BIS(1,2-CYCLOPENTYLENEDITHIO)- AND BIS(1,2-CYCLOHEXYLENEDITHIO)TETRATHIAFULVALENES

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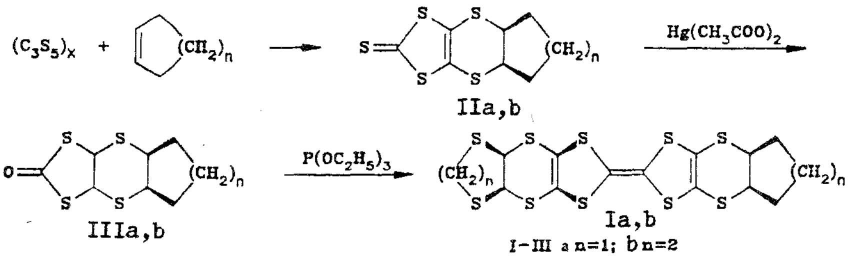
UDC 547.738

New homologs of bis(ethylenedithio)tetrathiafulvalene, viz., bis(cyclopentylenedithio)tetrathiafulvalene and bis(cyclohexylenedithio)tetrathiafulvalene, were obtained via a known scheme and characterized.

In the course of research on the interrelationship between the structure and the electrophysical properties of crystals of ion-radical salts of tetrathiafulvalene derivatives it was assumed that it is necessary to create certain deviations from the coplanarity of the structure in the electron-donor component in order to achieve high electrical conductivity of the organic metals [1]. With this end in mind we undertook the synthesis of previously unknown homologs of bis(ethylenedithio)tetrathiafulvalene — bis(cycloalkylene)tetrathiafulvalenes Ia, b.



The starting 1,3-dithiole-2-thiones IIa, b were obtained by the reaction of $(C_3S_5)_x$, which is presumably an oligomer of 1,3-dithiole-2,4,5-trithione, with cyclopentene and cyclohexene [2]. This reaction, like the known [2+4]-cycloaddition of tetrathiooxalate to alkenes [3, 4], is stereospecific. The cycloalkylene residue is cis-oriented with respect to the newly formed 1,4-dithiene ring.

One's attention is directed to the appreciable hypsochromic shift of the long-wave band of 4,5-(cis-cyclopentylenedithio)-1,3-dithiole-2-thione (IIa) in the electronic absorption spectrum [λ (in ethanol) 395 nm ($\log\varepsilon$ 4.11)] as compared with the spectra of IIb [414 nm (4.02)] and unsubstituted 4,5-ethylenedithio-1,3-dithiole-2-thione [410 nm (3.97)]. This can be ascribed to the effect of the relatively rigid conformation of the cis-cyclopentylene residue, which affects the conjugation of the sulfur atoms of the dithiene ring with the dithiole part of the molecule in this way.

1,3-Dithiole-2-thiones IIa, b were converted by a known reaction [5] to dithiolones IIIa, b, which form tetrathiafulvalenes when they are heated with triethyl phosphite.

The tetrathiafulvalene derivatives Ia, b obtained crystallize well; however, each of them is probably a mixture of geometrical isomers, in one of which both cis-cycloalkenyl substituents are located on the same side of the tetrathiafulvalene plane, whereas they are located on opposite sides of the plane in the other. The possible existence of these isomers is not reflected in the spectroscopic properties and the measured oxidation potentials (see Table 1). Their existence will be demonstrated (or excluded) by an investigation of the structure of the crystals.

The properties of Ia, b and the previously described [6] cycloalkenylene analogs of bis(ethylenedithio)tetrathiafulvalene are compared.

EXPERIMENTAL

The IR spectra of suspensions of the compounds in Nujol were recorded with a Specord IR-75 spectrometer. The electronic absorption spectra were obtained with a Specord UV-vis spectrophotometer. The PMR spectra were

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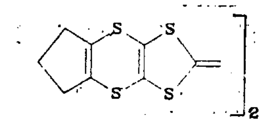
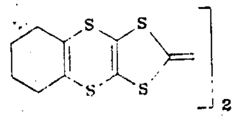
Riga Technical University, Riga 226048. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 10, pp. 1317-1319, October, 1991. Original article submitted April 28, 1990.

