ANALYSIS OF THE STRUCTURE OF 2,5-DIMETHYL-4-METHYLENE-1,3-OXATHIOLANE BY NMR SPECTROSCOPIC METHODS

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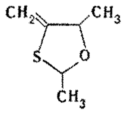
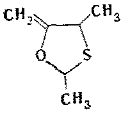
The ^{1}H and ^{13}C NMR spectra of 2,5-dimethyl-4-methylene-1,3-oxathiolane were analyzed by comparison of the calculated and experimental parameters with the aid of a paramagnetic shift reagent. The data obtained from the NMR spectra were used for the establishment of the structures of the products of isomerization and alcoholysis of 2,5-dimethyl-4-methylene-1,3-oxathiolane.

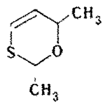
An unsaturated oxygen- and sulfur-containing heterocycle,* to which one of the following structures (I-IV) can be assigned on the basis of the results of elementary analysis and the IR and mass spectra, is formed in the reaction of sodium sulfide with acetylene in the presence of water:



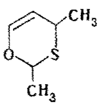
I



II



III



IV

With the aid of ^{1}H and ^{13}C NMR spectroscopy we were able to unambiguously prove that the heterocycle obtained is 2,5-dimethyl-4-methylene-1,3-oxathiolane (I) and that the cis to trans ratio is 55 : 45.

Inasmuch as there are no data in the literature on the NMR spectra of compounds of this type, we encountered difficulty in the interpretation of their ^{1}H and ^{13}C NMR spectra. We found it necessary to additionally use some special NMR spectroscopic methods: 1) a study of the PMR spectra of solutions in aromatic solvents; 2) an analysis of the changes in the PMR spectra in the presence of paramagnetic shift reagents (PSR); 3) ^{1}H$-\{^1$H$\}$ double homonuclear resonance under "total decoupling" and "INDOR" conditions; 4) recording of the ^{13}C NMR spectra at various temperatures under conditions of complete noise decoupling with the protons; 5) ^{13}C$-\{^1$H$\}$ double heteronuclear resonance by the "off-resonance" method; 6) a study of the NMR spectra of some derivatives of the heterocycle under consideration.

These methods in conjunction made it possible to find the chemical shifts (CS) of all of the ^{1}H and ^{13}C nuclei and the ^{1}H$-^1$H spin–spin coupling constants (SSCC) and to make the complete assignment of all of the signals in the ^{1}H and ^{13}C spectra (Fig. 1), the parameters of which are presented in Table 1.

Methods 3 and 5 have been widely used for the identification of coupled ^{1}H and ^{1}H and ^{1}H and ^{13}C nuclei and the assignment of them to a definite isomer, especially in the case of protons with close CS.

In the case of six-membered rings III and IV, in the ^{1}H spectrum one should expect the signals of two olefinic protons in the cis configuration with an SSCC of ~9 Hz for III or 6 Hz for IV [2] in the fact of a difference of the order of 1 ppm (III) or 2 ppm (IV) in their CS [3, 4]. As seen from Fig. 1 (spectrum a) and

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*The reaction was discovered by B. A. Trofimov, S. V. Amosova, and V. K. Voronov.

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TABLE 1. Parameters of the ^1H and ^{13}C NMR Spectra of Isomeric 2,5-Dimethyl-4-methylene-1,3-oxathiolanes[a]

^1H CS, ppm			$^1H-^1H$ SSCC, Hz			^{13}C CS, ppm			
No.[b]	cis	trans	No.[b]	cis	trans	No.[b]	No. of protons[c]	cis	trans
1	1,48	1,46	1—2	5,8	5,9	2	1	80,30	81,24
2	5,27	5,46	3—4	6,1	6,4	4	0	152,05	152,76
3	1,33	1,25	5—6	1,2[d]	1,2[d]	5	1	81,28	80,54
4	4,30	4,75	[(4—6) + (4—5)]/2	2,1[e]	1,6[e]	6	3	20,65	22,27
5	4,82[f]	4,82[f]	2—4	0,2	0,4	7	2	98,40	98,82
	4,63[d]	4,65[d]							
6	4,82[f]	4,82[f]							
	4,73[d]	4,76[d]				8	3	18,10	19,59

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[a] For pure liquids at 25° with tetramethylsilane as the internal standard (for both ^1H and ^{13}C); the accuracy in the measurement of the CS was ±0.01 ppm, and the accuracy in the measurement of the SSCC was ±0.1 Hz.

[b] The numbers of the ^1H and ^{13}C nuclei are indicated in conformity with Fig. 1.

