

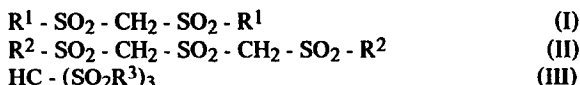
THE REVERSIBLE ANODIC COUPLING OF ANIONS  
 OF POLYSULPHONES IN BASIC MEDIA

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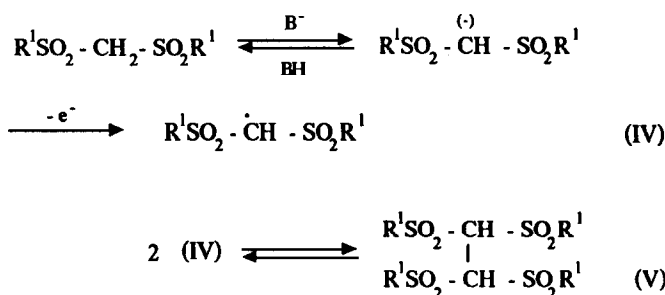
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**Summary:** The electrochemical oxidation of acidic sulphones (1,3-disulphones, 1,3,5,-trisulphones and trisulphonyl methanes) was conducted in organic medium in the presence of a base. In certain cases dimers may be obtained: these are not thermally stable and, upon heating cleave in radicals detectable by e.s.r. spectroscopy.

The electrochemical oxidation of anions derived from enolates and other carbanions is now well established<sup>(1)</sup> for leading to symmetrical dimers with a central C-C bond formation. The chemical duplication of basic forms of monosulphones by Cu<sup>II</sup> was described<sup>(2,3)</sup>. Other chemical coupling processes were also reported<sup>(4)</sup>. It can be expected that polysulphones:

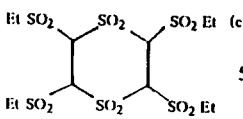


may activate strongly intermediate CH<sub>2</sub> groups and facilitate the anodic oxidation in conducting solvents rendered basic. The mastery of technical conditions leads to a CH-CH bond here substituted by four and even six strongly withdrawing groups and one should foresee a drop of the thermal stability (in term of homolytic cleavage) for such a linkage. The preliminary preparative results are gathered in the table and demonstrate at least with some disulphones (I) the occurrence of a coupling process. The scheme below shows a radical process but the existence of a mechanism implying dimer anion radical as a transient (addition of the radical to the anion) as proposed<sup>(5)</sup> by Amatore and Verpeaux for simpler substrates could be also taken into account.



However, single coupling processes cannot be considered as a general case since trisulphones (II) lead to a six-membered ring where two CH groups are implicated but with always an electricity consumption of the order of one electron per mole. One could then expect a chemical closure of the ring during the work up.

Finally trisulphone (III, R = CH<sub>3</sub>), if the coulometric measurements in the course of oxidation are taken into account (average result : n = 1 electron per mole), was assumed to couple but a large amount of the starting material is recovered after work up. The reason for that could be thermal homolytic cleavage of the dimer (in the course of the treatments of electrolysis solution and extracts where heatings are unavoidable) with multiple pathways which allow to pass from the free radical to the starting sulphone (III) (e.g. hydrogen atom abstraction from solvents).

Entry	Substrate	Experimental conditions			Main electrolysis product		
		Electrolyte	Anode Potential V vs Ag/Ag+ 0.1M	n (F. mole-1)	Nature	yield (%)	m.p (°C)
n°1	I (R <sup>1</sup> = Me)	MeOH + LiClO <sub>4</sub> 0.1M +Na metal (a)	+0.4	0.85	Dimer	45	260
n°2	I (R <sup>1</sup> = Et)	-id-	+0.4	0.80	Dimer (b)	78	92
n°3	I (R <sup>1</sup> = n.Pr)	-id-	+0.4	1.20	Dimer	56	157
n°4	I (R <sup>1</sup> = CF <sub>3</sub> )	-id-	+0.5	1.35	Dimer	45	>300
n°5	II (R <sup>2</sup> = Et)	-id-	+0.4	0.95	 Et SO <sub>2</sub> SO <sub>2</sub> SO <sub>2</sub> Et (c)	50	140
n°6	III (R <sup>3</sup> = Me)	Pyridine / TEAP 0.1M	+1.25	0.69	starting material		
		MeOH / LiClO <sub>4</sub> 0.1M +Na <sup>(a)</sup>	+0.7	0.95	-id-		

**Table :** Potentiostatic electrolyses of polysulphone at a graphite rod. n values correspond to, at least, a decay of 95% of the initial current. (a) stoichiometric amount towards the sulphone.

(b) <sup>1</sup>H n.m.r.(60MHz, CDCl<sub>3</sub>) δ in ppm : 4,46(s, 2xCH), 3,42(q, 4xCH<sub>2</sub>), 1,45(t, 4xCH<sub>3</sub>).

(c) <sup>1</sup>H n.m.r.(60MHz, CD<sub>3</sub>COCD<sub>3</sub>) δ in ppm : 5,2(s, 4xCH), 3,40(q, 4xCH<sub>2</sub>), 1,40(t, 4xCH<sub>3</sub>).

Consecutively to this first assumption, the thermal stability of the obtained dimers (suggesting the reversibility of the coupling process) was checked without and with a spin trap like tertibutylphenylnitron (BPN); the dimer of (I) (entry n°2) of the table is taken as an example. While perfectly stable at room temperature, it appears to be homolytically cleaved at 270°C (emergence of a singlet assignable to radical (IV)). Additionally the signal intensity is much higher in the presence of BPN in the case where (IV) is progressively trapped and accumulated in solution even at more moderate temperatures (60°C).

The reversibility of the coupling for radical derived from polysulphone is of high interest as a controlled source of free radicals and usable as a catalyst in polymerization processes.

#### REFERENCES

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