Varian MAT-112 chromatographic mass spectrometer at an ionizing voltage of 80 eV. Monitoring of the purity of the starting substances and the individuality of the reaction mixtures were carried out by gas-liquid chromatography (GLC), thin-layer chromatography (TLC), and column chromatography on silica gel (40/100) by elution with hexane—ether in various ratios.

The starting phenylcyclopropanes were synthesized by previously described methods. The o- and p-nitrophenylcyclopropanes were obtained by fractional distillation of the products of nitration of the corresponding hydrocarbons by the method in [3]. The aromatic ring-halogenated arylcyclopropanes were synthesized from the corresponding nitro derivatives as described in [4, 5]. p-Tolylcyclopropane, p-methoxyphenylcyclopropane, and p-dicyclopropylbenzene were synthesized by the Mannich—Kishner method [6, 7]. 1-Bromo-2-phenylcyclopropane, with bp 118-126°C (18 mm) and n_D^{20} 1.5696, was obtained from gem-dibromophenylcyclopropane by the method in [8]. 1-Methyl-1-phenyl-2-chlorocyclopropane, with bp 101-104°C (10 mm) and n_D^{20} 1.5690, was obtained from 1-methyl-1-phenyl-2,2-dichlorocyclopropane by the method in [9].

The reaction of arylcyclopropanes with sodium nitrite and trifluoroacetic acid in chloroform was carried out at —5°K by the general method presented in [1]. The characteristics and yields of the isoxazolines obtained are presented in Tables 3 and 4.

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INVESTIGATION OF SUBSTITUTED 2- AND 3-THIOLENE 1,1-DIOXIDES BY PMR SPECTROSCOPY WITH THE AID OF A LANTHANIDE SHIFT REAGENT

T. Ya. Lavrenyuk, A. V. Turov, M. Yu. Kornilov,
I. E. Boldeskul, and T. E. Bezmenova

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The reaction of lanthanide shift reagent $Eu(FOD)_3$ with 3-phenyl- and 3- and 4-chloro-2-thiolene 1,1-dioxides and with 3-phenyl-3-thiolene 1,1-dioxide was investigated by PMR spectroscopy. The geometrical structure of the adduct of the lanthanide shift reagent with 4-chloro-2-thiolene 1,1-dioxide was found.

Derivatives of 2- and 3-thiolene 1,1-dioxides display high biological activity [1], and a thorough study of their structures and conformational compositions is therefore urgent. Studies in which the conformations of the molecules of a number of thiolene 1,1-dioxides in solution were determined by PMR spectroscopy have been made [2]. Lanthanide shift reagents are effective agents for the analysis of the PMR spectra of these compounds [3].

In the present research we used europium(III) 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedionate [$Eu(FOD)_3$] as the lanthanide shift reagent to ascertain the three-dimensional structures of I-IV.

Petrochemistry Branch, Institute of Physical Organic Chemistry and Coal Chemistry, Academy of Sciences of the Ukrainian SSR, Kiev 252160. T. G. Shevchenko Kiev State University, Kiev 252601. Institute of Organic Chemistry, Academy of Sciences of the Ukrainian SSR, Kiev 252660. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 3, pp. 314-317, March, 1984. Original article submitted February 9, 1983; revision submitted August 23, 1983.

TABLE 1. Chemical Shifts (ppm) for Derivatives of 2- and 3-Thiolene 1,1-Dioxides (the lanthanide-induced shifts are given in parentheses)

Compound	2-H	5-H	4-H
3-Phenyl-2-thiolene 1,1-dioxide	6,87 (4,56)	3,40 (5,00)	3,25 (2,14)
3-Chloro-2-thiolene 1,1-dioxide	6,70 (5,03)	3,46 (5,54)	3,08 (2,35)
3-Phenyl-3-thiolene 1,1-dioxide	4,15 (2,93)	4,05 (2,88)	6,35 (0,89)
4-Chloro-2-thiolene 1,1-dioxide[a]	6,75 (1,82)	3,42; 3,80 (1,60), (1,84)	5,06 (0,97)
3-Methyl-3-thiolene 1,1-dioxide[b]	3,69 (2,81)	3,80 (2,90)	5,68 (1,07)

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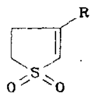
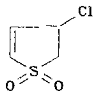
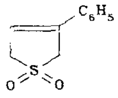
[a] $\delta_{3\text{-H}}$ 6.75 ppm; lanthanide-induced shift 0.66 ppm. [b] δ_{Me} 1.88 ppm; lanthanide-induced shift 0.52 ppm.