[c] This is the number of directly connected ^1H nuclei found during recording of the ^{13}C spectrum by method 5 (see the text).

[d] 20 mole % in cumene.

[e] The finding of the true values of the SSCC was hindered by superimposition of the signals of the AB portion of both isomers; the half-sum of the SSCC, which characterized the ABX degenerate spin system [1], is presented.

[f] This is the center of the multiplet of the H^5 and H^6 protons (cis, trans).

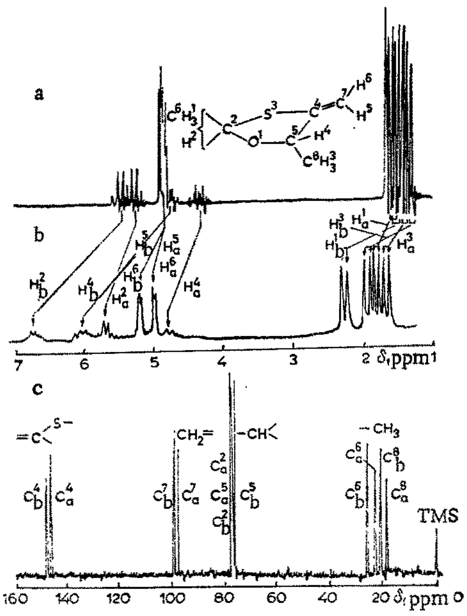


Fig. 1. NMR spectra of 2,5-dimethyl-4-methylene-1,3-oxathiolane: a) PMR spectrum; b) PMR spectrum in the presence of the paramagnetic shift agent; c) ^{13}C NMR spectrum.

Table 1, the H^5 and H^6 CS practically coincide. Recording of the ^1H NMR spectrum in an aromatic solvent (cumene) enabled us to find the $^1H^5-^1H^6$ SSCC, which was 1.2 Hz for both isomers; this excludes their cis configuration at the double bond.

The isomeric composition of oxathiolane I shows up graphically in the ^{13}C NMR spectrum during complete noise decoupling with the protons [Fig. 1 (spectrum c) and Table 1]; the spectrum contains 12 signals grouped in pairs. Moreover, in the CS region corresponding to carbon atoms with sp^2 hybridization there are two signals of ^{13}C nuclei ($\delta \sim 152$ ppm) that do not contain directly connected protons and two signals of carbon atoms ($\delta \sim 98$ ppm) that each contain two protons directly bonded with them. In the case of compounds of the III and IV type, all of the olefinic carbons should each contain one connected proton, i.e., they should be observed in the ^{13}C spectrum, recorded by methods 5, as doublets; this is not actually observed. All of this, together with ^{13}C CS, which do not agree with the values characteristic for the $-C=C-S-$ and $-C=C-O-$ fragments [5, 6] in six-membered heterocycles III and IV, makes it possible to exclude the latter from further consideration.

The choice between structures I and II can be made on the basis of an analysis of the CS of the $^1H^6$, $^{13}C^4$, $^{13}C^5$, and $^{13}C^7$ signals. Proceeding from the results that we previously obtained in a study of 5-methylene-1,3-dioxolanes [7, 8], in the NMR spectra of oxathiolane II one should have expected CS of the order of 3.90-4.40 ppm but not 4.80 ppm for the protons of the exocyclic methylene group, and CS of ~80 ppm instead of

TABLE 2. Observed and Calculated ΔCS ^{1}H Values in the PMR Spectrum of 2,5-Dimethyl-4-methylene-1,3-oxathiolane Containing Eu(DPM)$_3$ [a]

Compound	ΔCS (ppm) on atoms					
	1	2	3	4	5 [b]	6 [b]
1-cis (exptl.)	1,00	1,41	1,03	1,41	0,41	0,41
1-trans (exptl.)	1,00	1,61	0,84	1,58	0,42	0,42
1-cis,1-trans (calc.)	1,00	1,84	1,00	1,84	0,60	0,52

[a] The values were normalized with respect to the ΔCS $^1H^1$ values.
[b] The experimental ΔCS values for the center of the multiplet are indicated.

