Oxidation of organic sulfides and disulfides with a *tert*-butyl hydroperoxide—aluminum tri-*tert*-butoxide system

E. A. Zaburdaeva^{*} and V. A. Dodonov

N. I. Lobachevsky Nizhny Novgorod State University, 23 prosp. Gagarina, 603950 Nizhny Novgorod, Russian Federation. Fax: +7 (831) 462 3085. E-mail: zaea4@rambler.ru

Methyl phenylethynyl and phenyl phenylethynyl sulfides are selectively converted into methyl phenylethynyl and phenyl phenylethynyl sulfones, respectively, under the action of system *tert*-butyl hydroperoxide—aluminum tri-*tert*-butoxide in benzene at 20 °C. The analogous oxidation of diphenyl disulfide results in *S*-phenyl benzenethiosulfonate.

Key words: oxidation, aluminum tri-*tert*-butoxide, *tert*-butyl hydroperoxide, activated dioxygen, alkynyl sulfides, sulfones, diphenyl disulfide, *S*-phenyl benzenethiosulfonate.

Sulfides and their oxygen-containing derivatives, sulfoxides and sulfones, are incorporated in natural organic compounds and polymers and widely used in different fields.¹ The sulfones are usually obtained by the oxidation of initial sulfides with organic peroxy acids, in particular, *m*-chloroperbenzoic acid. The reactions occur in two steps: first, sulfides are converted into sulfoxides, which then transform into sulfones at 20 °C with high yields. Currently, catalytic systems based on 30% hydrogen peroxide in water-soluble solvents in the presence of derivatives of transition metals, for example, titanium^{2,3} and vanadium^{2,4–6} compounds are often used in the synthesis of sulfones. It is of note that such catalytic systems allow high conversion degrees (>90%), however, it is difficult to accomplish the process selectively.

In the present study, we offer a single-step preparative method for the synthesis of phenylethynyl sulfones by oxidation of the respective sulfides under the action of the system $Bu^tOOH-(Bu^tO)_3Al$. It was earlier shown^{7,8} that the latter oxidizes dialkyl, dibenzyl, and diphenyl sulfides to sulfones in virtually quantitative yields. The oxidant is the dioxygen formed in successive reaction of two moles of *tert*-butyl hydroperoxide with aluminum *tert*-butoxide in benzene or CCl_4 and located in the coordination sphere of the Al atom.

The aim of the present work was to study the oxidation of sulfides containing the phenylethynyl fragment under the action of the system $Bu^tOOH-(Bu^tO)_3Al$.

The oxidation of methyl phenylethynyl sulfide (1a) and phenyl phenylethynyl sulfide (1b) containing the alkynyl group at the S atom with the $Bu^tOOH-(Bu^tO)_3Al$ system results in the respective sulfones 2a,b (Scheme 1).

The reactions were carried out at a molar ratio substrate : Bu^tOOH : $(Bu^tO)_3Al = 1 : 2 : 1$ (benzene, 20 °C),

Scheme 1

Ph−C≡C−S−R + 2 Bu^tOOH
$$\xrightarrow{(ButO)_3Al}$$

1a,b
→ Ph−C≡C− $\stackrel{||}{=}$ -R + 2 Bu^tOH
 $\stackrel{||}{=}$
2a,b

R = Me (a), Ph (b)

i.e., under the conditions comparable to those described earlier.⁷ The oxidation occurs at the sulfur atom of the sulfides, the yields of sulfones **2a,b** are 92% and 47%, respectively. According to GLC data, in the case of compound **1a**, ~50% of the starting sulfide is converted into sulfone **2a** already in 50 min after the mixing of components, and after 20 h the reaction is fully completed.

The oxidation of compound **1b** under analogous conditions is also completed in 24 h, but it occurs substantially more slowly, and sulfone is formed in lower yield: after 1 h, compound **2b** was not observed in the reaction mixture, only after 3.5 h the yield of the sulfone reached 17.2%, and after 24 h it was 41%. Longer duration of the reaction resulted in a slight increase of the yield of compound **2b** (up to 47%).

The important feature of the accomplished experiments, judging from the GLC data, is the absence of sulfoxides in the reaction mixture in all steps of the reaction. It is of note that the studied systems on the basis of aluminum and titanium alkoxides oxidize phenylalkenes to dioxetanes and products of their further conversion.⁹ However, in the accomplished experiments, the triple bond does not undergo oxidation.

Published in Russian in Izvestiya Akademii Nauk. Seriya Khimicheskaya, No. 1, pp. 177-179, January, 2011.

