REACTIONS OF HYDROPEROXIDES COMMUNICATION 9. OXIDATION OF SULFUR-CONTAINING COMPOUNDS WITH HYDROPEROXIDES IN THE PRESENCE OF MOLYBDENUM SALTS

G. A. Tolstikov, U. M. Dzhemilev, N. N. Novitskaya, and V. P. Yur'ev UDC 542.943.7:547.73:547.459

Very many papers have been devoted to the oxidation of the sulfur atom in sulfur-containing compounds. Hydrogen peroxide, nitric acid, hexavalent chromium salts, potassium permanganate, periodates, hypochlorites, and other inorganic oxidizing agents are used for this purpose [1-4]. Among the organic reagents the peracids [5] have found the most extensive use. The oxidation of the S-S of disulfides to monosulfoxides by treatment with pyridine N-oxide is known [6]. The reaction of alkyl and aralkyl hydroperoxides with sulfides was described some time ago. It was shown that the complete oxidation of methyl cyclohexyl sulfide to the sulfoxide with tert-butyl hydroperoxide at 60°C occurs in 64 h [7]. In recent years the oxidation of organic compounds with hydroperoxides in the presence of variable valence metals has found extensive use [8]. In particular, a reagent composed of hydroperoxide and molybdenum salt is an active oxidizing agent. The oxidation of sulfides proceeds rapidly under the action of hydroperoxides in the presence of molybdenum acetylacetonate [9]. The oxidation of the dimethyl, diethyl, dibutyl and diphenyl sulfides to the corresponding sulfoxides and sulfones with hydroperoxides is possible in the presence of Group IV and Group VII metals [10]. The information on the catalyzed hydroperoxide oxidation of sulfides is summarized exhaustively in two recent papers [9, 10].

The purpose of the present paper was to make a more careful study of the catalyzed oxidation of organosulfur compounds of variable structure. Sulfides (I)-(IV) are smoothly oxidized by tert-amyl hydroperoxide (TAHP) in the presence of $MoCl_5$ to the corresponding sulfoxides (V)-(VIII) or sulfones (IX)-(XI), in which connection the oxidation rate of diacetoxy sulfide (III) is noticeably lower than the transformation rate of compounds (I)-(II), which is associated with the shielding effect of the acetoxy group. Under optimum conditions the yields of the oxidation products are close to quantitative



Institute of Chemistry, Bashkir Branch, Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 12, pp. 2744-2748, December, 1972. Original article submitted August 20, 1971.

© 1973 Consultants Bureau, a division of Plenum Publishing Corporation, 227 West 17th Street, New York, N. Y. 10011. All rights reserved. This article cannot be reproduced for any purpose whatsoever without permission of the publisher. A copy of this article is available from the publisher for \$15.00.

(XXIX)-(XXXI) (XXIII)-(XXV) $X = S, SO, SO_2$ CH3 CH₃ -(CH2)2-X (CH2)3-CH3 CH3-(CH2)3 ĊHa CHa (XXVI) -(XXVII

$$X = SO, SO_{2}$$

Cyclic sulfides of the 2-methyl-1-thiadecalin type form sulfoxide (XII) and sulfone (XIII) very easily. It should be mentioned that previously [11] sulfoxide (XII) was obtained as an oil, whereas we obtained a preparation with mp 56-58°. The tricyclic dichloro sulfide (XIV), obtained by the reaction of norbornadiene with SCl₂ [12], is oxidized smoothly, giving sulfoxide (XV) and sulfone (XVI). The advantages of the hydroperoxide method can be seen distinctly on the examples of the oxidation of the isomeric sulfolene adducts (XVII) and (XVIII) with SCl₂. We checked the oxidation of these compounds under the conditions given in [13] and showed that the sulfones, obtained by the action of H_2O_2 , are substantially contaminated with sulfoxides. Oxidation with TAHP gives completely pure sulfoxides (XIX)-(XX) and sulfones (XXI)-(XXII); the melting point of the compounds is higher than that given in [13].

The unsaturated sulfide (XXIII) is not oxidized by H_2O_2 even under drastic conditions, whereas sulfoxide (XXIV) is easily formed by the action of TAHP. The yield of sulfone (XXV) is 60% when the oxidation is run in refluxing dioxane.

