Letters to the Editor

Brominative aromatization of cyclohexyl methyl sulfide

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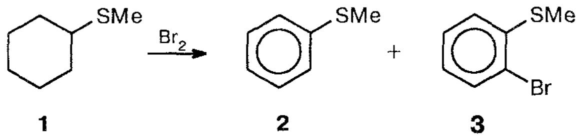
Sulfur in organic compounds is usually used as an "assisting element"[1] in different chemical transformations.[1,2] For example, the S atom acts as an acceptor of Br_2 in the first stage of the aromatization of 1,2-bis(alkylthio)cyclohexenes,[3] cyclohexene-5,6-dihydro-1,4-dithiines, cyclohexene-5,6-dihydro-1,4-oxathiines,[3,4] and cyclohexanone ethylenedithioacetals (through their rearrangement into the corresponding cyclohexene-5,6-dihydro-1,4-dithiines).[4–6] In these compounds (or intermediates) the S atom is located at the double bond. For the first time, we performed the aromatization of methyl cyclohexyl sulfide (**1**) (which is totally saturated) with bromine, and the mixture of products (**2** and **3**) was isolated.



1 **2** **3**

Compound **3** has been prepared previously[7] by another route. It should be noted that **3** is not the product of the bromination of **2**, because in the bromination of **2** only the *p*-bromo derivative is formed.

Bromine (2.46 g, 0.015 mol) in $CHCl_3$ (5 mL) was added dropwise to a solution of sulfide **1** (2 g, 0.015 mol) in $CHCl_3$ (30 mL) with stirring and cooling by a salt-ice mixture bath, then the temperature of the reaction mixture was increased to the ambient temperature, where it was kept for 1 to 2 h. The treatment was repeated twice. The mixture was washed with aqueous $NaHCO_3$ and water, dried over Na_2SO_4, and evaporated and distilled *in vacuo*; the fraction with b.p. 60—115 °C (2—3 Torr) was collected. The products were separated by column chromatography (silica gel, heptane). Methyl phenyl sulfide (**2**) (0.68 g, 35 %) and *o*-bromophenyl methyl sulfide (**3**) (0.31 g, 10 %) were obtained. Compound **2** was identical (TLC, NMR) to an authentic sample prepared by methylation of thiophenol.[8] Compound **3**: n_D^{16} 1.6358. Found (%): C, 41.38; H, 3.40. C_7H_7BrS. Calculated (%): C, 41.39; H, 3.47. ^1H NMR (250 MHz, $CDCl_3$—CCl_4, 1:1), δ: 2.49 (s, 3 H, SMe); 7.01 (t, 1 H, C_6H_4, J = 8 Hz); 7.12 (d, 1 H, C_6H_4, J = 8 Hz); 7.29 (t, 1 H, C_6H_4, J = 8 Hz); 7.53 (d, 1 H, C_6H_4, J = 8 Hz). ^{13}C NMR ($CDCl_3$—CCl_4, 1:1), δ: 15.63 (SCH_3); 121.78, 125.24, 125.46, 127.60, 132.57, 139.75 (C_6H_4).

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Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 1, pp. 188—189, January, 1995.

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Received October 14, 1994

Chemiluminescence of the 9,10-anthrasemiquinone radical ion during autooxidation of 9,10-dibromoanthracene in the diphenylmethane—Bu^tOK—DMSO system

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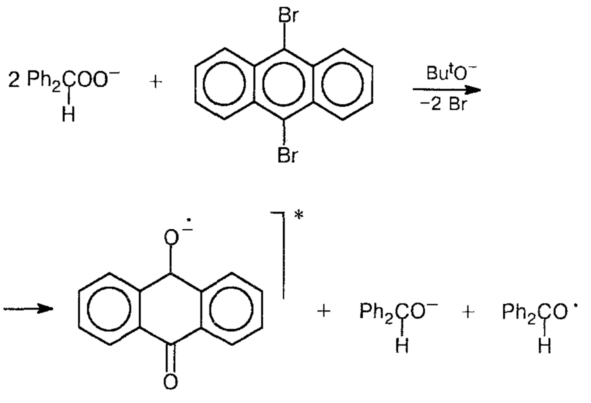
Chemiluminescent (CL) systems in which radicals are the photon emitters are known.[1,2] We found the CL-reaction of the oxidation of 9,10-dibromoanthracene (DBA) in the diphenylmethane (DPM)—Bu^tOK—DMSO system, in which the 9,10-anthrasemiquinone radical ion is the photon emitter. DBA is routinely used in CL investigations to obtain the photophysical parameters of the triplet excited state of molecule, *e.g.*, formed in the course of the disproportionation of $RO_2^{\cdot}$ radicals;[3] it is assumed that the activator is not involved in the reaction. We revealed that this is not true in all cases. Oxidation of DPM in DMSO in the presence of Bu^tOK is accompanied by CL, and the Ph_2CO^* triplet is an emitter, which is confirmed by the coincidence of the CL spectra and the phosphorescence spectra of the reaction medium and Ph_2CO. Addition of DBA causes an increase in light emission. The CL spectrum contain a component that we assigned to emission of the 9,10-anthrasemiquinone radical ion formed as the result of DBA oxidation in addition to the band of the radiative deactivation of singlet excited DBA. The CL spectrum of the radical ion with the maximum at 580 nm coincides with the photoluminescence spectrum of the reaction mixture excited with λ = 500 nm light. The formation of the radical ion is confirmed by the identity of the absorption spectrum of the reaction mixture with that of the radical ion generated from anthraquinone in a strong basic medium (Bu^tOK—DMSO): λ_{max} = 513 and 547 nm. The ESR spectrum of the reaction mixture (g = 2.0049±0.0002) is also identical to that of the radical ion.

The data obtained show that during the oxidation of DBA in the DPM—Bu^tOK—DMSO system the 9,10-anthrasemiquinone radical ion in the excited state is formed, whose deactivation causes the long-wave CL component. The role of DPM is to generate peroxyanions from the corresponding carbanions. Apparently, the latter are involved in the oxidation of DBA, which proceeds *via* the formation of an intermediate diperoxide that subsequently decomposes to the radical ion:



In the absence of DPM in the DMSO—Bu^tOK system saturated with oxygen, DBA does not form the 9,10-anthrasemiquinone radical ion.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 1, pp. 189—190, January, 1995.