1066-5285/11/6001-185 © 2011 Springer Science+Business Media, Inc.

The conversion of diphenyl disulfide (3) under the same conditions at a molar ratio substrate : $Bu^{t}OOH : (Bu^{t}O)_{3}Al = 1 : 2 : 1 \text{ was } 53\%$, and *S*-phenyl benzenethiosulfonate (4) was formed as the only product (Scheme 2).

Scheme 2

Ph−S−S−Ph + 2 Bu^tOOH
$$\xrightarrow{(ButO)_3Al}$$

3
→ Ph−S−S−Ph + 2 Bu^tOH
0
4

With doubled amounts of $(Bu^tO)_3Al$ and Bu^tOOH , the conversion of disulfide **3** increased to 93%, no formation of the disulfone was observed.

The proposed synthesis method can be used in preparative organic chemistry for the oxidation of other sulfides to sulfones under mild conditions.

Experimental

NMR spectra were recorded on a Varian INOVA 400 instrument in C_6D_6 ; IR spectra were recorded on an IR Prestige-21 spectrometer (Shimadzu) in a thin layer; high resolution GC-MS analysis (HRMS) was performed on a Finnigan MAT 95 instrument.

Gas chromatography analysis of the starting sulfides and the respective sulfones was performed on an Agilent-6890 instrument (capillary column HP-5, 15000×0.25 , carrier gas — nitrogen); GC-MS analysis was performed on the instrument of the same company equipped with a mass-detector Net Work-5973 (column HP-5-MS, carrier gas — helium). Samples were injected at 70 °C or 90 °C, then the temperature was increased in 15 min to 300 °C. The calculation was made using internal standard method, the internal standard was nonane.

Benzene (c.p.) was purified by distillation from P_2O_5 and stored over metallic sodium. Aluminum tri-tert-butoxide was obtained by the reaction of tert-butyl alcohol with aluminum according to the earlier described procedure¹⁰ followed by sublimation (160-170 °C, 1 Torr). Found (%): Al, 11.52. C12H27AlO3. Calculated (%): Al, 10.96. All operations with (Bu^tO)₃Al were carried out under argon. Bu^tOOH was synthesized according to the earlier described procedure,¹¹ the concentration of the latter was at least 99.5-99.8%. Ph₂S₂ (99%) (Acros) was used. Methyl and phenyl phenylethynyl sulfides (1a,b) were synthesized according to the known procedure¹² by metalation of phenylacetylene with butyllithium with subsequent treatment of the obtained phenylethynyl lithium with MeSO₂SMe and PhSO₂SPh, respectively. Sulfide 1a was purified by distillation, b.p. 49-51 °C (7.5 • 10⁻³ Torr). ¹H NMR (400 MHz, δ): 7.40-7.36 (m, 2 H); 6.95-6.93 (m, 3 H); 1.88 (s, 3 H). ¹³C NMR (75 MHz, δ): 131.2, 127.8, 127.5, 127.1, 123.5, 91.9, 81.3, 18.3. Sulfide 1b was isolated by column chromatography, eluent - pentane with addition of 2% triethylamine. ¹H NMR (400 MHz, δ): 7.41–7.35 (m, 4 H); 7.00–6.85

(m, 6 H). ¹³C NMR (75.5 MHz, δ): 132.5, 131.3, 128.7, 127.6, 127.2, 125.9, 125.7, 122.6, 97.8, 75.5.

Disulfide 3 and S-phenyl benzenethiosulfonate (4) were identified by TLC on Silufol UV-254, eluent hexane—ether (9:1) with UV detection.

Methyl phenylethynyl sulfone (2a). To a solution of (Bu^tO)₃Al (3 mmol) and sulfide 1a (3 mmol) in benzene (10 mL), Bu^tOOH (6 mmol) was added. After 50 min, the formation of methyl phenylethynyl sulfone (2a) in amount equivalent to that of the sulfide 1a was determined by GLC and GC-MS. After 20 h, only sulfone 2a was present in the reaction mixture. The solvent and volatile components were condensed in a trap cooled with liquid nitrogen. The colorless powder-like residue was hydrolyzed with aqueous NH₄Cl, extracted with ether, the extract was dried with Na₂SO₄, and ether was removed. Sulfone 2a was isolated in a form of colorless crystals, m.p. 65–66 °C. IR, v/cm⁻¹: 2185 (C=C); 1304, 1129 (SO₂); 687 (C-S).¹³ HRMS, *m/z*: 180.0236. $C_9H_8O_2^{32}S_1$. Calculated: M = 180.0245. ¹H NMR (400 MHz, δ): 7.01–7.06 (m, 1 H); 6.82–6.87 (m, 2 H); 6.68–6.73 (m, 2 H); 2.38 (s, 3 H). ¹³C NMR (75 MHz, δ): 127.7, 127.6, 127.4, 127.3, 117.6, 90.1, 85.6, 45.7.

