give the product in quantitative yield. The product was identical to ketol II obtained in the preceding experiment.

Di(2-dicyanomethylenecyclohexyl) Sulfide (III). A 2-g sample of diketone I, 1.3 g of malononitrile, and a few drops of piperidine were dissolved in 50 ml of alcohol, and the mixture was allowed to stand at room temperature for 2 days. The precipitated crystals were removed by filtration, washed with alcohol, and dried to give 1.5 g (52%) of III with mp 172-173° (acetonitrile). Found: C 66.7; H 5.8; N 17.3; S 10.0%. $C_{18}H_{18}N_4S$. Calculated: C 67.1; H 5.6; N 17.4; S 10.0%. IR spectrum: 2227 ($C\equiv N$) and 1605 ($C=C$) cm^{-1}.

Leuckart Reaction for I and II. A mixture of 26 g of diketone I or ketol II, 70 ml of formamide, and 70 ml of 85% formic acid was refluxed for 2 h, after which 400 ml of HCl (1 : 1) was added, and the mixture was refluxed for another hour. It was then cooled slowly to room temperature, and the precipitated crystals of α-IV hydrochloride were removed by filtration to give 9.3 g (37%) of a product with mp 253-255°. The mother liquor was cooled with ice to precipitate 3.2 g (13%) of β-IV hydrochloride with mp 301-302°. The hydrochlorides were dissolved in water, the solutions were made alkaline with NaOH, and the precipitated bases were recrystallized from 50% alcohol. The products were obtained in quantitative yield. The α isomer was obtained as colorless prisms with mp 71.5-72.5° and R_f 0.25. Found: C 67.7; H 10.2; N 6.4; S 15.4%. $C_{12}H_{21}NS$. Calculated: C 68.2; H 10.0; N 6.6; S 15.2%. The picrate had mp 188-189° (dec.). Found: N 13.0%. $C_{18}H_{24}N_4O_7S$. Calculated: N 12.7%. The β isomer was obtained as colorless plates with mp 99-99.5° and R_f 0.1. Found: C 67.6; H 10.1; N 6.3; S 15.0%. $C_{12}H_{21}NS$. Calculated: C 68.2; H 10.0; N 6.6; S 15.2%. The picrate had mp 198° (dec.). Found: N 13.0%. $C_{18}H_{24}N_4O_7S$. Calculated: N 12.7%.

LITERATURE CITED

1. V. I. Vysotskii, K. G. Chuprakova, and M. N. Tilichenko, Zh. Obshch. Khim., 46, 785 (1976).
2. M. N. Tilichenko and T. I. Akimova, Zh. Organ. Khim., 6, 976 (1970).
3. M. N. Tilichenko, Scientific Yearbook of Saratov State University [in Russian], (1954), p. 504.
4. M. N. Tilichenko and V. I. Vysotskii, Dokl. Akad. Nauk SSSR, Ser. Khim., 119, 1162 (1958).
5. M. N. Tilichenko and V. T. Kharchenko, 29, 2370 (1959).
6. M. N. Tilichenko and V. T. Kharchenko, 30, 2283 (1960).

STUDY OF THE REACTION OF SULFUR HALIDES WITH UNSATURATED COMPOUNDS

XIII.* OXIDATION OF THIABICYCLOTRIDECENES

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UDC 547.732'818'897:542.943

The oxidation of thiabicyclotridecenes with various oxidizing agents proceeds selectively and, depending on the amount and strength of the oxidizing agent, gives sulfoxides, epoxy sulfoxides, or epoxy sulfones. The sulfur atom is initially oxidized, after which the double bond either undergoes epoxidation or hydroxylation.

