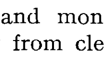
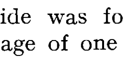
Electrochemical Reduction of 1,2-Diphenylthiiren Dioxide and Monoxide

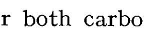
By Albert J. Fry,* Kjell Ankner, and Vijay K. Handa
(*Hall-Atwater Laboratory of Chemistry, Wesleyan University, Middletown, Connecticut* 06457)

Summary The cathodic reduction of 1,2-diphenylthiiren dioxide and monoxide was found to afford products resulting from cleavage of one or both carbon–sulphur bonds.

1,2-Diphenylthiiren dioxide (**1**)[1] and the corresponding monoxide (**2**)[2] are considerably more stable thermally than the corresponding saturated substances, and it has been postulated that this stability derives in part from a conjugative effect such that the central ring may be considered a Hückel $4n + 2$ ($n = 0$) system. To the extent that this view has any validity, injection of electrons into (**1**) and (**2**) should produce non-Hückel (and therefore unstable) species. We have investigated the electrochemical reduction of (**1**) and (**2**) and find that this is indeed the case.

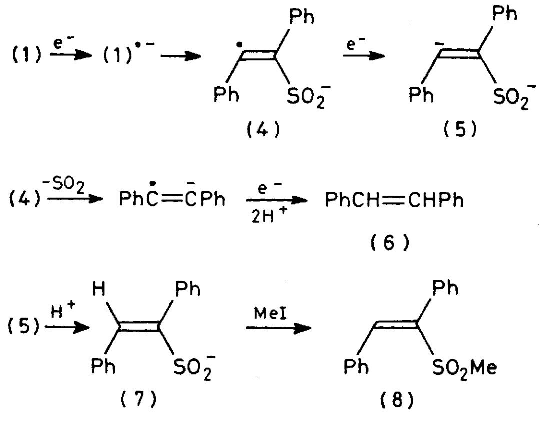

(1)


(2)


(3)

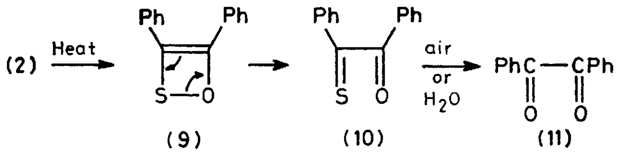
Cyclic voltammetry has shown[3] that the open-chain conjugated sulphone (**3**) undergoes reversible one-electron reduction to a stable radical anion in dimethylformamide (DMF) containing 0·1 M tetraethylammonium perchlorate (TEAP) at a sweep rate of 250 mV s^{-1}. In contrast, the cyclic voltammograms of (**1**) and (**2**) show no trace of a re-oxidation wave upon scan reversal after the reduction peak potential [$-1·73$ and $-1·98$ V *vs.* Ag/0·01 M Ag^+ for (**1**) and (**2**), respectively, at a scan rate of 500 mV s^{-1}] even at the fastest scan rate employed (10 V s^{-1}). We estimate from these data that the radical anions from (**1**) and (**2**) decompose a minimum of 3×10^3 times faster than that from (**3**). This considerably diminished stability presumably derives at least partly from the non-Hückel character of the radical anions of (**1**) and (**2**), although relief of ring strain by ring opening (*vide infra*) may also play a role.

The products from electrochemical reduction of (**1**) and (**2**), all of which arise from cleavage of at least one carbon–sulphur bond, pose intriguing mechanistic problems. Reduction of (**1**) at $-1·8$ V in DMF–0.1 M TEAP resulted in uptake of only 0·76 F/mol. The organic extracts contained *trans*-stilbene (**6**) (30%). When electrolysis was carried out in the presence of a small amount of acetic acid, 1·94 F/mol were consumed. Addition of methyl iodide to the catholyte, heating for 2 h, and work-up afforded (**6**) (40%) and the vinyl sulphone (**8**)[4] (27%). Controlled-potential electrolysis of (**2**) at $-2·0$ V under these conditions resulted in uptake of 2·4 F/mol and afforded diphenylacetylene (**14**) (80%) and benzil (**11**) (10%).

