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Cathodic Coupling of 1, 3, 5 - tri (Aryl and Alkylsulfonyl) Benzenes into Tetra and Penta-substituted Biaryls

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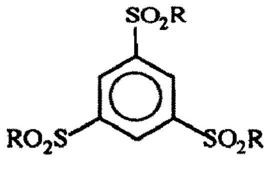
Abstract : Tri [aryl and alkylsulfonyl] benzenes cathodically lead in non aqueous conditions to unexpected coupling products either tetra or pentasulfonylbiphenyls depending on the structure of the starting compounds.

Everyone knows[1] now the interest of the activation of specific carbon atoms in organic molecules by alkyl and arylsulfonyl groups. As a matter of fact, at least during the last two decades, a special attention was paid to the activation by one or two sulfonyl groups. Therefore, the cathodic behaviour of aromatic sulfones was found[2] to be strongly changed by a higher substitution : it was then observed both an increasing stabilization of relevant anion radicals and a progressive increase of normal potentials. Since sulfonyl groups may act both as strongly electron withdrawing and leaving groups, it appeared[3, 4] then that reactions implying electron transfer(s) onto complex sulfones are most of the time very difficult to foresee in detail. Although 1, 2, 4, 5 - tetrasulfonylbenzenes were found[5] to be among the best acceptors of organic chemistry (with the relevant formation of surprisingly stable anion radicals leading exclusively to cleavage reactions), it was amazing to realize that the electrochemical reduction of 1, 3, 5 - trisulfonylbenzene occurs in a very unexpected way since aryl-aryl couplings were observed. As a matter of fact the present preliminary communication, aims to describe in detail the cathodic behaviour of trisulfones **1**.



