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SYNTHESIS OF 2-THIABICYCLO[3.2.0]HEPT-3-ENES BY REACTION OF ACETYLENE WITH SODIUM SULFIDE

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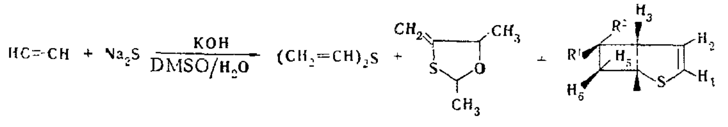
The previously unknown 2-thiabicyclo[2.3.0]hept-3-ene and exo- and endo-6-methyl-2-thiabicyclo[3.2.0]hept-3-enes were synthesized in one step from acetylene and sodium sulfide in aqueous dimethyl disulfoxide.

It was recently observed [1, 2] that 2,5-dimethyl-4-methylene-1,3-octathiolane (I) is formed along with the major product – divinyl sulfide [1] – in the reaction of acetylene with sodium sulfide in aqueous dimethyl sulfoxide (DMSO):



I

II–IV

II $R^1=R^2=H$; III $R=H$, $R^2=CH_3$; IV $R^1=CH_3$, $R^2=H$

Under special conditions [3] oxathiolane I is obtained in 15-28% yield.

Continuing these studies we isolated three new individual compounds (II-IV) in an overall yield of ~3% from the reaction products by preparative gas–liquid chromatography (GLC).

According to the PMR, IR, and mass spectrometric data and the results of elementary analysis, the lowest-boiling of the three compounds is 2-thiabicyclo[3.2.0]hept-3-ene (II) and the other two are its 6-methyl substituted derivatives [exo (III) and endo (IV) forms].

The IR spectra of II-IV contain intense $\nu_{C=C}$ bands at 1570-1590 cm^{-1}. The low frequency and the high intensity of these bands are not characteristic for cycloalkenes [4] but are customary for the $H_2C=CHS$ group-

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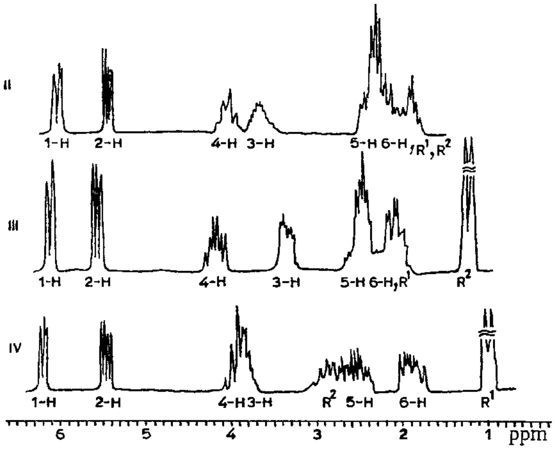


Fig. 1. PMR spectra of 2-thiabicyclo[3.2.0]-hept-3-enes (II-IV).

ing [4, 5]. The two weak bands of C_{sp^2}−H bonds at 3040 and 3060 cm^{-1} make it possible to assume that the hydrogen atoms are attached to different carbon atoms, and the absence of the absorption at 3090 cm^{-1} that is characteristic for terminal ethylene sulfides [4-6] indicates the absence of this fragment. In addition, the position of the bands of the C_{sp^2}−H deformation vibrations (890-910 and 960-970 cm^{-1}) and stretching vibrations of the C−S bond (narrow very intense bands at 690-700 cm^{-1}) is not characteristic for the $CH_2{=}CHS$ grouping [4-6]. Thus the IR spectra provide a basis for the assumption that all three of the investigated compounds contain a CH=CHS fragment. In addition, the band of a methyl group (1375 cm^{-1}), which is absent in the spectrum of II, is completely unambiguously identified in the IR spectra of III and IV.

The molecular-ion peak in the mass spectra of the investigated compounds is the second most intense peak. The most intense peak (m/e 84) corresponds to the thiophene structure (here and subsequently, the m/e values are presented for the corresponding ions). The subsequent fragmentation of the substance on electron impact proceeds via the usual pathways [7]. In the case of III and IV one observes an intense peak at 97, which is not observed in the mass spectrum of II. The formation of this intermediate ion, which is evidently a stable thiapyrylium ion, can be explained by a rearrangement similar to the rearrangement of alkylbenzenes [8].

