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Cathodic Reduction of SO_2 in the Presence of Organic Dihalides

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The reaction of the electrolytically generated $SO_2^{\cdot-}$ anion radical with 1,ω-dihalides is used for the synthesis of sulfur containing heterocycles like oxathiolane-, oxathiane-, thiane- and thiepane-oxides. 1,2-Dihalides are reductively deblocked to give olefines.

(Keywords: Sulfur dioxide reduction; Sulfones; Sulfinic esters, cyclic)

Kathodische Reduktion von SO_2 *in Gegenwart organischer Dihalogenide*

Die Reaktion des elektrolytisch erzeugten $SO_2^{\cdot-}$-Anionradikals mit 1,ω-Dihalogeniden führt zu schwefelhaltigen Heterocyclen wie Oxathiolan-, Oxathian-, Thian- und Thiepanoxiden. 1,2-Dihalogenide geben durch reduktive Eliminierung Olefine.

In previous work we have shown that an electrosynthesis of sulfones can be achieved by cathodic reduction of sulfur dioxide in aprotic media in the presence of organic halides[1a–c].

The reaction proceeds via the free anion radical $SO_2^{\cdot-}$ which is in equilibrium with the complexed form $S_2O_4^{\cdot-}$, a strongly blue coloured species[2]. The mechanism of the formation of sulfones has recently been shown to run as follows[3a]:

$$SO_2^{\cdot-} + RX \longrightarrow RSO_2^{\cdot} + X^-$$

$$RSO_2^{\cdot} + SO_2^{\cdot-} \longrightarrow RSO_2^- + SO_2$$

$$RSO_2^- + RX \text{ (or } R'Y) \rightarrow RSO_2R \text{ (or } RSO_2R') + X^- \text{ (or } Y^-)$$

We wish to report now on the use of 1,ω-dihalides in this reaction sequence which should lead either to cyclic sulfur containing com-

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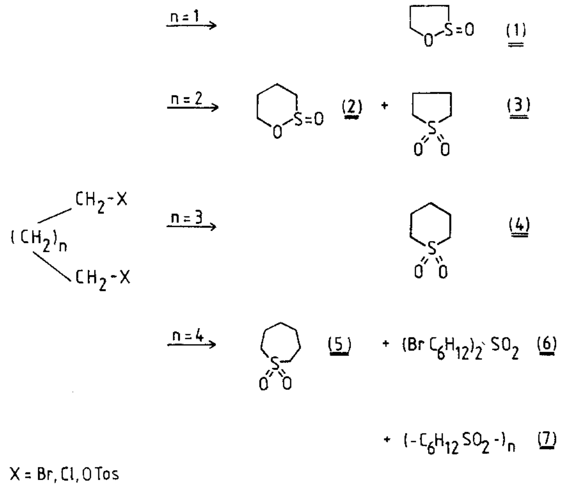
pounds or to polymeric sulfones, depending on the chain length of the starting material. One example of ring formation using α,α-dibromo-*o*-xylylene and resulting in 1-oxa-2-thiatetrahydronaphtalene-S-oxide and benz(c)dihydrothiophene-1,1-dioxide has already been given[1a]. Now the results summarized in the scheme are presented.

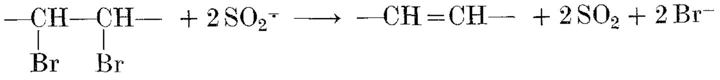


Hitherto only a few examples of the cyclic compounds of type **1** and **2** are known, which were obtained by rather elaborate reaction steps[4]. Both types have been reported to be useful as starting compounds for SO_2 extrusion reactions forming cyclopropanes or olefines, respectively, upon photolytic or thermal decomposition[5]. We think that the electrolytical way seems to offer an economic access to these cyclic sulfinic esters.

Attack on the oxygen atom of the intermediate sulfinate anion forming the sulfinic acid ester has already been observed in the reaction of $SO_2^{\overline{\cdot}}$ with monohalides, where about 10-25% of *n*-alkylsulfinic-*n*-alkylesters can be obtained[3b]. The sulfinate is a distinct intermediate since by careful, slow addition of organic halide to the blue radical solution of $S_2O_4^{\overline{\cdot}}$ sulfinates can be obtained in medium yields (e.g., 30% of allylsulfinate or 39% of benzylsulfinate, both analyzed as sulfones after addition of excess methyliodide). In the case of the dihalides ring size is probably the determining factor deciding attack on either the sulfur or the oxygen atom.

The yield of the seven membered sulfone **5** may probably be improved by dilution techniques. Similar experiments with slow addition of the reagents have successfully been tried with mixtures of halides of comparable reactivity in order to get mixed sulfones in highest purity[1c]. Besides **5** some di-(6-bromohexyl-)-sulfone (**6**) and polymeric sulfones can be isolated.