The oxidation of sulfides is currently attracting considerable attention [1]. Research directed toward the study of the effect of the character of the oxidizing agent and steric factors on the degree of oxidation of the sulfur atom may be of particular interest. In this respect, convenient experimental subjects are 13-thia-

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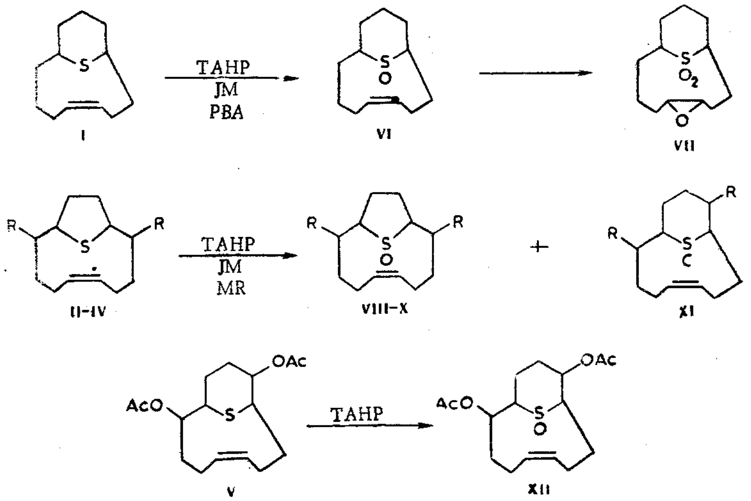
*See [9] for communication XII.

Bashkirsk Branch, Institute of Chemistry, Academy of Sciences of the USSR, Ufa. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 4, pp. 475-478, April, 1976. Original article submitted March 24, 1975.

bicyclotridecene derivatives I-V, obtained by the addition of sulfur dichloride to trans,trans,cis- and trans, trans,trans-cyclododecatrienes [2, 3]. Depending on the type of substituent attached to C-2 and C-9 (C-10), one can change the degree of shielding of the sulfur atom and thereby regulate the oxidation process. It has been shown [3, 4] that I-V are cis-disubstituted (in the heteroring) thiabicyclans with an endo orientation of the substituents attached to C-2 and C-9 (C-10).

We have investigated the oxidation of thiabicyclans I-V with various oxidizing agents – the Jones mixture (JM) [5], the Milas reagent (MR) [6], perbenzoic acid (PBA) [7], and tert-amyl hydroperoxide (TAHP) in the presence of $MoCl_5$ [8].



Sulfoxides VI and IX, respectively, were obtained in no higher than 50% yields on treatment of 13-thiabicyclo[7.3.1]-cis-5-tridecene (I) and 2,9-diacetoxy-13-thiabicyclo[8.2.1]-cis-5-tridecene (III) with a fourfold excess of JM in acetone. Sulfones were not detected even when a large excess of JM was used. The presence of a sulfoxide group is confirmed by the absorption band at 1020-1055 cm^{-1}.

The oxidation of sulfides I-V with an equimolar amount of TAHP in the presence of $MoCl_5$ makes it possible to obtain sulfoxides in almost quantitative yields. The double bond in the sulfides is not involved in the reaction. Rearrangement of the skeleton with expansion of the thiacyclopentane ring to thiacyclohexane XI [9] was observed in the oxidation of adduct II to the sulfoxide.

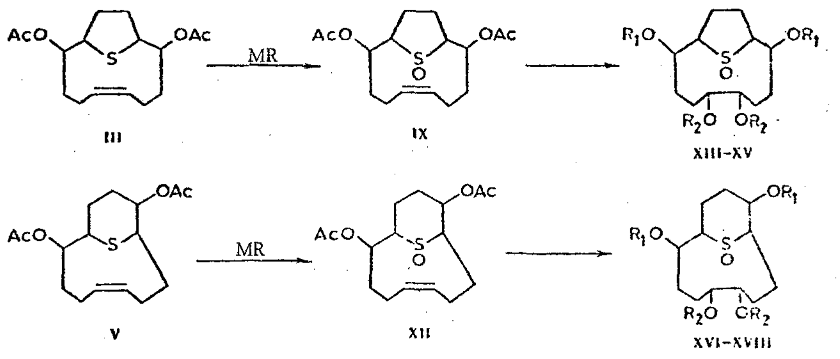
Excess TAHP brings about epoxidation of the double bond. Thus the reaction of unsubstituted sulfide I with 5 moles of TAHP gives epoxy sulfone VII. The structure of VII is confirmed by its IR spectrum, which contains bands at 755, 770, and 820, and at 1125 and 1285 cm^{-1}, which are characteristic, respectively, for epoxy and sulfone groupings. In addition, the epoxy group is determined by titration by the method in [10]. The PMR spectrum does not contain signals in the region of protons attached to a double bond, but the $HC-SO_2$ protons and the protons of the epoxy group give a four-proton signal – a multiplet centered at ~2.8 ppm – and the multiplet of the remaining methylene protons is centered at ~ 2.06 ppm.