The oxidation of compounds **1b** and **3** was performed analogously. The conversion of sulfides into respective sulfones was monitored by GLC and MS. No formation of sulfoxides was observed.

The characteristics of phenyl phenylethynyl sulfone (**2b**) are presented in Refs 14, 15.

S-Phenyl benzenethiosulfonate (4) was obtained at the ratio 3 : (Bu^tO)₃Al : Bu^tOOH = 1 : 2 : 4. From the reaction mixture after hydrolysis, a colorless crystalline substance was isolated without special purification, m.p. 43 °C; according to different data, ¹⁶ *S*-phenyl benzenethiosulfonate (4) has melting point in a range of 36–53 °C. IR, v/cm⁻¹: 1325, 1141 (SO₂).^{13 1}H NMR (400 MHz, δ): 7.27–7.24 (m). ¹³C NMR (75 MHz, δ): 125.8, 129.5, 130.0, 130.9, 131.2, 134.0, 135.9. The obtained sample coincided by the *R*_f value with the authentic *S*-phenyl benzenethiosulfonate sample in TLC analysis.

The authors express their acknowledgment to V. Yu. Malakhov and A. E. Gavryushin for the help in registration and interpretation of the spectra and chromatograms.

This work was performed within the collaboration program "Mikhail Lomonosov II" between the Ministry of Education and Science of the Russian Federation (Project No. 2.2.2.3.16148) and German Academic Exchange Service (Project A/07/72363), and was financially supported by the Russian Foundation for Basic Research (Project No. 08-03-97050-Volga region_a).

References

- Poluchenie i Svoistva Organicheskikh Soedinenii Sery [Preparation and Properties of Organic Sulfur Compounds], Ed. L. I. Belen 'ky, Khimiya, Moscow, 1998, 560 pp. (in Russian).
- K. Kaczorowska, Z. Kolarska, K. Mitkab, P. Kowalski, *Tetrahedron*, 2005, 61, 8315.
- 3. Ch. V. Reddy, J. G. Verkade, J. Mol. Catal. A: Chem., 2007, 272, 233.
- F. Gregori, I. Nobili, F. Bigi, R. Maggi, G. Predieri, G. Sartori, J. Mol. Catal. A: Chem., 2007, 286, 124.

- N. Moussa, A. Ghorbel, J. M. Fraile, J. A. Mayoral, J. Mol. Catal. A: Chem., 2006, 255, 62.
- 6. M. R. Maurya, A. K. Chandrakar, S. Chand, J. Mol. Catal. A: Chem., 2007, 278, 12.
- V. A. Dodonov, E. A. Zaburdaeva, L. P. Stepovik, *Izv. Akad. Nauk, Ser. Khim.*, 2004, 1663 [*Russ. Chem. Bull., Int. Ed.*, 2004, 53, 1729].
- E. A. Zaburdaeva, V. A. Dodonov, L. P. Stepovik, I. A. Kapuskina, *Phosph. Sulf. Silicon Relat. Elements*, 2005, 180, 1521.
- I. M. Martynova, L. P. Stepovik, V. A. Dodonov, *Zh. Obshch. Khimii*, 2001, **71**, 1681 [*Russ. J. Gen. Chem. (Engl. Transl.*), 2001, **71**].
- Organic Synthesis. An Annual Publication of Satisfactory Methods for the Preparation of Organic Chemicals, John Wiley and Sons, Inc., New York, 1940–1945.

- 11. V. Karnojitzki, *Les Peroxides Organiques*, Hermann, Paris, 1958.
- 12. L. Brandsma, *Preparative Acetylenic Chemistry*, 2nd ed., Elsevier, Amsterdam, 1988, 129.
- K. Nakanishi, *Infrared Absorption Spectroscopy*, Holden-Day, Inc., San Francisco, 1962.
- 14. N. Riddell, W. Tam, J. Org. Chem., 2006, 71, 1934.
- 15. A. Pelter, J. Chem. Soc., Perkin Trans. 1, 1990, 2775.
- 16. SIGMA-ALDRICH Catalog Handbook of Chemicals, 2009–2010, 2136.

Received December 20, 2009; in revised form October 28, 2010

187