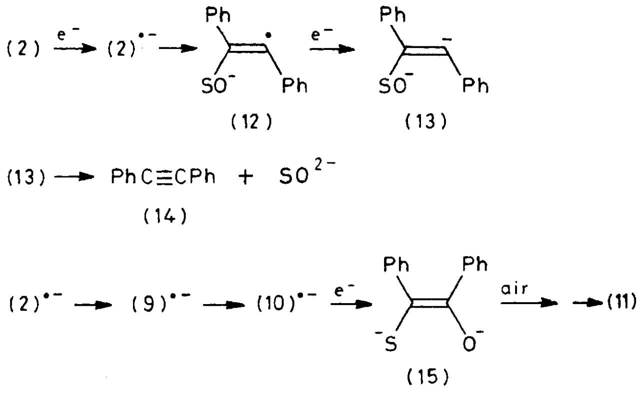


SCHEME 1.

The products of electrochemical reduction of (**1**) may be accounted for by the sequence of reactions shown in Scheme 1. Loss of SO_2 might occur from either (**4**) or (**5**), but not from the sulphinate ion (**7**) since similar ions are known to be stable.[5] Formation of (**6**) and (**8**) involves several protonation steps; in the absence of acetic acid protonation would be by adventitious water in the DMF. This would form hydroxide ion, which is known to destroy (**1**),[1] thus accounting for the low coulometry result in the absence of acetic acid.



The products from (**2**) are somewhat harder to rationalize. Diphenylacetylene (**14**) and benzil (**11**) have been isolated from the photolysis and thermolysis, respectively, of (**2**).[2] The latter reaction is thought to proceed by ring expansion to (**9**) and thence to monothiobenzil (**10**). We suggest the sequence of reactions shown in Scheme 2 to account for



SCHEME 2.

these products. The route to (**14**), the major product, is analogous to the initial steps in Scheme 1, but since SO is not as good a leaving group as SO_2,[2] (**13**) may decompose by a different path, namely ejection of SO^{2-},[6] the conjugate base of the (as yet) unknown HOSH. Alternatively, ring expansion of $(\mathbf{2})^{\cdot -}$ [possibly by way of (**12**)] would generate the radical anion of (**9**). Subsequent ring opening and reduction would lead to the di-anion (**15**), related to the known enediolate[7] and enedithiolate[8] ions. Finally, air oxidation would convert (**15**) into (**10**) and thence into (**11**).

Financial support by the National Science Foundation for this research is gratefully acknowledged, as is funding by the National Science Foundation, Dreyfus Foundation, and Wesleyan University for the Varian XL-200 n.m.r. spectrometer used in this research.

(*Received*, 29*th October* 1980; *Com.* 1167.)

---

[1] L. A. Carpino, L. V. McAdams, III, R. H. Rynbrandt, and J. W. Spiewak, *J. Am. Chem. Soc.*, 1971, **93**, 476.
[2] L. A. Carpino and H.-W. Chen, *J. Am. Chem. Soc.*, 1979, **101**, 390.
[3] K. Ankner, B. Lamm, and J. Simonet, *Acta Chem. Scand., Ser. B*, 1977, **31**, 742.
[4] M. Oki and A. Kimura, *Bull. Chem. Soc. Jpn.*, 1965, **38**, 682.
[5] W. E. Truce and A. M. Murphy, *Chem. Rev.*, 1951, **48**, 69.
[6] T. J. Wallace, H. Pobiner, J. E. Hoffman, and A. Schriesheim, *J. Chem. Soc.*, 1965, 1271.
[7] D. C. Johnson and P. R. Gains, *Anal. Chem.*, 1973, **45**, 1670.
[8] F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' 4th edn., Wiley-Interscience, New York, 1980, pp. 185—187.