

## Chain Contraction in Anodic Oxidation of *gem*-Polysulphides

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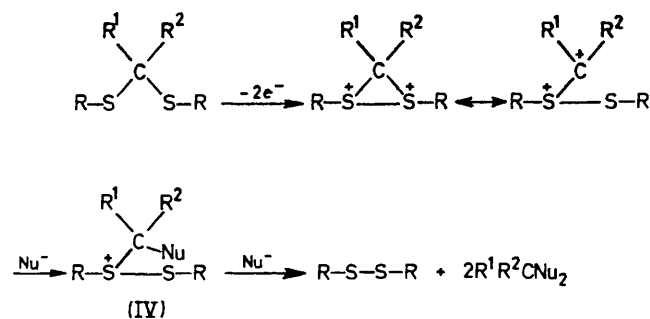
**Summary** Anodic oxidation of some aromatic *gem*-polysulphides results, unexpectedly, in chain contraction giving in dry solvents an  $\alpha$ -disulphide or, in wet solvents, a thiosulphonate.

ANODIC oxidation of sulphides in aqueous organic solvents generally affords the sulfoxide and the sulphone.<sup>1</sup> In aprotic solvents, complex sulphonium salts<sup>2,3</sup> have been isolated following electro-oxidation. We here report some unexpected results from the anodic oxidation of the *gem*-polysulphides (I; R = Ar). In pure MeCN containing



$\text{LiClO}_4$  (0.1M) oxidation of (I) at a platinum anode gives neither the sulfoxide (and sulphone) nor the sulphonium salt. After the passage of  $2 \text{ F mol}^{-1}$ , the main product is the  $\alpha$ -disulphide (II; R = Ar). Carbonyl compounds are generally also present after work up resulting from attack of water on carbocations formed by cleavage of the  $-\text{C}-\text{S}^+-$  bonds. In  $\text{MeCN}-\text{H}_2\text{O}$  (90:10 v/v)  $-\text{S}-\text{S}-$  bond formation

still occurs. After passage of  $6 \text{ F mol}^{-1}$ , the thiosulphonate  $\text{RSSO}_2\text{R}$  (III) is the major product.



SCHEME

This type of oxidation does not depend on the solvent or its acidity since the results are the same in both MeCN and  $\text{MeNO}_2$ , in the presence or absence of pyridine or  $\text{NaCO}_3$ . Further, we have checked that the  $\alpha$ -disulphide is not

TABLE. Products of anodic oxidation of *gem*-disulphides

Substrate	X	$E^a/V$	Dry MeCN			MeCN-H <sub>2</sub> O (90:10 v/v)		
			Coulometry F mol <sup>-1</sup>	Products (%) <sup>b</sup>		$E/V$	Coulometry F mol <sup>-1</sup>	Product (%) <sup>b</sup>
				(II)	(III)			(III)
$(p\text{-XC}_6\text{H}_4\text{S})_2\text{CH}_3$ .. ..	MeO	+1.2	2.9	70	20	+1.2	5.9	85
	Me	+1.2	1.85	80	—	+1.2	5.7	90
	H	+1.4	2.2	75	10	+1.2	6.1	80
	NO <sub>2</sub>	+1.8	2.3	50	—	—	—	—
$(p\text{-XC}_6\text{H}_4\text{S})_2$ .. ..	H	—	—	—	—	+1.4	3.6	80

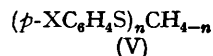
<sup>a</sup> Potentials with respect to the Ag/Ag<sup>+</sup> (0.01M) electrode. <sup>b</sup> Yields are measured by n.m.r. analysis of the mixture after work up.

formed by oxidation (1) of the thiol which could be produced by hydrolysis of the substrate.



The results may, however, be rationalised by an E.E.C.C. mechanism (Scheme) involving a dicationic intermediate.

Similar formation of -S-S- bonds (in both dry and wet media) is observed following anodic oxidation of more complex polysulphides. Thus with (V;  $n = 3$ , X = Me, OMe, or F), compounds (II; R =  $p\text{-XC}_6\text{H}_4$ ) are formed,



together with  $p\text{-XC}_6\text{H}_4\text{SCHO}$ . For higher molecular weight compounds (V;  $n = 4$ , X = H, Me, OMe, and F) insolubility prevents electrolysis on a normal scale, but only -S-S- derivatives are present after work-up in the expected yields; dithiocarbonate (-S-CO-S-) intermediates which are possible could be also oxidized according to the Scheme.

One-step chain contraction in *gem*-polysulphides seems to be possible only by electrochemical means. When R is aliphatic, the results are different because the intermediate sulphonium salt (IV) is relatively stable and can be isolated.

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<sup>2</sup> P. T. Cottrell and C. K. Mann, *J. Electrochem. Soc.*, 1969, **116**, 1449.

<sup>3</sup> S. Torii, Y. Patsuyama, K. Kawasaki, and K. Uneyama, *Bull. Chem. Soc. Japan*, 1973, **46**, 2912; S. Torri and K. Uneyama, *Tetrahedron Letters*, 1972, **44**, 4513.