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ELECTROCHEMICAL BROMINATION OF DMSO IN ALKALINE MEDIA: THE SYNTHESIS OF 1,1,1-TRIBROMO- AND HEXABROMODIMETHYLSULFONES

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The reaction of DMSO with chlorine and bromine in aqueous media leads to oxidation of the organic substrate. In acid media, the reaction product is dimethylsulfone [1]. In slightly basic media, the completely halogenated derivative $(CX_3)_2SO_2$ is obtained (the yield for X = Br is 70% [2]).

The electrolysis of aqueous bromide solutions containing DMSO leads to the same prod-The yield of (CBr₃)₂SO₂ (I) in this case, however, is less than upon chemical bromination and decreases with increasing alkali content in the electrolyte, which corresponds to the evidence for the cleavage of (I) by concentrated alkali [3]. The use of sodium carbonate instead of alkali in the electrosynthesis permits an increase in the yield of (I) to 50%. However, carrying out the reaction in the presence of NaHCO3 unexpectedly led to previously unreported 1,1,1-tribromodimethylsulfone CBr₃SO₂CH₃ (II). The structure of this product was confirmed by convergent synthesis by the oxidation of CBr₃SCH₃ using CrO₃ in acetic acid. Sulfone (I) is formed, in all likelihood, as the result of purely bulk bromination of DMSO through a base catalysis mechanism by analogy to the electrosynthesis of CHBr₃ from acetone [4]. In both cases, the yield of the bromo derivatives increases with decreasing temperature and increasing substrate concentration. The same pH range is optimal. Sodium bicarbonate apparently cannot have a specific effect on the bromination reaction which proceeds in the electrolyte bulk, since NaHCO3 has been used to optimize the bromination of various sulfur compounds to give (I) [3, 5], while the formation of "unsymmetrical" derivatives, i.e., products containing bromine at only one methyl group, was not observed. Hence, we may assume that the electrochemical synthesis of (II) proceeds through the formation of an intermediate, apparently a complex of DMSO with halogens [6] in the adsorption layer and the subsequent electrochemical oxidation of this intermediate.

EXPERIMENTAL

The PMR spectra were obtained on a Tesla BF-467 spectrometer at 60 MHz with TMS as the internal standard in CCl₄ solution. A sample of CBr_3SCH_3 which is the starting compound for the convergent synthesis of (II) was obtained according to Truce [7] and Boberg [8].

Electrosynthesis of Hexabromodimethylsulfone (I). A 600 ml aqueous solution containing 120 g KBr, 100 g $Na_2CO_3 \cdot 10H_2O$, and 23.4 g DMSO was added to a diaphragmless electrolyzer containing a 100-cm² ruthenium-titanium oxide anode and 20-cm² stainless steel cathode and a 6 A current was passed at 7-10°C (19 A·h was introduced). The precipitate was filtered off, dried over P_2O_5 , and extracted with benzene. The solvent was distilled off in vacuum to give 14.4 g (50% current yield) (I), mp 135°C [5]. When the reaction was carried out in the presence of 5.6 g KOH instead of Na_2CO_3 , the yield of (I) is 6.8 g (24% current yield).

A. N. Frumkin Institute of Electrochemistry, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 2, pp. 471-472, February, 1988. Original article submitted April 6, 1987. Electrosynthesis of 1,1,1-Tribromodimethylsulfone (II). A current of 6 A was passed through the electrolyzer described above containing 600 ml of an aqueous solution containing 120 g KBr, 70 g NaHCO₃, and 7.8 g DMSO at 20-22°C (27 A·h was introduced). The extraction of (II) was carried out as in the case of (I) to give 11.8 g (36% yield, 28% current yield) (II), mp 235-237°C (from toluene-hexane). PMR spectrum (δ , ppm): 3.47 s (3H). Found, %: C 7.45; H 1.10; Br 71.87. C₂H₃Br₃O₂S. Calculated, %: C 7.26; H 0.91; Br 72.46.

<u>Preparation of (II) by the Oxidation of 1,1,1-Tribromomethyl Methyl Sulfide</u>. A sample of 61.7 g (0.21 mole) 1,1,1-tribromomethyl methyl sulfide in 100 ml glacial acetic acid was added dropwise, with rapid stirring and cooling to $18-21^{\circ}$ C over 5 h, to 51.8 g fine-crystalline CrO₃ in 300 ml glacial acetic acid. The reaction mixture was stirred at this temperature for an additional 1 h and then poured into 2 liters cold water and neutralized with NaHCO₃. The precipitate was filtered off and dried over P₂O₅ to give 37.9 g (55%) (II), mp 235-236°C (from toluene-hexane).

CONCLUSIONS

The electrochemical bromination of DMSO in alkaline media leads to the formation of $(CBr_3)_2SO_2$ (in the presence of Na_2CO_3) or $CBr_3SO_2CH_3$ (in the presence of $NaHCO_3$).

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HYPOPHOSPHOROUS ACID AS A HYDRIDE ION DONOR

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Ionic hydrogenation of hydrogenolysis requires proton and hydride ion donors. Hypophosphorus acid, H_3PO_2 (I), is presumably both a proton donor and hydride ion donor. In order to check this hypothesis, we selected the ionic hydrogenation of 1-methylcyclohexene (II). This compound readily undergoes ionic hydrogenation to give methylcyclohexane by the action of hydride ion donors such as Et_3SiH and strong acids such as CF_3CO_2H [1]. However, 1-methyl-cyclohexene in the presence of (I) is not converted to methylcyclohexane at 40°C over 4 h with a ten-fold excess of acid. The lack of a reaction between (I) and (II) may be explained either by assuming that H_3PO_2 is a poor proton donor or a poor hydride ion donor. The reaction of (I) with (II) does not proceed in the presence of Et_3SiH which is an active hydride ion donor. Thus, H_3PO_2 is a poor proton donor. However, when CF_3CO_2H is added to a reaction mixture of (I) and (II) in order to increase the acidity of the medium, ~5% methylcyclohexane was found in the reaction products. Hence, the P-H bond may serve as a hydride ion donor.

When a carbocation such as the tropylium cation participates in the reaction, then, despite its low activity as a hydride ion acceptor, the reduction proceeds even by the action of 50% aqueous solution of (I) and cycloheptatriene is formed in ~25% yield. In this case, the reaction of (I) with the tropylium ion proceeds to give the mono- and dicycloheptatrienyl

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