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ELECTROCHEMICAL REDUCTION OF α,α'-DIBROMO-DIBENZYLSULFONE, -SULFOXIDE, AND -SULFIDE

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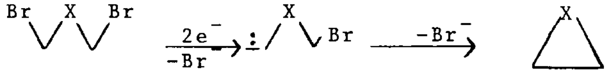
Abstract: The electrochemical reduction of the title compounds in dimethylformamide affords in all cases stilbene as a major product, leading to the conclusion that cyclization to a three-membered ring containing sulfur is a common feature in these reductions. Other products isolated in the reductions help to shed light upon the course of the reactions.

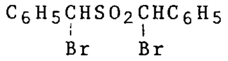
We have for some time been investigating the electrolytic reductive cyclization of 1,3-dibromides (**1**) as a possible synthetic route to three-membered ring species (**2**). We have found that cyclization is general for X=CH_2,[2] carbonyl,[3] and phosphinate,[4] although **2** is unstable in the latter two cases. Our interest in the



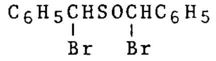
(1)

1 **2**

possible generality and synthetic utility of this process has now led us to explore the electrochemical reduction of α,α'-dibromodibenzylsulfone (**3**), -sulfoxide (**4**), and -sulfide (**5**).[5] We wish to report our results, which further amplify the generality of the process represented by eq. 1.


$C_6H_5CHBrSO_2CHBrC_6H_5$

3


$C_6H_5CHBrSOCHBrC_6H_5$

4

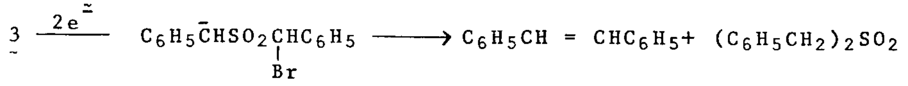

$C_6H_5CHBrSCHBrC_6H_5$

5

α,α'-Dibromodibenzylsulfone (**3**).

Sulfone **3** exhibits a single polarographic wave at -0.9V (vs Ag/Ag^+)[6] in dimethylformamide (DMF) containing 0.1M tetraethylammonium perchlorate (TEAP), the height of the wave corresponding to uptake of two electrons. Cyclic voltammetry at a platinum cathode indicated, as expected,[7] that this wave is totally irreversible.

Controlled-potential electrolysis at -0.8V of **3** (dl/meso = 2:1) consumed 1.8-2.1 Faraday/mole of **3** and afforded stilbenes (**7**) (84%) and dibenzylsulfone (**8**) (5%). These products appear to arise respectively by (a) cyclization of bromocarbanion **6** to an episulfone with subsequent thermal loss of sulfur dioxide[8] to



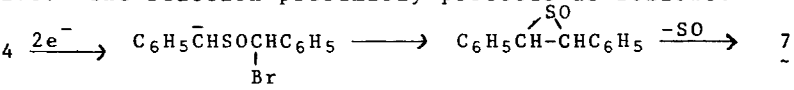
$$\mathbf{3} \xrightarrow{2e^-} C_6H_5\bar{C}HSO_2\underset{Br}{C}HC_6H_5 \longrightarrow C_6H_5CH = CHC_6H_5 + (C_6H_5CH_2)_2SO_2$$

6 **7** **8**

afford **7**, or (b) protonation of **6** by supporting electrolyte or adventitious water, followed by reductive removal of the second halogen atom in precedented fashion[4] to afford **8**.

Trans and *cis*-stilbene are formed in a 1:1 ratio by reduction of a 2:1 *dl*:*meso* mixture of diastereomers of **3**, hence reduction is not stereospecific. Interruption of electrolysis after passage of 1.0 Faraday/mole of **3** and workup showed that the *dl*:*meso* ratio had become 1.3:1, but that the *cis*:*trans* ratio of **7** was still 1:1. Stereochemical integrity of the starting material on the way to **7** may be lost in a number of ways. Episulfones presumably extrude SO_2 stereospecifically, but they undergo rapid base-catalyzed isomerization.[8] Either **6** or hydroxide ion (formed by reaction of water with **6** on the path to **8**) could epimerize the intermediate episulfone and/or the dibromide **3**.[9] Carbanion **6** itself tends to react non-stereospecifically in DMF,[8] providing a third pathway for loss of stereochemistry.

α,α-Dibromodibenzylsulfoxide (**4**). Racemic dibromide **4** exhibits a single two-electron polarographic wave at -1.1 V (vs Ag/Ag$^+$)[6] in DMF - 0.1M TEAP; cyclic voltammetry at platinum or carbon indicated this wave to be totally irreversible. Controlled potential electrolysis at a carbon cloth[10] cathode (-0.8V) proceeded cleanly and rapidly to afford *trans*-stilbene (**7**) as the only product by TLC (85% crude; 57% after chromatography and recrystallization). However, unlike the electrolysis at carbon, in which the catholyte remained almost colorless throughout, electrolysis at a mercury pool cathode produced a dark solution with a black precipitate (HgS?)[11] coating the electrode surface, and the electrolysis was considerably slower. The products were stilbene (**7**) (71%) (*trans*:*cis* = 6.8) and benzaldehyde (20%). It was found that **4** undergoes hydrolysis to benzaldehyde in DMF if a trace of base is present. Probably the only difference between the electrolyses at carbon and mercury is the fact that the slower electrolysis at the latter material permits time for hydrolysis of **4** to become competitive. The reaction presumably proceeds as follows:

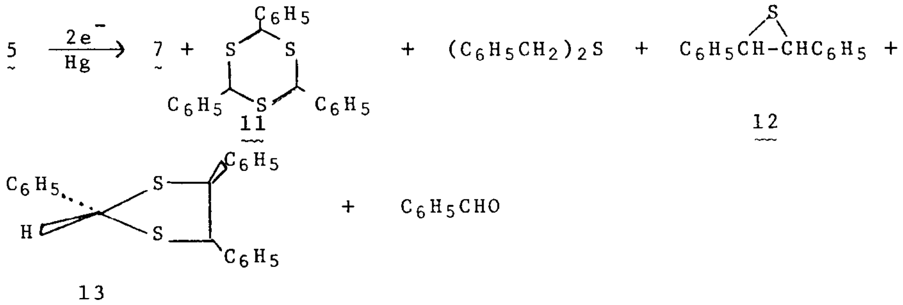


$$\mathbf{4} \xrightarrow{2e^-} C_6H_5\bar{C}HSO\underset{Br}{C}HC_6H_5 \longrightarrow C_6H_5\overset{SO}{CH\text{-}CH}C_6H_5 \xrightarrow{-SO} \mathbf{7}$$

9 **10**

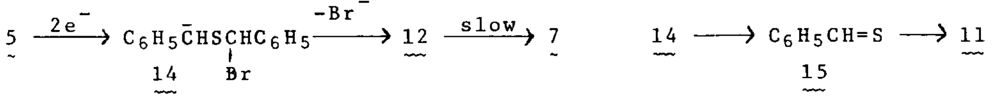
Cis or *trans*-1,2-diphenylthiirane oxides (10) would not survive our electrolysis and workup conditions. *Trans*-10 has $t_{1/2}$ = 10-17 hr at 25°C; it decomposes cleanly to *trans*-stilbene and sulfur monoxide, while *cis*-10 decomposes 5-8 times faster to a 60:40 *cis*:*trans*-stilbene mixture.[12] Since electrolysis at carbon produces only *trans*-7, carbanion 9 presumably cyclizes stereospecifically to *trans*-10; under the slower reaction conditions epimerization of 4 can presumably compete, resulting ultimately in a small amount of *cis*-7.

α,α'-Dibromodibenzylsulfide (5). This material decomposes (in what appears to be autocatalytic fashion) and was used directly after preparation. Like 3 and 4 it exhibits a single two-electron irreversible polarographic wave at -0.9V (vs Ag/Ag+). Controlled-potential electrolysis of a 3.4:1 *dl*/*meso* mixture at mercury afforded a mixture of two major and four minor products which could be separated by a combination of preparative TLC and medium pressure liquid chromatography (mplc).[13] They are: *trans*-stilbene (7) (38%), *unsym*-1,3,5-triphenyltrithiane (mp. 161°) (11) (44%), 1,2-diphenylthiirane (12) (*trans*:*cis* = 2.1) (2%), benzaldehyde (2%), dibenzylsulfide (1%), and the thioacetal 13[14](2%) (mp. 128-130°; NMR($CDCl_3$): AB quartet at δ4.96 and 5.13 (J=9.7 Hz)(2H), 5.93 (s,1H), 7.2-7.8(m,15H); mass spec:m/e:334(parent),212,180,122. When electrolysis is interrupted before completion, the proportion of 12 in the mixture is noticeably higher.



Its stability under the reaction conditions was investigated by preparation of an authentic sample. It was found that crude 12[16] is rapidly converted to *trans*-stilbene (and a black precipitate of HgS) upon stirring a DMF solution over mercury, although a sample purified by mplc proved to be stable under these conditions.

Isolation of compounds 11 and 13 is strong evidence for the intermediacy of thiobenzaldehyde (15) in the reaction. We suggest the following scheme to account for the products:



$$5 \xrightarrow{2e^-} \underset{14}{C_6H_5\bar{C}HS\underset{Br}{C}HC_6H_5} \xrightarrow{-Br^-} 12 \xrightarrow{slow} 7 \qquad 14 \longrightarrow \underset{15}{C_6H_5CH{=}S} \longrightarrow 11$$

$$12 + 15 \longrightarrow 13$$

The trithiane 11 is a common product from reactions generating 15.[17] Thioacetal

13 could be formed by ionic or radical opening of 12 in a reaction precedented for episulfoxide 10.[12]

Apparently bromoanion 14 has two major fragmentation pathways available: cyclization to 12 or fragmentation to 15. In contrast, reaction of 5 with ultrasonically dispersed mercury[18] proceeded cleanly to trans-stilbene (95%) together with traces of benzaldehyde and dibenzylsulfide. It is not clear to us why 15 is not formed in this reaction.

Conclusions. Reductive cyclization of 1,3-dibromides (eg. 1) is efficient in this series of compounds, as with those previously investigated by us, and thus appears to be a very general process. The cyclized materials generally extrude sulfur to form alkenes. This may have some value as a source of strained alkenes, a possibility we are investigating.

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References and Notes

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