The oxidation of some di- and trisulfides was studied. Thus, 5,5,10,10-tetramethyl-6,9-dithiatetradecane is easily converted to disulfoxide (XXVI) and disulfone (XXVII). The degree of trithiane oxidation can be distinctly regulated, to produce the mono-, di-, or trisulfoxides (XXIX)-(XXXI). The total insolubility of the trisulfoxide makes it impossible to effect further oxidation.

Catalyzed hydroperoxide oxidation was used by us to obtain the oxidized derivatives of sulfur-containing aromatic compounds. Thiophene is destroyed by excess hydroperoxide with the formation of sulfonic acids, which were not identified. The oxidation of benzothiophene under mild conditions makes it possible to establish chromatographically that sulfoxide (XXXII) is formed as the sole reaction product. However, while attempting to isolate it we always obtained a mixture of sulfide, sulfoxide and sulfone. This is associated with the rapidly progressing disproportionation of the sulfoxide, which up to now has not been isolated in the pure state [14]. Benzothiophene sulfone (XXXIII) is formed in quantitative yield. 2,3-Dichlorobenzothiophene is also easily oxidized, giving sulfoxide (XXXIV) and sulfone (XXXV) in quantitative yield.

Phenoxathiin is oxidized so vigorously that we observed the quantitative formation of sulfoxide (XXX . VI) within 2-3 min after refluxing the reactants in benzene. Further oxidation gives the sulfone (XXXVII). 3-Chlorophenathiazine is converted to the sulfoxide and sulfone (XXXVIII)-(XXXIX) under the same conditions.

For the thianthrene derivatives (XL) and (XLV) we obtained compounds that correspond to all of the possible degrees of oxidation of the sulfur atoms, (XLI)-(XLIV) and (XLVI)-(XLIX).

Thianaphtheno[2,3-c]thianaphthene when reacted gives the monosulfoxide (L), monosulfone (LI) and disulfone (LII); only the monosulfone is formed in oxidation by H_2O_2 [15]

(XXXII)-(XXXIII) X = S0, SO₂, R = H; (XXXIV)-(XXXV) X = S0, SO₂; R = Cl $\begin{array}{c} (XXXVIII) - (XXXIX) Y = NH, R = CI; \\ X = SO SO \end{array}$ (XL)--(XLIV) R = HX=S, SO, SO2