Epoxy sulfoxides are formed in the case of disubstituted sulfides. Oxidation to the sulfone is evidently hindered by the presence of electronegative substituents attached to C-2 and C-9 (C-10). In addition, an examination of three-dimensional models of sulfides II-V shows that approach of the oxidizing agent to the sulfur atom is hindered on the side of the cis-C-1–C-2 and cis-C-9–C-10 bonds and, correspondingly, on the large ring side.

It is interesting to note the fact that diacetoxy sulfide III is oxidized selectively to sulfoxide IX without involvement of the double bond when a small excess of MR is used. Hydroxylation of the double bond is realized when a large excess of MR is used and gives 2,9-diacetoxy-5,6-dihydroxy-13-thiabicyclo[8.2.1]-tridecane 13-oxide (XIII). A sulfone is not detected in this case also.

Sulfoxide XIII is converted to 2,5,6,9-tetrahydroxy-13-thiabicyclo[8.2.1]tridecane 13-oxide (XIV) on saponification with alcoholic alkali. Treatment of XIII with acetic anhydride in anhydrous pyridine gives 2,5,6,9-tetraacetoxy-13-thiabicyclo[8.2.1]tridecane 13-oxide (XV).

The formation of sulfoxides VI and IX was established in the oxidation of sulfides I and II with an equimolar amount of PBA. The oxidation of sulfides I and III with excess PBA gives epoxy sulfoxides.



EXPERIMENTAL METHOD

The IR spectra of mineral oil or hexachlorobutadiene suspensions of the compounds were recorded with a UR-20 spectrometer. The PMR spectra of the compounds were obtained with a Tesla BS-487B spectrometer (80 MHz) with hexamethyldisiloxane as the internal standard. Neutral Al_2O_3 (activity II) and benzene–alcohol (9 : 1) were used for thin-layer chromatography (TLC). The starting sulfides were obtained by the method in [2, 3].

General Method for the Oxidation of Sulfides to Sulfoxides. 1) TAHP and $MoCl_5$. tert-Amyl hydroperoxide purified through the sodium salt and vacuum fractionated was used for the oxidations. A mixture of equimolar amounts of the sulfide and TAHP, as well as $MoCl_5$ (5-10 mg per gram of substance), was refluxed in benzene for 15-30 min with monitoring of the oxidation reaction by TLC. The sulfoxides were obtained in quantitative yields.

2) With the Jones Mixture in Acetone. The oxidation was carried out in acetone solution with the gradual addition of threefold and fourfold excesses of the Jones mixture, after which the mixtures were allowed to stand for 15-30 min. They were then extracted with ether, the ether extracts were washed to neutrality with water and dried, and the solvent was removed by distillation.

3) With the Milas Reagent. The starting sulfides were dissolved in a small volume of chloroform, excess MR (60%) and a granule of OsO_4 were added, and the mixture was allowed to stand for 15-30 min. The solvents were removed by distillation, and the residues were crystallized. All of the sulfoxides obtained by oxidation with JM, PBA, MR, and TAHP were identical.