a : R = Me
b : R = Et
c : R = nBu
d : R = Ph

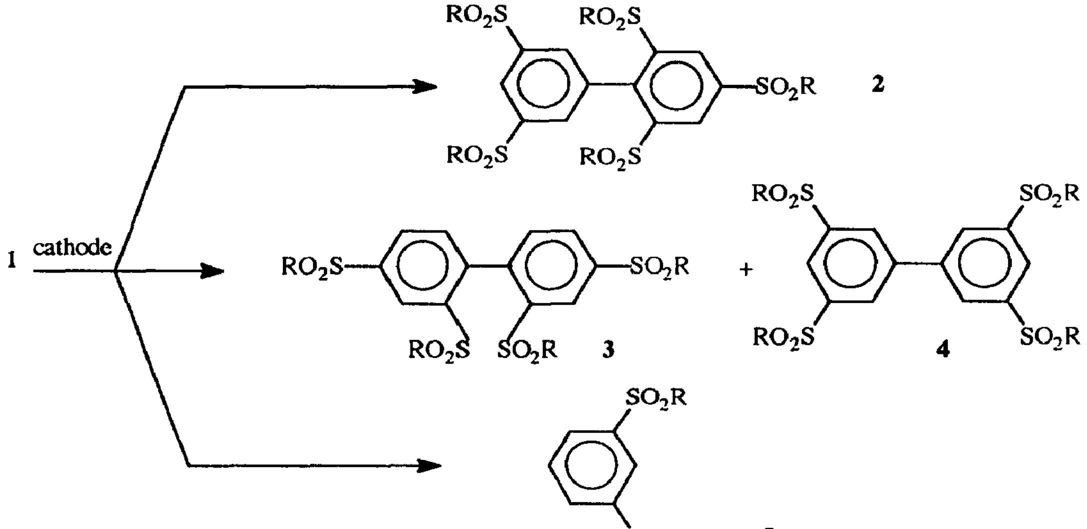
1

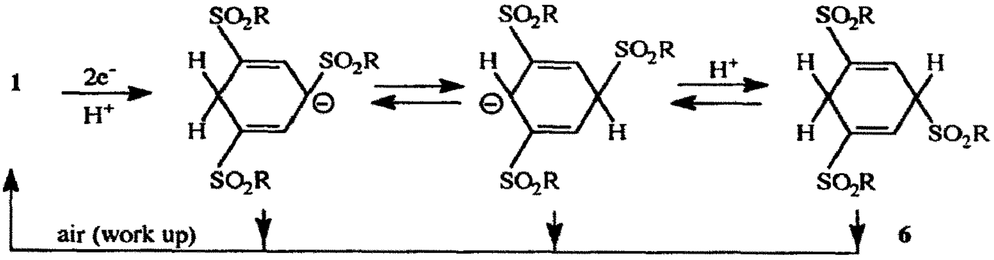
The electrochemical reduction of substrates **1** when carried out in aprotic electrolyte (Dimethylformamide -DMF - containing ammonium salts) at metallic electrodes (e.g. stirred mercury pool and platinum sheet) affords most of the time coupling products (**2**, **3** and **4**). Disulfones **5** obviously issued from the two electron cleavage of **1** were often obtained but in small amount. Additionally, although potentiostatic electrolyses were in all cases completed until the residual current has reached a value 5 % inferior to that observed at the start, it was found that various amounts of **1** remained present after work up. In some reduction experiments conducted especially on **1d** in various electrolytes with an average consumption of two moles of electron per mole of **1**, it was amazing to recover mostly the starting trisulfone.

Recovering starting material (especially from **1d**) can be reasonably explained by formation of the corresponding dihydrocompounds. This formation in the catholyte is supported by amperometry in the course of potentiostatic electrolyses. Bubbling air through the cell allowed the progressive reappearance of trisulfones **1** in catholyte.

In order to explain the formation of coupling products **2**, **3** and **4**, a main question arises : are dihydrocompounds (or better their basic forms) involved in the obtaining of biaryls ? With **1d**, the answer to this question is probably "*yes*" since the product distribution is strongly affected if electrophiles are added *before* start or *after* electrolysis completion. This fact seems to be supported by the high stability of **1d** anion radical. Contrariwise, the obtaining of coupling products for **1b** and **1c** *via* nucleophilic displacement taking into account basic forms from **6** as a major mechanism does not fit with experiments : **1b** and **1c** exhibit in cyclic voltammetry (CV) an irreversible first cathodic step the height of which always accounts for a one electron step. Adding proton donor (phenol, acetic acid), even in a large excess has no affect at all on the CV peak shape. Therefore, although cathodic coupling of ArX type compounds (X : leaving group attached to an aryl ring Ar) was reported to be very unlikely to occur without the use of catalyst such as "zero" metals, it is here expected that anion radicals (for **1b** and **1c**) are strongly donating species toward starting compounds. Thus, with aromatic polysulfones, new rather fast reactions -particularly coupling- can be foreseen since alkyl sulfonyl groups (less bulky than aryl) play here a double role : first as strong electron-withdrawing substituents and second as potential leaving anions after charge transfer(s).

Furthermore the cathodic reduction of compounds **1** was carried out in aprotic deuteriated dimethylsulfoxide (electrolyte : nBu_4NBF_4 0.1 M). ^1H NMR spectra of the catholyte after total completion of electrolyses (solution maintained under inert athmosphere) exhibited (especially with the products issued from compounds 1a-c) the presence of *only* 6 aromatic protons the coupling of which appeared in agreement with the writing of a dimeric dianion $[\mathbf{1} - \mathbf{1}]^{=}$ (see scheme below). Additionnally, it is worth mentioning the addition of the anion radical of 1 to the substrate seems to be the determining rate. Such a proposal fits quite well with the theory, since the found slope of Ep = f (log v) - v being the sweep rate in CV - was 31 ± 0.03 mV per decade of v