With 1,2-dibromides only olefines are formed in almost quantitative yields



$$-\underset{\substack{|\\ \mathrm{Br}}}{\mathrm{CH}}-\underset{\substack{|\\ \mathrm{Br}}}{\mathrm{CH}}- \; + 2\,\mathrm{SO}_2^{\cdot-} \longrightarrow -\mathrm{CH}{=}\mathrm{CH}- \; + 2\,\mathrm{SO}_2 + 2\,\mathrm{Br}^-$$

Whether this reductive elimination occurs via nucleophilic attack of the $SO_2^{\cdot-}$ radical or by simple electron transfer is not quite clear. Substitution should form episulfones or β-sultines, both of which would be unstable under the reaction conditions used[6]. From stereochemical considerations it is expected that *dl*- and *meso*- stilbenedibromides should give either *trans* or *cis* stilbene, respectively, but in both cases the reaction with $SO_2^{\cdot-}$ results in pure *trans* stilbene. Both stereoisomers of the stilbenes are stable under the reaction conditions employed. Electron transfer may be dominant since the reduction potentials of the 1,2-dihalides lie rather close to the $SO_2/SO_2^{\cdot-}$ redox potential, thus favouring a catalytic reduction of the halide as observed by *Simonet* et al.[7] in the reaction of aromatic anion radicals with halidas.

Similarly *dl*- and *meso*-dimethyl-2,3-dibromosuccinate gave dimethylfumarate quantitatively comparable to the direct electrochemical reduction of the dibromo compounds[8].

The reaction of 1,2-dihalides disclosures one limit of the electrochemical sulfones synthesis. However homogeneous reduction yielding olefines may be a useful alternative in deblocking reactions of protected double bonds, a reaction which has been tried by *Husstedt* et al.[9]. Use of $SO_2^{\cdot-}$ would require less negative potentials and, therefore, lower cell voltages than the direct electrochemical conversion used by those authors.

Further work will be done in the field of homogeneous reactions of the $SO_2^{\cdot-}$ anion radical, e.g. with aldehydes and nitro compounds.

Experimental

Reactions are normally carried out by galvanostatic production of the anion radical on Pt or glassy carbon electrodes in dimethylformamide (*DMF*) or acetonitrile (*AN*), respectively, the solvent containing tetraalkylammonium salts as supporting electrolyte and being saturated with gaseous sulfur dioxide in an H-cell as described previously[1a]. The resulting blue solution of the complex radical can react with the organic halide directly in the electrolysis cell or the radical solution can be transferred to a separate reaction vessel.

Most runs can be done in *AN* of laboratory grade but this will give some lower current yields than using samples of purified solvent, while chemical yields still remain high.

If *DMF* is used, great care must be taken to remove traces of formaldehyde, because even low aldehyde concentrations of about $3 \cdot 10^{-5} M$ are able to destroy more than $0.01 M$ solutions of the $SO_2^{-\cdot}$ radical by some catalytic mechanism. Best quality *DMF* was obtained by repeated, careful distillation and by the use of activated alumina similar to the procedure used by *Oelschläger*[10]. Clean solutions of *DMF* are stable at daylight for at least 10 days in contradiction to reported properties of this solvent.

If *X* is *OTos* and the supporting electrolyte contains only perchlorate anions, the reactions proceeds very slowly at all temperatures. If bromides salts are used, halide exchange will occur prior to attack by $SO_2^{-\cdot}$ so that reasonable yields of the desired products are obtainable[3].

General procedure

To 100 ml of *AN*, containing $0.2 M$ tetraethylammoniumbromide, held at 60-80 °C and saturated with gaseous sulfur dioxide, 20-50 mmol of dihalide are added. At current densities of 20-80 mA/cm^2, electrolysis is continued until a blue colour of unused $S_2O_4^{-\cdot}$ persists. After solvent evaporation the products are dissolved in CH_2Cl_2, washed with water and dried. Product isolation is usually done by vacuum distillation. Gas chromatographic analysis can be done on 10% carbowax 20 M columns at 160-180 °C. All compounds gave satisfactory spectral data in accordance with reported values. Yields given are based on the amount of organic compound consumed, current yields are usually 10-15% lower.

1,2-Oxathiolane-2-oxide (**1**)

From 1,3-dibromopropane: 60-85%, from 1-bromo-3-chloropropane 35-45%, from 1-bromo-3-tosyloxypropane (in bromide electrolyte) 20-30% (cf. ref. [4]).

1,2-Oxathiane-2-oxide (**2**) and *Tetramethylenesulfone* (**3**)

From 1,4-dibromobutane 37-54% of **2** and 25-45% of **3**, from 1,4-ditosyloxybutane (in bromide electrolyte) 40-45% of **2** and **3** (cf. ref. [4]).

Thiane-1,1-dioxide (**4**)

From 1,5-dibromopentane, 60-70%, m.p. 97-98 °C (ref. [11] 98 °C).

Thiepane-1,1-dioxide (**5**), *Di-(6-bromohexyl-)-sulfone* (**6**) and *Polymer* (**7**)

From 1,6-dibromohexane: 25-30% of cyclic sulfone (**5**), m.p. 69-71 °C (ref. [11] 71 °C); 3-5% of bromosulfone (**6**), m.p. 108-110 °C. ^1H-NMR ($CDCl_3$/*TMS*): δ 1.6-2.1 (m; 16 H), 3.0 (t; 4 H), 3.5 (t; 4 H). MS (70 eV): $m/e = 313, 311$ (42%, *M*-OH), 165, 163 (43%, BrC_6H_{12}—). IR (KBr): 1320, 1115 cm^{-1} (SO_2); and 50-65% of polymeric sulfone (**7**), m.p. 165-170 °C.

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