spectra of the obtained new chromophore derivatives of anthraquinone **6-10** with the starting dithiocarbamates **1-5** [5]. The electronic spectra of these compounds, recorded in methanol solutions, are characterized by the presence of two main bands of absorption maxima at 250–290 and 360–410 nm, which refer to the dithiocarbamate substituent [14] and the conjugate anthracene ionic system [1].

A comparison of the UV spectra (Fig. 2) of the starting dithiocarbamate derivative **1** with product **6** indicates the following. In the UV spectrum of dithiocarbamates **1**, there is a clearly pronounced absorption maximum at λ_{max} = 252 nm and a shoulder at λ_{max} = 402 nm. The absorption band in the short-wave region of 250–290 nm can be attributed to electron $\pi \rightarrow \pi^*$ transitions in S–C=S and N–C=S fragments [14, 15] and anthracenedione ring [1].

In the range of 250–290 nm for perchlorate salts **7-10** several absorption maxima of different intensities are observed. The most intense band is in the short-wavelength region with a maximum absorption at λ_{max} = 273 nm, while the absorption at λ_{max} = 252 nm, characteristic for the starting compound **1**, becomes less intense. Such changes in the intensity can be explained by the formation of salt. Another absorption peak in the range 360–400 nm corresponds to the $n \rightarrow \pi^*$ transition. In the products **6-10** obtained, this absorption maximum shifts toward smaller wavelengths. In particular, 32 nm bathochromic shift appears in the UV spectrum of compound **6** with a clearly pronounced absorption maximum at λ_{max} = 370 nm compared to compound **1**, for which λ_{max} = 402 nm. This is the evidence of the transition of a pair of electrons of the sulfur atom from the unequal *n*-orbitals to the loosening π^* orbital, which agrees well with the authors' studies [14, 15]. Similar behavior is observed for other perchlorate salts **7-10**. The protonation reaction (9,10-dioxo-9,10-dihydroanthracen-1,5-diyl) bis diethylcarbamodithioate) **5** leads to dipperchlorate salt **10**.

4. Conclusions

The features of the protonation of dithiocarbamate derivatives of 9,10-anthracenedione **1-5** with H_2SO_4-AcOH with subsequent treatment with 70% $HClO_4$ were first investigated and it was found that the result of the reaction is the formation of perchlorate salts of **6-10** on the dithiocarbamate fragment. This fact is probably explained by the effect of the present sulfur containing substituent at position 1 of the anthracenedione ring, significantly reducing the basicity of the oxygen atom of the carbonyl group at position 9 of anthracenedione, decreasing its protonation ability in the reaction.

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ПРОТОН-ІНІЦІЙОВАНЕ ПЕРЕТВОРЕННЯ ДИТІОКАРБАМАТІВ 9,10-АНТРАЦЕНДІОНУ

Анотація. *Досліджено протон-ініційоване перетворення дитіокарбаматних похідних 9,10-антрацендіону за умов кислотно-каталізованої циклодегідратації при дії суміші H_2SO_4-AcOH та подальшому обробленні перхлоратною кислотою. На основі даних спектральних методів (^1H, ^{13}C ЯМР, ІЧ-, УФ-спектроскопії) встановлено, що реакція зупиняється на стадії протонування атома Сульфуру тіокарбонільної групи з утворенням перхлоратних солей. УФ спектри одержаних перхлоратів характеризуються гіпсохромним зсувом з чітко вираженим максимумом поглинання.*

Ключові слова: *9,10-антрацендіон, дитіокарбамати, кислотно-каталізована циклодегідратація, перхлорати, спектральні дослідження.*