13-Thiabicyclo[7.3.1]-cis-5-tridecene 13-Oxide (VI). This compound was obtained as a colorless oil with n_D^{20} 1.4250. Found: C 68.2; H 9.1; S 15.3%. $C_{12}H_{20}OS$. Calculated: C 68.0; H 9.4; S 15.1%.

5,6-Epoxy-13-thiabicyclo[7.3.1]tridecane 13,13-Dioxide (VII). This compound was obtained from 5 moles of TAHP per mole of sulfide after refluxing for 2 h. Crystallization of the product from methanol gave VII with mp 135-137°. Found: C 59.0; H 8.2; S 13.2; O_{oxide} 6.6%. $C_{12}H_{20}O_3S$. Calculated: C 59.0; H 8.2; S 13.1; O_{oxide} 6.5%. IR spectrum: 765, 775, 820, 920, 1270, 1300 $(-\underset{O}{C-C}-)$, 1125, 1285, and 1320 (SO_2) cm^{-1}. PMR spectrum (in CCl_4), δ, ppm: 2.75-3.25 (4H, $H-C-SO_2$ $H-\underset{O}{C-C}-H$), and 1.5-2.1 (16H, $-CH_2-$).

2,9-Diacetoxy-13-thiabicyclo[8.2.1]-cis-5-tridecene 13-Oxide (IX). This compound had mp 163-165° and R_f 0.5. Found: C 58.7; H 7.6; S 9.8%. $C_{16}H_{24}O_5S$. Calculated: C 58.5; H 7.3; S 9.8%. IR spectrum: 735 (cis-HC=CH), 1050 (SO), 1245 and 1755 ($OCOCH_3$) cm^{-1}. PMR spectrum (in $CDCl_3$), δ, ppm: 5.4 m (2H, HC=CH), 4.6 t (2H, HCOAc), 3.0 m (2H, HCSO), and 1.96 s (6H, $OCOCH_3$).

2,9-Dihydroxy-13-thiabicyclo[8.2.1]-cis-5-tridecene 13-Oxide (X). This compound had mp 160-165° and R_f 0.0. IR spectrum: 720 (cis-CH=CH), 1015 (SO), 3100, and 3300 (OH) cm^{-1}.

2,10-Diacetoxy-13-thiabicyclo[7.3.1]-cis-5-tridecene 13-Oxide (XII). This compound had mp 135-137° (from alcohol). Found: C 58.6; H 7.1; S 10.0%. $C_{16}H_{24}O_5S$. Calculated: C 58.5;

H 7.3; S 9.8%. IR spectrum: 735, 3015 (cis-HC=CH–), 1060 (SO), 1250, and 1750 ($OCOCH_3$) cm^{-1}. PMR spectrum (in $CDCl_3$), δ, ppm: 5.0-5.8 (2H, HC=CH; 2H, HCOAc), 2.5-3.2 m (2H, HCS; 2H, HCC=), and 2.08 s and 2.0 s (6H, $OCOCH_3$).

2,9-Diacetoxy-5,6-dihydroxy-13-thiabicyclo[8.2.1]tridecane 13-Oxide (XIII). A granule of osmic acid was added to a solution of 4.6 g of III in 20 ml of chloroform, after which 16.1 ml of the MR was added with stirring, and the mixture was allowed to stand overnight. The solvent was removed by distillation, and the solid residue was crystallized from alcohol to give 5 g (90%) of XIII with mp 225-228°. Found: C 53.4; H 6.9; S 8.9%. $C_{16}H_{26}O_7S$. Calculated: C 53.0; H 7.2; S 8.8%. IR spectrum: 1050 (SO), 1240 and 1745 ($OCOCH_3$), and 3300-3400 (OH) cm^{-1}.

2,5,6,9-Tetrahydroxy-13-thiabicyclo[8.2.1]tridecane 13-Oxide (XIV). This compound, with mp 135-140°, was obtained by saponification of XIII. Found: C 51.6; H 8.0; S 12.0%. $C_{12}H_{18}O_5S$. Calculated: C 51.8; H 8.0; S 11.5%. IR spectrum: 1050 (SO) and 3300-3400 (OH) cm^{-1}.