Starting trisulfone (Ep)	Solvent	Applied Potential V (Electrode Matérial)	Electricity amount (F. mole^{-1})	Isolated Product distribution (%)				
				2	3	4	5	1
1a (- 0.96 V)	DMF	- 1.00 (Pt)	1.4	34	-	-	-	-
1b (- 0.99 V)	DMF	- 1.00 (Hg)	1.7	38	-	-	16	10
1c (- 0.96 V)	DMF	- 0.95 (Hg)	1.6	31	7	7	-	11
1d (- 0.48 V)	DMF[a]	- 0.80 (Pt)	1.8	-	-	35	-	40
	DMF[b]	- 0.80 (Pt)	1.9	-	-	-	-	85
	DMSO[c]	- 0.80 (Pt)	1.4	-	-	-	-	60
	Acétonitrile[d]	- 0.80 (Pt)	2.1	-	-	-	-	45
	DMF[e]	- 0.80 (Pt)	2.2	-	-	56	-	10

Table 1 : Preparative potentiostatic electrolyses were carried out with about 2 millimoles of trisulfone. Reference electrode : Ag/AgI/I$^-$ in all cases. Two compartment cell. Current densities at the start : 4-5 mA.cm^{-2}. Electrolysis duration : about 7 hours. Peak potential values are given for a sweep rate of 0.1 V s^{-1}. Platinummicro electrode. Supporting electrolyte 0.1 M Bu_4NBF_4. With 1d, electrolyses could be conducted in the presence of electrophile or proton donor in excess . In other cases, strong acid solution or electrophiles in excess were added during or after electrolysis in order to trap electrogenerated organic anions.

For example :

(a) : addition of 4 equivalents of concentrated HCl after completion of the electrolysis.

(b) : addition of 2 equivalents of acetic acid in course of the electrolysis.

(c) : reaction conducted in the presence of methyl iodide (4 equivalents).

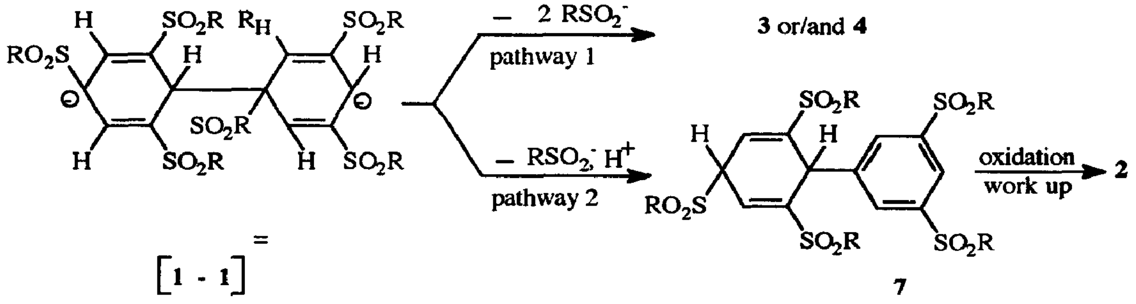
(d) : reaction conducted in the presence of methyl iodide (4 equivalents).

(e) : addition at the end of the electrolysis of 3 equivalents of trimethylsilane bromide.

instead of 30 mV. A coupling anion radical - anion radical should lead to a slope of 20 mV per decade of v at room temperature.

Therefore other pathways like those taking into account basic forms of **6** as nucleophiles prepared prior to the electrolyses of **1b** or **1c** (affording then aryl radicals by cleavage of C - S bonds) have to be rejected. Under such conditions such $S_{NR}1$ like reactions should lead to the formation of "mixed" biaryls **2**. As a matter of fact such biaryls were never found in any product distribution issued from the recipe described above. Lastly, it is worth mentioning that **2b** and **2c** were found to be easier to reduce than relevant starting compounds. Bubbling air after completion of electrolyses allows the progressive appearance of **2** (as seen by CV. or amperometry) and this seems fully compatible with a conversion such as **7** —> **2**.

$$1^{\cdot -} + 1 \rightleftarrows [1-1]^{\cdot -} \xrightarrow{e^-} [1-1]^{=}$$



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