0009-3122/91/2710-1053$12.50 ©1992 Plenum Publishing Corporation

TABLE 1. Electronic Absorption Spectra and Electrochemical Oxidation Potentials (E) of Tetrathiafulvalenes

Compound	λ_{max} (in dioxane), nm (log ε)	E^1, V	E^2, V
Ia	314 (4,16), 343 (4,23), 470*	0,68	0,97
Ib	326 (4,17), 351 (4,10), 460 sh (2,60)	0,66	0,92
Bis(cyclopenten-1,2-ylenedithio)tetrathiafulvalene [6] 	313 (4,52), 348 (4,42), 490 (2,81)	0,81	1,07
Bis(cyclohexen-1,2-ylenedithio)tetrathiafulvalene [6] 	316 (4,65), 345 (4,47), 490 (2,85)	0,74	1,02

*Weakly expressed inflection.

obtained with a Perkin—Elmer R-12A spectrometer (80 MHz) with hexamethyldisiloxane (HMDS) as the internal standard. The electrochemical oxidation potentials were determined in solution in benzonitrile with a PL-50-1 potentiostat by means of a three-electrode scheme relative to a silver chloride electrode; the working electrode was a glass-graphite electrode, and the inert electrolyte was tetrabutylammonium perchlorate. The determinations were carried out by A. Édzhina.

4,5-(cis-1,2-Cyclopentylenedithio)-1,3-dithiole-2-thione (IIa, $C_8H_8S_5$). A mixture of 9.8 g (50 mmole) of $(C_3H_5)_x$ [2], 10 ml (11 mmole) of cyclopentene, and 10 ml of benzene was heated in a sealed ampul at 55-60°C for 6 h, after which the reaction mixture was extracted with hot ethanol with the addition of activated charcoal. Recrystallization of the product from ethanol gave 9.28 g (70%) of yellow plates with mp 116°C. Electronic absorption spectrum, λ_{max} (in ethanol), nm (log ε): 275 (3.86), 395 (4.11). PMR spectrum (in $CDCl_3$), δ, ppm: 1.73-2.29 (6H, m, CH_2), 3.82 (2H, t, CHS).

4,5-(cis-1,2-Cyclohexylenedithio)-1,3-dithiole-2-thione (IIb, $C_9H_{10}S_5$). A mixture of 0.8 g (50 mmole) of $(C_3H_5)_x$, 10 ml (99 mmole) of cyclohexene, and 10 ml of benzene was heated at 80-85°C for 5 h, after which it was extracted with hot ethanol with the addition of activated charcoal. The solvent was evaporated, and the residue was dissolved in benzene—hexane (2:3) and purified by chromatography with a column packed with silica gel by elution with benzene—hexane (2:3). This procedure gave, after recrystallization from benzene—hexane, 6.75 g (48%) of yellow crystals with mp 86-87°C. Electronic absorption spectrum, λ_{max} (in ethanol), nm (log ε): 280 (3.89), 414 (4.02). PMR spectrum (in $CDCl_3$), δ, ppm: 1.64-1.96 (8H, t, CH_2), 3.70 (2H, t, CHS).

4,5-(1,2-Cyclopentylenedithio)-1,3-dithiol-2-one (IIIa, $C_8H_8OS_4$). A mixture of 1.8 g (7 mmole) of IIa, 2.6 g of mercury acetate, 37 ml of $CHCl_3$, and 28 ml of glacial acetic acid was refluxed for 6 h, after which the HgS was removed by filtration, the filtrate was diluted with water, and the chloroform layer was separated and washed with water. Evaporation of the solvents gave 1.3 g (76%) of IIIa with mp 35°C (from methanol). IR spectrum: 1673, 1603 cm^{-1}.

4,5-(1,2-Cyclohexylenedithio)-1,3-dithiol-2-one (IIIb, $C_9H_{10}OS_4$). This compound was obtained under similar conditions in 82% yield and had mp 40°C (from ethanol). IR spectrum: 1672, 1602 cm^{-1}.

