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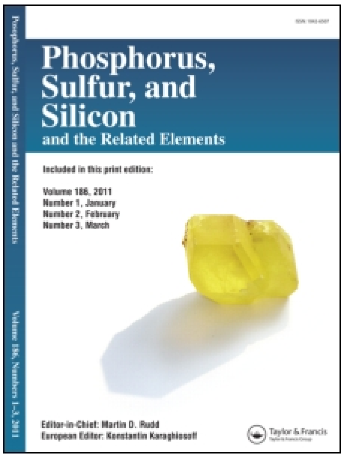

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A STEREOSELECTIVE CATHODIC COUPLING OF ARYL STYRYL SULFONES

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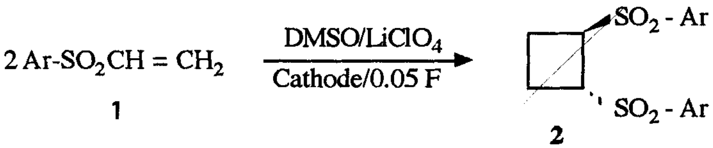
Abstract The cathodic coupling of unsaturated sulfones (title compounds) performed in aprotic media in the presence of lithium salts as electrolyte affords d,l dimers almost exclusively.

Aryl vinyl sulfones were reported(1) to lead, under cathodic process either to the cleavage of the carbon-sulfur bond or to the saturation of the activated double bond. First, the cyclodimerization, catalyzed cathodically,(2) of arylvinylsulfones **1** which affords in good yields cyclobutane **2** was an unexpected success. The electrical consumption was reported to be very low (scheme 1) :



1

2

SCHEME 1

However, the extension of such successful reaction to β-substituted vinylsulfones failed.

$Ar\text{-}SO_2\text{-}CH = CH\text{-}R$ R = alkyl or aryl

Thus, with arylvinylsulfones substituted in β-position with alkyl R chains, it was found(3) the isomerization, by electrogenerated bases, of the α,β isomer to β,γ isomer, known to be more stable ; moreover the reactivity of electrogenerated bases by Michaël addition leads to many side-products of little interest.

Concerning faradic coupling of unsaturated sulfones, let us to recall here briefly that numerous works have been devoted to the cathodic reduction of styrenes substituted in β-position with Electron Withdrawing Groups (nitrile, ketones, esters). Linear or cyclic hydrodimers are obtained.

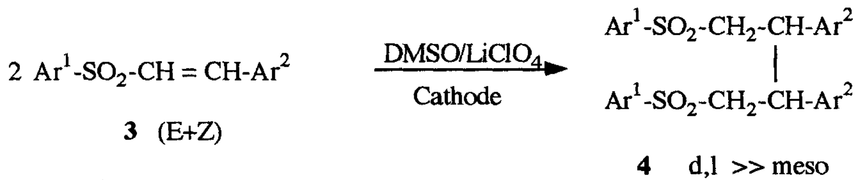
We present here the case of arylstyrylsulfones **3**. These sulfones are easily synthesized from procedures described in literature. A large number of sulfones **3** has been prepared :

Ar^1-SO_2-CH = CH - Ar^2 **3**

3a	$Ar^1 = C_6H_5$	$Ar^2 = C_6H_5$	**3f**	Ar^1 = p-H_3C-C_6H_4	Ar^2 = p-Cl-C_6H_4
3b	Ar^1 = p-H_3C-C_6H_4	$Ar^2 = C_6H_5$	**3g**	Ar^1 = p-H_3C-C_6H_4	Ar^2 = 2-pyridyl
3c	Ar^1 = o-H_3CO-C_6H_4	$Ar^2 = C_6H_5$	**3h**	Ar^1 = p-H_3C-C_6H_4	Ar^2 = 2-naphthyl
3d	Ar^1 = p-H_3CO-C_6H_4	$Ar^2 = C_6H_5$	**3i**	Ar^1 = p-H_3C-C_6H_4	Ar^2 = p-biphenyl
3e	Ar^1 = p-H_3C-C_6H_4	Ar^2 = p-Anis.	**3j**	Ar^1 = p-H_3C-C_6H_4	Ar^2 = 9-anthryl

All of these substrates show two reduction peaks from cyclic voltammetry data.

Preparative scale electrolyses, under specific conditions, DMSO-$LiClO_4$ as an electrolyte and low current density, yield linear dimers **4** according to the chemical pathway shown in scheme 2 :



$$2\ Ar^1\text{-}SO_2\text{-}CH=CH\text{-}Ar^2 \xrightarrow[\text{Cathode}]{DMSO/LiClO_4} \begin{array}{c} Ar^1\text{-}SO_2\text{-}CH_2\text{-}CH\text{-}Ar^2 \\ | \\ Ar^1\text{-}SO_2\text{-}CH_2\text{-}CH\text{-}Ar^2 \end{array}$$

3 (E+Z)

4 d,l >> meso

SCHEME 2

d,l isomers were obtained in high yield in the presence of lithium cation which plays here a major role.Table shows the ratio of the d,l and meso isomers, total yields are very high excepted with sulfones **3h** and **3j** which undergo cleavage process.

Table : Macroelectrolyses of sulfones **3** in DMSO/$LiClO_4$.

SULFONES	Charge ($F.M^{-1}$)	Coupling products (isolated yields %) **4 d,l**	**4 meso**	SULFONES	Charge ($F.M^{-1}$)	Coupling products (isolated yields %) **4 1,l**	**4 meso**
3a	1	71	(5)	**3f**	1	(53)	(5)
3b	1	68	(5)	**3g**	1	(64)	(5)
3c	1.2	67	(5)	**3h**	1.4	(43)	(8)
3d	1	74	(5)	**3i**	1	(74)	(5)
3e	1.2	60	(5)	**3j**	1.7	(0)	(0)

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