I,II


III


IV

I R=C_6H_5; II R=Cl

The PMR spectra of thiolene dioxides I, II, and IV in the absence of a lanthanide shift reagent do not make it possible to assign the signals. Assignment of the signals becomes possible when Eu(FOD)$_3$ is used. Thus the two multiplets at 3-3.5 ppm in the spectra of 2-thiolene dioxides I and II are converted to triplets with spin-spin coupling constant (SSCC) J = 7 Hz. Since the weak-field multiplet (see Table 1) experiences stronger paramagnetic shifts, it may be concluded that it corresponds to the protons of the 5-methylene group, which is closer to the coordination center of the substrate. The fact that the signals of the methylene protons have the form of triplets in the spectra of I and II modified with Eu(FOD)$_3$ indicates a planar structure of the dihydrothiophene ring (compared with [2]) or its rapid (on the NMR time scale) inversion. However, a planar structure of I and II in solutions is unlikely in view of the fact that thiolene dioxide I has a nonplanar structure in the crystalline state [4].

In the spectrum of 3-thiolene 1,1-dioxide IV the methylene groups in the 2 and 5 positions give two closely located narrow signals (J < 1 Hz). Under the influence of the lanthanide shift reagent they are shifted almost identically to weak field; the weak-field signal displays a greater width than the high-field signal. It might be expected that $J_{45} > J_{24}$, and we therefore assigned the broader weak-field signal to the 5-H protons (see Table 1).

In the spectrum of III the protons of the methylene group give a doublet of doublets (J_{gem} = 15 Hz, J_{vic} = 7 and 5 Hz); this indicates magnetic nonequivalence due to their diastereotopic character. The nonplanar structure of III follows from the results of x-ray diffraction analysis of a compound with a similar structure (see also [5]). It is also important that both the chemical shifts and the magnitudes of the lanthanide-induced shifts are different for the signals of the protons of the CH_2 group. The SSCC do not change when the lanthanide shift reagent is added. This indicates that the conformation of the III molecule remains unchanged when the shift reagent is added.

To refine the assignments of the spectral lines and to determine the preferred conformation of 4-chloro-2-thiolene 1,1-dioxide in solution we used the method in [6] after calculating the position of the lanthanide ion in the adduct with the shift reagent. This was possible, since we had data on the induced shifts of the five nonequivalent protons of III (for a three-dimensional molecule one must have at least four independent parameters of lanthanide-induced shifts). We assumed that the dihydrothiophene ring of the III molecule has the same structure as that in 4-phenyl-2-thiolene 1,1-dioxide, the geometry of which was previously studied by x-ray diffraction analysis [7]. Calculations of the induced shifts of the signals of the methylene protons of III were carried out for two possible variants of the assignment of the weak-field component of the doublet of doublets, viz., to pseudoequatorial and pseudoaxial 2-CH_2 protons. In the calculations it was assumed that the lanthanide is coordinated to an identical extent with both oxygen atoms; the resulting induced

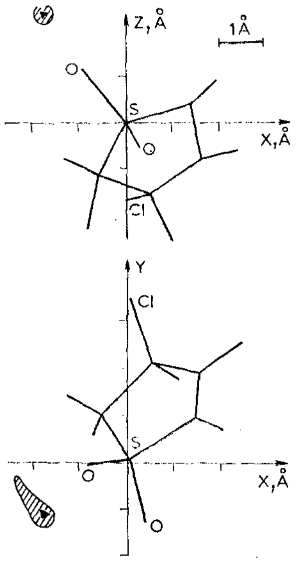


Fig. 1

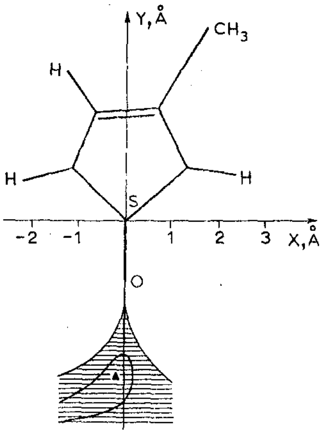


Fig. 2

Fig. 1. Results of calculation of the geometrical structure of the adduct of Eu(FOD)$_3$ with 4-chloro-2-thiolene 1,1-dioxide. Two orthogonal projections of the molecule are given. The probability of the localization of the lanthanide ion in the shaded region is 95%. The calculation gives the best agreement between the calculated and experimental lanthanide-induced shifts for the point designated by ▲.

Fig. 2. Results of a calculation of the geometrical structure of the adduct of Eu(FOD)$_3$ with 3-methyl-3-thiolene 1,1-dioxide. The shaded region has the same significance as in Fig. 1. The most probable location of the lanthanide in the adduct is designated by ▲.

shifts then turn out to be the values that would be expected if the coordination center were located at the middle of a line connecting the oxygen atoms of the thiolene 1,1-dioxide. It has been previously shown [8] that this approximation is the best one.