لمله

Com - pound	T_, ℃	Time,h	Yield, %	Mp, °C	Empirical formula	Found,%			Calculated,%		
						с	н	s	С	Ħ	s
VI VII VIII X XI XII XIX XXII XXII XXII		$ \begin{vmatrix} 1 & 1 \\ 1, 5 \\ 1, 5 \\ 1, 5 \\ 0, 5 - 2 \\ , 5 \\ 0 \\ 3 - 4 \\ 0 \\ 1, 5 - 2 \\ 1 \\ 1, 5 \\ 0, 5 \\ 1 \\ 1 \\ 2 - 3 \\ 2 - 3 \\ 1 \\ 3 \end{vmatrix} $	95 90 85 95 95 90 90 90 90 85 90 60 95 100 95 100 90 90 90 90 95 95	$\begin{array}{c} 96-98\\74-75\\224-225\\176-177\\124-125\\56-58\\230-232\\275-276\\171-173\\227-229\\178-180\\220-222\\125-126\\148-150\\126-128\\159-161\\220-221\\278-280\\292dec.\\352-352,5\\192-193\\308-310\\ \end{array}$	$\begin{array}{c} C_{12}H_{20}Cl_2OS\\ C_{16}H_{26}O_5S\\ C_{28}H_{28}Cl_3N_2O_5S\\ C_{12}H_{20}Cl_2O_2S\\ C_{16}H_{26}O_{9}S\\ C_{10}H_{30}OS\\ C_{8}H_{12}Cl_2O_5S_3\\ C_{8}H_{12}Cl_2O_5S_3\\ C_{8}H_{12}Cl_2O_5S_3\\ C_{8}H_{12}Cl_2O_5S_3\\ C_{8}H_{12}Cl_2O_5S_3\\ C_{8}H_{12}O_5S_3\\ C_{8}H_{10}O_5S_3\\ C_{8}H_{10}O_5S_3\\ C_{16}H_{34}O_2S_2\\ C_{16}H_{34}O_2S_2\\ C_{16}H_{16}O_2S_2\\ C_{14}H_{8}O_2S_2\\ C_{14}H_{8}O_4S_2\\ \end{array}$	51,3 57,8 58,61 55,1 64,3 225,55,52 225,56 332,42 53,84,12 59,22,25,66 53,8,84,12 59,22,25,55,22 53,84,22 53,	7,79,53,66,79,63,3,43,44,4,4,5,6,2,6,6,33,4,34,44,6,5,5,4,4,6,5,5,4,4,2,2,6,1,2,5,4,4,6,5,5,4,4,2,2,6,1,2,5,4,4,2,2,6,1,2,5,4,4,2,2,6,1,2,5,4,4,2,2,6,1,2,5,4,4,2,2,6,1,2,2,1,2,1,2,1,2,1,2,1,2,1,2,1,2	$\begin{array}{c} 11,8\\9,7\\5,4\\11,5\\9,1\\16,9\\27,8\\25,8\\27,5\\25,8\\27,5\\432,2\\19,3\\34,0\\32,2\\19,3\\18,5\\14,4\\21,5\\21,5\\221$	50,8 58,22 58,52 58,55,55,52 27,41 255,95 27,91 225,99 324,00 322,22 433,83 40,863,41 660,60 63,14 660,63,14 660,65,65 665,656 655,252	$\begin{array}{c} 7, 7, 4, 6, 7, 5, 7, 4, 2, 4, 2, 5, 3, 5, 6, 8, 7, 5, 2, 0, 7, 5, 3, 3, 3, 3, 3, 5, 6, 8, 7, 5, 2, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0,$	$\begin{array}{c} 11,3\\ 7,6\\ 10,7\\ 9,2\\ 27,1\\ 25,9\\ 34,0\\ 22,2\\ 19,9\\ 13,6\\ 22,2\\ 21,0\\ 20,0\\ 2$

TABLE 1. Oxidation of Sulfur-Containing Compounds with tert-Amyl Hydroperoxide in the Presence of $MoCl_5$ or $Mo(CO)_6$



Thus, the advantages of catalyzed hydroperoxide oxidation, such as the possibility of sharply regulating the degree of oxidation of the sulfur atom, the high yields, and also the simplicity of running the reaction and the convenience of isolating the products, make this method the most universal of the known methods for the oxidation of organosulfur compounds.

EXPERIMENTAL METHOD

The tert-amyl hydroperoxide used in the work, after purification via the Na salt and vacuum-distillation, had a purity of 90-96%. The IR spectra were recorded on a UR-20 spectrophotometer using either a Nujol mull or a film. The chromatographing was run on Al_2O_3 (III activity). The completeness of oxidation was checked by TLC.

<u>Oxidation Method</u>. To a solution of the compound being oxidized and the catalyst (either 5-10 mg of $MoCl_5$ or $Mo(CO)_6$ per gram of sulfide) in either benzene or $CHCl_3$ (50-100 ml per gram of sulfide) was added the hydroperoxide. The mixture was kept at 0-80°C for 0.5-8 h. When preparing the sulfoxides the oxidation was run with a strictly equimolar amount of TAHP, while 2-3 M of the hydroperoxide were used when preparing the sulfones. The IR spectra of all of the obtained sulfoxides contained characteristic frequencies in the 1035-1070 cm⁻¹ region. The sulfonyl group is characterized by absorption at 1120-1130 and 1310-1320 cm⁻¹.

<u>Preparation of Dichlorodicyclohexyl Sulfoxide (VI)</u>. To a solution of 1 g of dichlorodicyclohexyl sulfide and 0.01 g of $MoCl_5$ in 50 ml of benzene was added 0.45 g of TAHP (98%). The mixture was heated at 60° for 1 h, washed with water, dried over Na_2SO_4 , and evaporated to dryness. We obtained 0.9 g of (VI); $\nu_{S=O}$ 1040 cm⁻¹.