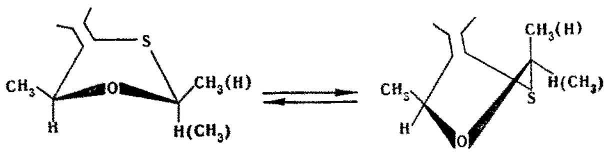
TABLE 3. Parameters of the PMR Spectra of the Products of the Reaction of Oxathiolane I with Methanol (pure liquid)

Compound	R^1	R^2	R^3	R^4	δ, ppm						SSCC, Hz		% (± 3)
					H	CH$_3$	R^1	R^2	R^3	R^4	CH$_3$—H	R$_1$—R$_2$	
VIa	CH$_3$	H	OCH$_3$	CH$_3$	5,15	1,46	1,18	3,65	3.23	1,47	5,8	6,3	45
VIb	CH$_3$	H	CH$_3$	OCH$_3$	5,18	1,45	1,13	3,85	1,46	3,24	5,8	6,4	10
VIc	H	CH$_3$	CH$_3$	OCH$_3$	5.28	1,39	3,97	1,14	1.45	3.25	6,1	6,4	35
VId	H	CH$_3$	OCH$_3$	CH$_3$	5,31	1,41	4,22	1,13	3,27	1,44	5,9	6,5	10

98 ppm for the ^{13}C nucleus directly connected to it. The ^{13}C atom, which has sp^3 hybridization and contains a sulfur atom in the α position should have a CS of ~40 ppm [9] for II rather than 80 ppm, as follows from the experiments. Finally, the SSCC of the olefinic protons in heterocycles of the II type have a different absolute value (3.0 Hz [8] instead of 1.2 Hz). Thus the disparity between the parameters of the NMR spectra and structure II is obvious.

Inasmuch as there is no description of the ^{1}H and ^{13}C NMR spectra of 4-methylene-1,3-oxathiolanes in the literature, we undertook an attempt to make an approximate calculation of the CS of the ^{1}H and ^{13}C signals for heterocycle I, proceeding from known additive schemes for ^{1}H-substituted ethylenes [3, 4] and 1,3-dioxolanes [8]* and for ^{13}C in alkenes [9], saturated heterocycles [10], and substituted aliphatic compounds [11, 12]. The results of the calculation not only are in satisfactory agreement with the experimental ^{1}H and ^{13}C CS of I but also provide a basis for the assignment of the observed ^{1}H signals to the cis and trans isomers. The definitive assignment was made on the basis of a number of well-known principles: The methyl groups attached to C$^{5(4)}$ in 1,3-dioxolanes have a deshielding effect on the proton attached to C^2 in the cis position relative to them [8, 13, 14], whereas a methyl group attached to C^2 has an effect on the cis proton attached to C$^{5(4)}$; as a rule, the long range spin–spin coupling constants of the protons attached to C^2 and C$^{5(4)}$ have greater absolute values when they are mutually trans oriented [8, 15]; steric interaction of substituents, specifically in substituted cyclopentanes [16] and 4-methylene-1,3-dioxolanes, leads, as a rule, to a shift in the signals of the ^{13}C nuclei bonded to them to the region of stronger shielding [17]. Allowance for the principles enumerated above enabled us to confidently assign the corresponding $^1H^2$ and $^1H^4$ and $^{13}C^6$ and $^{13}C^8$ signals to the cis and trans configurations.

Inasmuch as heterocycle I contains an exocycle double bond, it cannot have such conformational lability as 1,3-dioxolane or cyclopentane. Two conformations of the "half-chair" type are apparently the most populated conformations for each isomer.



Steric interaction between the CH$_3$ groups in the cis isomers should lead to a shift of their ^{13}C signals to stronger field as compared with the corresponding signals of the trans isomer. It therefore might have been assumed that the CS of the signals of these carbons would be more sensitive to redistribution of the populations of the conformations, let us say, as the temperature changes. In fact, as the temperature rises

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*When we used increments of this scheme for 4-methylene-1,3-oxathiolanes we found it necessary to take into account the high rigidity of the latter.

from 25 to 55°, for example, ΔCS $^{13}C^6$ in the cis isomer is 0.13 ppm as compared with 0.04 ppm in the trans isomer. This is in good agreement both with the assignment of the signals and with the fact that the differences in the shielding of the CH_3 groups of the isomers are actually due mainly to steric interaction.

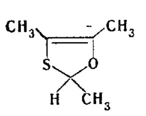
Inasmuch as all of the protons in the isomers of I under consideration are involved in spin–spin coupling, whereas all of the ^{13}C nuclei in turn couple with the protons, the careful performance of experiments involving double homonuclear ($^1H-\{^1H\}$) and heteronuclear* ($^{13}C-\{^1H\}$) resonance enabled us to make the complete assignment of all of the remaining ^1H and ^{13}C signals. This is impossible to do directly from the ^1H and, particularly, the ^{13}C NMR spectra, inasmuch as the ratio of the unseparated isomers formed in the reaction is close to unity.