Two orthogonal projections of the III molecule are presented in Fig. 1; the cross section of the region of the probable location of the lanthanide ion in the adduct is designated on the same scale. It is apparent that the center of the region, i.e., the most probable location of the lanthanide ion in the adduct, is found at a distance of 2.5 Å from the assumed center of coordination at angle φ = 130° to the perpendicular drawn from the sulfur atom to the line that connects the oxygen atoms. This result was obtained for the variant in which the signal of the pseudoaxial proton of the 5-CH$_2$ group is assumed to be the weak-field signal (see Table 1). The correlation of the calculated and experimental induced shifts (Δ_{calc} and Δ_{exp}) becomes considerably worse in the case of the alternative assignment of the signals of the methylene group. The good agreement between the Δ_{calc} and Δ_{exp} values indicates the correctness of the geometry of the III molecule that we used. Thus III in solution has a nonplanar conformation with the $C_{(5)}$ atom outside of the plane of the ring.

It must be noted that the geometrical structure of the adduct of the lanthanide shift reagent with the substrate that we found for III differs from the structure of the adducts of thiolene 1,1-dioxides presented in [3], in which it was shown that the lanthanide is located on the bisector of angle O–S–O. To ascertain the reasons for the disparity between our data and the literature data we calculated the location of the lanthanide ion in the adduct of Eu(FOD)$_3$ with yet another derivative of this heterocycle, viz., 3-methyl-3-thiolene 1,1-dioxide, under the assumption of a planar conformation of the thiolene ring (precisely this geometry for this compound was used by Wrobel and co-workers [3]). The corresponding contour map is presented in Fig. 2. It is apparent that the size of the region in which the probability of localization of the lanthanide ion is 95% (shaded region) is extremely significant; the point for which a minimum deviation of Δ_{calc} from Δ_{exp} is observed (the most probable position of the lanthanide ion in the adduct) does not lie on the bisector of angle O–S–O. The result obtained by Wrobel and co-workers [3] is evidently explained by the fact that the calculations of the geometrical structure were carried out using an insufficient number of starting parameters.

Thus the use of lanthanide shift reagents for the analysis of the PMR spectra of thiolene 1,1-dioxides makes it possible to simplify the spectra and to establish the preferred conformation of compounds in solution when data on the induced shifts for a sufficient number of magnetic nuclei are available.

EXPERIMENTAL

The PMR spectra of 0.2 mole/liter solutions of the substrate in $CDCl_3$ were recorded with a Tesla BS-487B spectrometer (80 MHz). The lanthanide shift reagent was introduced into the solutions in powdered form in successive portions up to a reagent/substrate molar ratio of 0.6, and the PMR spectrum was measured each time. The location of europium in the adducts was calculated with an SM-1 computer by means of the DINIYa program [6].

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ELECTROCHEMICAL MODELING OF THE OXIDATIVE DEHYDROGENATION OF 4H-THIOPYRANS

I. M. Sosonkin, A. N. Domarev,
N. I. Kozhevnikova, and V. G. Karchenko

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The oxidation of substituted 4H-thiopyrans on a rotating platinum disk electrode with a ring in acetonitrile was accomplished for the first time. It was established that the dehydrogenation of both tri- and pentasubstituted thiopyrans proceeds via a scheme involving the successive transfer of an electron, a proton, and an electron (an EPE process); 4H-thiopyrans are oxidized more readily than the corresponding oxygen analogs.

Up until now, the electrochemical oxidation of 4H-thiopyrans has not been studied. In order to study the effect of a sulfur atom in the heteroring we investigated the electrochemical behavior of these compounds.

We selected 2,4,6-triphenyl- (I) and 3,5-dimethyl-2,4,6-triphenyl-4H-thiopyran (II) as the subjects of our investigation due to the fact that, as shown in [1], as a consequence of the presence of methyl substituents in the $C_{(3)}$ and $C_{(5)}$ positions of the heteroring of II, its dehydrogenation in acidic media is realized via a different mechanism than that in the dehydrogenation of thiopyran I. In analogy with other heterocyclic compounds, one might have expected that cations with both retention [2] and elimination [3] of the substituent in $C_{(4)}$ position can be formed in the electrochemical oxidation of thiopyrans I and II. We therefore initially studied the electrochemical reduction of thiopyrylium cations III-VI — possible products of the oxidation of thiopyrans I and II — on a rotating platinum disk

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N. G. Chernyshevskii Saratov State University, Saratov 410601. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 3, pp. 318-320, March, 1984. Original article submitted March 1, 1983.