<u>Bis-3-chlorotetrahydrothiophene Dioxide 1,1,4,4-Sulfoxide (XXIX)</u>. To a solution of 0.5 g of (XXXIII) in 50 ml of absolute dioxane were added 5 mg of either $MoCl_5$ or $Mo(CO)_6$ and 0.37 g of TAHP (98%), and the mixture was heated for 2 h at 70-80°. Then the mixture was cooled to 0°, and the obtained precipitate was separated and washed with acetone. We obtained 0.45 g of (XXIX), mp 230-232°; $\nu_{S=O}$ 1080 cm⁻¹. Found: C 26.9; H 3.2; S 27.1%. C₈H₁₂Cl₂O₅S₃. Calculated: C 27.11; H 3.4; S 27.1%.

<u>Bisdihydrothiophene 1,1-Dioxide 4,4-Sulfone (XXV)</u>. A mixture of 0.5 g of sulfide (XXIII), 20 mg of MoCl₅ and 1 g of TAHP in 150 ml of dioxane was refluxed for 12 h, and then the solvent was evaporated. We obtained 0.32 g of (XXV), ν_{SO_2} 1130 and 1325 cm⁻¹.

<u>Thianaphtheno-[2,3-c]-thianaphthene Disulfone (LII).</u> To a mixture of 0.5 g of thianaphtheno-[2,3-c]-thianaphthene and 10 mg of either $MoCl_5$ or $Mo(CO)_6$ in 70 ml of benzene was added 0.6 g of TAHP (100%) in drops, and the mixture was refluxed for 3 h, after which it was cooled to 20° and allowed to stand overnight. The obtained crystals were separated and washed several times with acetone. We obtained 0.49 g of (LII), ν_{SO_2} 1130 and 1320 cm⁻¹.

The properties of the newly obtained compounds are summarized in Table 1. The melting points of the known products coincide with the literature data and are identical with those of the compounds synthesized by another method.

CONCLUSIONS

1. A study was made of the oxidation of complex alicyclic sulfides with hydroperoxides in the presence of molybdenum salts and it was established that hydroperoxide oxidation catalyzed by metals can serve as a convenient method for the preparation of pure sulfoxides and sulfones in high yields.

2. Sulfur-containing aromatic heterocycles can be oxidized to sulfoxides and sulfones by treatment with hydroperoxides in the presence of molybdenum compounds, with a clear-cut regulation of the degree of oxidation of the sulfur atoms.

LITERATURE CITED

- 1. E. N. Karaulova, Chemistry of Petroleum Sulfides [in Russian], Nauka (1970), p. 121.
- 2. E. N. Karaulova, in: Science Reviews. Chemistry of Petroleum and Gas [in Russian], Vol. 2, Izd. AN SSSR (1958), p. 130.
- 3. N. K. Kharasch, Organic Sulfur Compounds, Vol. 1, London (1961).
- 4. K. Weiland-Hilgetag, Experimental Procedures in Organic Chemistry [Russian translation], Khimiya (1968), p. 611.
- 5. D. Swern, Chem. Rev., 45, 1 (1949).
- 6. K. Jkuro, Tetrahedron Lett., 3791 (1968).
- 7. Y. Ayrey, D. Barnard, and C. Moore, J. Chem. Soc., 3179 (1954).
- 8. R. Landau, D. Brown, J. Russell, and D. Collar, Seventh World Petroleum Congress [Russian translation], Khimiya (1970), p. 75.
- 9. L. Khunen, Angew. Chem., 78, 957 (1966).
- 10. French Patent No. 1, 540, 284, Class CO7; Ref. Zh., Khim., 18N128P (1969).
- 11. V. Sh. Shaikhrazieva, Dissertation [in Russian], Moscow (1967).
- 12. F. Lautenschlager, J. Org. Chem., 31, 1679 (1966).
- 13. S. M. Lewis and W. Emmons, J. Org. Chem. 31, 3572 (1966).
- 14. H. D. Hartough and S. L. Meisel, Compounds with Condensed Thiophene Rings, London (1954).
- 15. M. G. Voronkov and V. E. Udre, Khim. Geterotsikl. Soedin., 43 (1968).