2,5,6,9-Tetraacetoxy-13-thiabicyclo[8.2.1]tridecane 13-Oxide (XV). A 0.3-ml sample (a fourfold excess) of acetic anhydride was added to a solution of 0.11 g of XI in 10 ml of anhydrous pyridine, and the mixture was allowed to stand overnight. The solvent was then removed by distillation, and the residue was crystallized from acetone to give a product with mp 214-216° in 85% yield. Found: C 53.4; H 6.6; S 13.2%. $C_{20}H_{30}O_9S$. Calculated: C 53.3; H 6.7; S 13.4%. IR spectrum: 1030 (SO), 1250, and 1750 ($OCOCH_3$) cm^{-1}.

2,10-Diacetoxy-5,6-dihydroxy-13-thiabicyclo[7.3.1]tridecane 13-Oxide (XVI). This compound, with mp 65-70°, was obtained by the method used to synthesize XIII. Found: C 52.8; H 7.4; S 9.0%. $C_{16}H_{26}O_7S$. Calculated: C 53.0; H 7.2; S 8.8%. IR spectrum: 1030 (SO), 1240, 1740 ($OCOCH_3$), and 3300-3500 (OH) cm^{-1}.

2,5,6,10-Tetrahydroxy-13-thiabicyclo[7.3.1]tridecane 13-Oxide (XVII). This compound, with mp 180-183°, was obtained by saponification of XVI. Found: C 51.6; H 8.0; S 11.8%. $C_{12}H_{18}O_5S$. Calculated: C 51.8; H 8.0; S 11.5%. IR spectrum: 1040 (SO) and 3300-3500 (OH) cm^{-1}.

2,5,6,10-Tetraacetoxy-13-thiabicyclo[7.3.1]tridecane 13-Oxide (XVIII). This compound, with mp 125-127°, was obtained by the method used to synthesize XV. Found: C 53.2; H 7.0; S 13.0%. $C_{20}H_{30}O_9S$. Calculated: C 53.3; H 6.7; S 13.4%. IR spectrum: 1040 (SO), 1245, 1745 ($OCOCH_3$), 1230, and 1730 ($OCOCH_3$) cm^{-1}.

LITERATURE CITED

1. E. N. Karaulova, The Chemistry of Petroleum Sulfides [in Russian], Moscow (1970).
2. N. N. Novitskaya, R. V. Kunakova, G. K. Samirkhanova, and G. A. Tolstikov, Zh. Organ. Khim., 9, 636 (1973).
3. N. N. Novitskaya, R. V. Kunakova, E. E. Zaev, G. A. Tolstikov, and L. V. Spirikhin, Zh. Organ. Khim., 11, 1434 (1975).
4. A. Sh Sultanov, N. N. Novitskaya, V. I. Khvostenko, G. A. Tolstikov, R. V. Kunakova, and S. R. Rafikov, Dokl. Akad. Nauk SSSR, 211, 866 (1973).
5. L. Fieser and M. Fieser, Reagents for Organic Synthesis, Vol. 1-3, Wiley.
6. R. A. Raphael (editor), Advances in Organic Chemistry, Vol. 1, Wiley (1960).
7. E. N. Prilezhaeva, The Prilezhaev Reaction, Electrophilic Oxidation [in Russian], Moscow (1973).
8. G. A. Tolstikov, U. M. Dzhemilev, N. N. Novitskaya, and V. P. Yur'ev, Izv. Akad. Nauk SSSR, Ser. Khim., 2744 (1972).
9. N. N. Novitskaya, R. V. Kunakova, L. K. Yuldasheva, E. E. Zaev, E. V. Dmitrieva, and G. A. Tolstikov, Izv. Akad. Nauk SSSR, Ser. Khim., No. 2, 196 (1976).
10. M. M. Chakrabarty, D. Bhattacharyya, and M. Kundu, Analyst, 95, 85 (1970).