The PMR spectra of II-IV have much in common (Fig. 1). The olefinic protons are represented by two multiplets (δ 5.60 and 6.20 ppm) corresponding to the CH=CH fragment (J = 6 Hz) in all cases. The position of the signals is typical for α,β-ethylene sulfides [9-12], and the magnitude of the J constant is characteristic for protons attached to a double bond included in a five-membered ring [13]. Compound II does not contain a methyl group, at the same time that III and IV are none other than methylated derivatives of II (δ_{CH_3} 1.20 and 0.98 ppm, respectively).

The PMR spectra make it possible to reject the alternative 2-thiabicyclo[3.1.1]hept-3-ene structure (V)

V

for the following reasons: in compounds with similar structures the J constant of the olefinic protons is considerably higher than the observed value (8-10 Hz) [14]; the protons of the bridge CH_2 groups in this bicyclic system should be equivalent in pairs, but this is not observed.

Structure II is also confirmed by the ^{13}C NMR spectrum, which contains six signals (rather than five, as would be the case for structure V, since the bridge carbon atoms in the latter are equivalent): 126.14, 124.71, 51.46, 45.44, 33.21, and 30.02 ppm. The two primary carbon atoms have sp^2 hybridization, whereas two of the tertiary and two of the secondary atoms of the subsequent four carbon atoms have sp^3 hybridization, respectively.

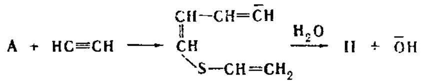
The signals of the methyl groups in the spectra of III and IV are doublets ($J \approx 6.6$ Hz) characteristic for the CH_3CH fragment in a ring, i.e., methylation is realized in the 6 or 7 position. The choice between these possibilities in favor of methylation at the C_6 atom follows from $^1H-\{^1H\}$ double-resonance experiments: the geminal proton with respect to the CH_3 group and the β proton (relative to the S atom) of the double bond couple quite strongly with the proton attached to the C_5 atom situated relative to each of them through three bonds.

Recording of the PMR spectrum in the presence of a paramagnetic shift reagent [(dipivaloylmethanato)-europium] makes it possible to conclude that II has an exo structure, since the signals of its methyl group undergo less of a paramagnetic shift and the signals of its methylidyne proton [$CH(CH_3)$] undergo a greater paramagnetic shift than observed for IV.

Let us now examine the probable scheme of the formation of bicyclic compounds II-IV. The successive addition of the doubly charged sulfide anion to two acetylene molecules in a protogenic medium, which leads primarily to divinyl sulfide, evidently proceeds through intermediate carbanion A:

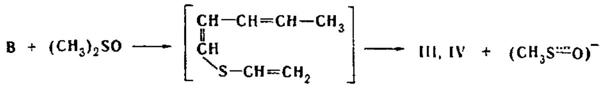
$$CH_2{=}CHSCH{=}\bar{C}H \quad A$$

In the absence of sufficient protons, the latter can add a third acetylene molecule to give vinyl 1,3-butadienyl sulfide, which is subsequently cyclized to 2-thiabicyclo[3.2.0]hept-3-ene (II):

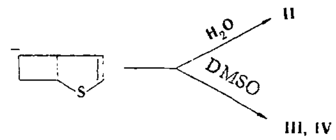


B

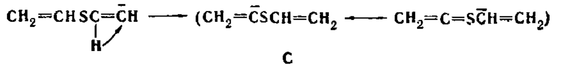
Bicyclic compounds III and IV may be formed as a result of methylation of vinylmercapto-1,3-butadienyl carbanion B by DMSO and subsequent cyclization:



The possibility of methylation of carbanions with DMSO under the conditions of reaction (1) was proved in [15]. One also cannot exclude the possibility that anion B itself undergoes cyclization and that the resulting bicyclic anion is subsequently stabilized either by a proton or by a method group from the medium:

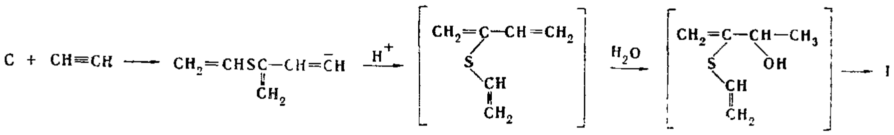


The formation of 2,5-dimethyl-4-methylene-1,3-oxathiolane (I) can also be better understood in the light of the data obtained. The isomerization of carbanion A should be advantageous, since the vacant orbitals of sulfur are included in this way in the charge distribution.