Bis(1,2-cyclopentylenedithio)tetrathiafulvalene (Ia, $C_{16}H_{16}S_8$). A mixture of 1.3 g (5 mmole) of IIIa and 5 ml of triethyl phosphite was heated at 100-110°C for 1 h, after which it was cooled, and the orange crystalline substance, with mp 190-205°C (dec., from pyridine), was removed by filtration. PMR spectrum (in $CDCl_3$), δ, ppm: 1.72-2.30 (6H, m, CH_2), 3.7-3.9 (2H, m, CHS). The yield was 0.8-0.9 g (67-71%).

Bis(1,2-cyclohexylenedithio)tetrathiafulvalene (Ib, $C_{18}H_{20}S_8$). This compound was obtained under similar conditions and had mp 205°C (dec., from pyridine). PMR spectrum (in $CDCl_3$), δ, ppm: 1.71 (8H, t, CH_2), 3.62 (2H, d, CHS). The yield was 70-75%.

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PYRROLES FROM KETOXIMES AND ACETYLENE.
46.* PYRROLES WITH STERICALLY HINDERED SUBSTITUENTS

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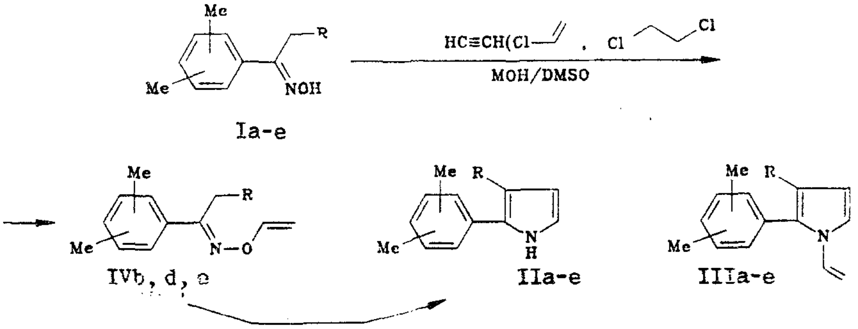
UDC 547.574.2+547.314.2+
536.423.4+547.741

The corresponding pyrroles and their N-vinyl derivatives were obtained by the catalyzed (by an MOH—DMSO superbase) reaction of acetylene and its crypto forms (vinyl chloride, 1,2-dichloroethane) with alkyl-2,4-, alkyl-2,5-, and alkyl-3,4-dimethylphenylketoximes. Reaction intermediates — O-vinylketoximes — were detected.

The condensation of ketoximes with acetylene in superbase media (the Trofimov reaction), which leads to pyrroles and N-vinylpyrroles, has been investigated quite extensively [2]. However, ketoximes with sterically bulky substituents that are capable of hindering the approach of the oximate anion to the acetylenic bond have not been involved in this reaction thus far.

The aim of the present research was to investigate the possibility of the use of such ketoximes, viz., alkyl 2,4-, 2,5-, and 3,4-dimethylphenyl ketone oximes Ia-e, in the reaction with acetylene and its crypto forms (vinyl chloride, 1,2-dichloroethane) under the influence of the MOH—DMSO catalytic pair (M = Li, K) and to synthesize the previously unknown sterically hindered pyrroles and N-vinylpyrroles, which are interesting models for the study of the dependence of the effects of conjugation on the degree of coplanarity of interacting π fragments.

Our research showed that, depending on the reaction conditions, ketoximes Ia-e can react with acetylene to give the corresponding pyrroles IIa-e or their N-vinyl derivatives IIIa-e (see Table 1).



I—IV a R=H, 2,4-Me_2; b R=H, 2,5-Me_2, c R=H, 3,4-Me_2, d R=Me, 2,5-Me_2; e R=Et, 2,5-Me_2; M=Li, K

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*For Communication 45 See [1] .

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Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 10, pp. 1320-1323, October, 1991. Original article submitted July 23, 1990.