The results obtained upon recording the spectrum in the presence of tris(dipivaloylmethanato)europium [Eu(DPM)$_3$] (Fig. 1, spectrum b) and comparison of the shifts of the lines (ΔCS) of the complex relative to their positions in the spectrum of a sample without an additive [18] constituted an independent confirmation of the above assignment of the signals of the protons of each of the isomers. The following facts are evident from a comparison of spectra a and b in Fig. 1: first, the $^1H^1-^1H^6$ ΔCS values in the spectrum of the trans isomer exceed the corresponding values for the cis isomer by a factor of approximately three; second, in each of the isomers, $\Delta CS^1H^1 \simeq \Delta CS^1H^3$, whereas $\Delta CS\ ^1H^2 \simeq \Delta CS\ ^1H^4$. As is well known [19], in the case of a pseudocontact coupling mechanism the ΔCS value for axially symmetrical complexes should be determined by the distance (r) from the coordinating ion to the resonating nucleus of the ligand and the angle (θ) between the corresponding radius vector and the axis of symmetry of the Eu^{3+} complex.

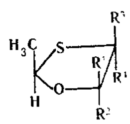
Using the equation in [20], $\Delta CS = K(3\cos^2\theta - 1)/r^3$ (where K is a constant) and assuming the distance from Eu^{3+} to the coordinating S or O atom in the ring is 3.0 Å [21] and approximate bond lengths (C–H 1.10 Å, C–O 1.40 Å, C–S 1.70 Å, C–C 1.55 Å, and C=C 1.35 Å) and angles between them (C–O–C 110°, C–S–C 100°, and O–C–S and O–C–C 110°) [22], averaged for the two conformations, we were able to show that the assumption of coordination of the paramagnetic ion with the S atom does not give even a rough qualitative correspondence between the observed and calculated ΔCS values. Moreover, a calculation of ΔCS ^1H starting from coordination exclusively at the oxygen atom gives not only qualitative but also good quantitative agreement with the experimental results (Table 2).

It follows from Table 2 that the adopted conformational model of heterocycle I is sufficiently competent* and coordination is realized at the oxygen atom. The absence of appreciable coordination at the sulfur atom [23] is apparently due to the considerably lower basicity of this center as compared with the oxygen atom. In fact, as is well known [24], direct bonding of a sulfur atom to an sp^2-hybridized carbon atoms leads to a pronounced decrease in its basicity. The considerable difference in the corresponding ΔCS values in the isomers is apparently due to the difference in their reagent–substrate dissociation constants. The certain amount of steric hindrance to complexing in the cis isomer is most likely responsible for this. We were unable to observe the ^{13}C NMR spectra of the complexes (≃15 mole %I in CCl_4).

Independent proof of the structure of heterocycle I was obtained in a study of its thermal isomerization to 2,4,5-trimethyl-1,3-oxathiole (V) and of isomeric products of addition to oxathiolane I of methanol (VIa-d).



V



VI a-d

The isomerization was carried out directly in the pickup of the NMR spectrometer; in a 10% solution in CCl_4 oxathiolane I underwent 70% isomerization to oxathiole V at 100° in 90 min. One's attention is drawn to the fact that the disappearance of the signals of both isomers proceeds symbatically. The parameters of the NMR spectrum of V (of the pure liquid at 25° with tetramethylsilane as the standard; the number of the proton, its CS in parts per million, the multiplicity, and the SSCC in hertz are indicated) are: $^1H^1$ 5.73, quartet, 5.9; $^1H^2$ 1.52, doublet, 5.9; $^1H^3$ 1.69, quartet, 1.0; $^1H^4$ 1.64, quartet, 1.0. The ^{13}C chemical shifts in parts per million are: $^{13}C^2$ 82.40, $^{13}C^4$ 101.10, $^{13}C^5$ 139.75, $^{13}C^6$ 23.50, $^{13}C^7$ 11.74, and $^{13}C^8$ 11.60. The

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*Off resonance and complete decoupling of the individual ^{13}C nuclei for finding the CS of the directly coupled protons.

†The results of a study of the isomeric I with PSR additives by ^1H and ^{13}C NMR methods for the elucidation of the problem of the conformation of the heterorings will be published separately.

assignment was proved by $^{13}C-\{^1H\}$ double NMR. The parameters of the ^1H NMR spectra of VIa-d and their percentages in the mixture of isomers are presented in Table 3. The identification of all of the signals is the spectrum of the mixture was accomplished by comparison with the PMR spectra of the individual components (isolated by means of preparative chromatography) and analysis of the ^1H CS in the spectra of the latter on the basis of known additive relationships [8].

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