C

The addition of isomerized carbanion C to acetylene, stabilization of the new carbanion by a proton from the medium, and hydration lead to oxathiolane I:



VI

The identification of the oxygen analog of sulfide VI in the products of the reaction of acetylene with selenium, which proceeds under similar conditions [16], may serve as additional proof for a scheme of this type.

All of these schemes predict an increase in the yields of I-IV as the concentration of water in the system decreases (as the protogenic character of the medium decreases), and this is actually observed.

The described one-step method for the synthesis of the new 2-thiabicyclo[3.2.0]hept-3-ene bridged heterocyclic system, despite the low yield, may become a preparative method owing to its exceptional simplicity and the accessibility of the starting substances and also because it is presently difficult to propose any other approaches to the construction of a system of this type. After the industrial incorporation of the new method for the preparation of divinyl sulfide [1] based on reaction (1), thiabicycloheptenes II-IV, being side products of this reaction, will not only become accessible compounds but even compounds that are needed.

EXPERIMENTAL

The ^1H and ^{13}C NMR spectra were recorded without a solvent with a high-resolution XL-100/12 spectrometer with tetramethylsilane as the internal standard. The mass spectra were recorded with a MKh-1303 spectrometer at an ionizing-electron energy of 50 eV, an accelerating voltage of 2 kV, and t_k 100°. Preparative GLC was accomplished with a Khrom-3 apparatus with 15% polyphenyl ether on Chromaton N-AW-HMDS as the stationary phase; the temperature of the 4 m × 10 mm column was 135°, the vaporizer temperature was 180°, and the carrier gas was helium.

2-Thiabicyclo[3.2.0]hept-3-enes (II-IV). A 30-liter reactor equipped with a stirrer was charged with 16 liters of DMSO, 3.8 kg of anhydrous sodium sulfide, 2.2 kg of H_2O, and 2.7 kg of KOH. The flask was heated to 90-95°, and acetylene was passed through the mixture continuously with stirring (100 rpm) at 2 atm. The feed rate was determined by absorption and was found to be 70-80 liters/h without reduction to the standard conditions.

After acetylene absorption had ceased, the mixture was removed from the flask and subjected to fractionation to give divinyl sulfide, with bp 82-87° (720 mm); 2,5-dimethyl-4-methylene-1,3-oxathiolane with bp 50-60° (30 mm); and 230 g of a fraction with bp 60-70° (30 mm) containing approximately equal amounts of I and thiabicycloheptene II-IV (in ~3% yield).

Preparative GLC of this fraction yielded the individual thiabicycloheptenes II-IV. 2-Thiabicyclo[3.2.0]-hept-3-ene (II) had n_D^{20} 1.5432, d_4^{20} 1.0736, and bp 62-63° (30 mm). Found: C 64.8; H 7.2; S 28,2%. C_6H_8S. Calculated: C 64.3; H 7.1; S 28.6%. Mass spectrum: 112, 84, 71, 58, 47, and 33. exo-6-Methyl-2-thiabicyclo-[3.2.0]hept-3-ene (III) had n_D^{20} 1.5286, d_4^{20} 1.0485, and bp 65-66° (30 mm). Found: C 66.4; H 8.02; S 25.1%. $C_7H_{10}S$. Calculated: C 66.6; H 7.9; S 25.4%. Mass spectrum: 126, 111, 98, 97, 84, 71, 58, 47, and 33. endo-6-Methyl-2-thiabicyclo[3.2.0]hept-3-ene (IV) had n_D^{20} 1.5287, d_4^{20} 1.0425, and bp 66-67° (30 mm). Found: C 66.6; H 8.0; S 25.2%. $C_7H_{10}S$. Calculated: C 66.6; H 7.9; S 25.4%. Mass spectrum: 126, 111, 98, 97, 84, 71, 58, 47, and 33.

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