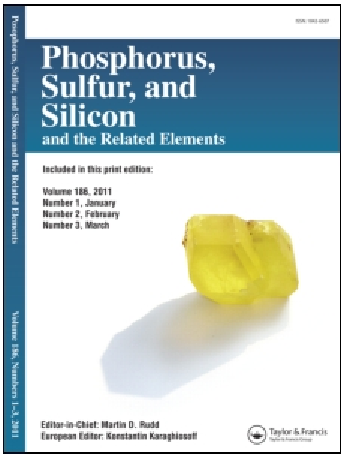

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

A Recent Survey on the Cathodic Behaviour of Sulfones: Is Cleavage the Unavoidable Fate?

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To cite this Article Simonet, Jacques(1993) 'A Recent Survey on the Cathodic Behaviour of Sulfones: Is Cleavage the Unavoidable Fate?', Phosphorus, Sulfur, and Silicon and the Related Elements, 74: 1, 93 — 112
To link to this Article: DOI: 10.1080/10426509308038103
URL: http://dx.doi.org/10.1080/10426509308038103

Phosphorus, Sulfur, and Silicon, 1993, Vol. 74, pp. 93–112
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A RECENT SURVEY ON THE CATHODIC BEHAVIOUR OF SULFONES : IS CLEAVAGE THE UNAVOIDABLE FATE ?

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Abstract It is proposed a survey on recent results concerning the cathodic behaviour of aromatic sulfones : scission of one C-S bond but also coupling, isomerization, cyclodimerization, etc. Selectivity of described reactions are mainly discussed as a function of the used electrolyte.

INTRODUCTION

If most sulfones are known to react with chemical reducing reagents like dissolved metals and amalgams, their ability to react via electron transfer (heteregeneously by means of a cathodically polarized electrode or homogeneously by means of anions or anions radicals possessing a sufficient reducing power) should depend on the level of their respective LUMO. In other words, the first charge transfer may occur more or less easily within an accessible range of potential (up to - 3 V vs Saturated Calomel Electrode -SCE-, this potential value being about the most reducing potential reached since there is not electrolyte-solvent couple electrochemically stable beyond this value) only if the sulfonyl group is directly branched to unsaturated system (e.g. an aromatic moiety). Obviously, redox potential range necessary to observe electron transfer(s) onto most of sulfones are however located within a range were both proton and water are reduced. Accordingly, the use of aprotic (or weakly protic) organic solvents appears most of the time absolutely necessary.

The conditions of the electrochemical reactivity of sulfones (electron transfer, cleavage, redox catalysis, occurence of acidic proton, action of electrogenerated bases in unbuffered media, cathodic elimination, etc.) were fully discussed along a preceding review(1) and therefore are not evoked here. Let us however recall the cleavage mechanism of aromatic sulfones according to the nature of substituents (electron withdrawing or donating) branched onto the aromatic system.

$$\mathrm{Ar\,SO_2\,R} \overset{e^-}{\rightleftarrows} [\mathrm{Ar\,SO_2\,R}]^{-\bullet} \tag{1}$$

$$[\mathrm{Ar\,SO_2\,R}]^{-\bullet} \xrightarrow{k_c^1} \mathrm{Ar}^\bullet + \mathrm{RSO_2}^- \tag{2}$$

$$[\mathrm{Ar\,SO_2\,R}]^{-\bullet} \xrightarrow[k_c^2]{} \mathrm{R}^\bullet + \mathrm{Ar\,SO_2}^- \tag{3}$$

$$\left[\begin{matrix}\mathrm{Ar}^\bullet\\ \mathrm{R}^\bullet\end{matrix}\right. + [\mathrm{Ar\,SO_2\,R}]^{-\bullet} \longrightarrow \begin{matrix}\mathrm{Ar}^-\\ \mathrm{R}^-\end{matrix} + \mathrm{Ar\,SO_2\,R} \tag{4}$$

or

$$\mathrm{Ar}^- \text{ and } \mathrm{R}^- \xrightarrow{\text{proton source}} \mathrm{Ar\,H \text{ and } RH} \tag{5}$$

$$\mathrm{Ar}^\bullet \text{ or } \mathrm{R}^\bullet \xrightarrow[\text{HS}]{\text{H-donor solvent}} \mathrm{Ar\,H} \text{ or } \mathrm{RH} + \mathrm{S}^\bullet \tag{6}$$

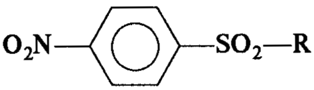
$$\mathrm{S}^\bullet + [\mathrm{Ar\,SO_2\,R}]^{-\bullet} \longrightarrow \mathrm{S}^- + \mathrm{Ar\,SO_2\,R} \tag{7}$$

The scheme above underlines the passage through an anion radical as an obligatory transient. The life time of this intermediate depends on the nature of substituents present on the Ar group. One may consider that with electron withdrawing substituents, the formation of the anion radical should correspond to the occupation of the LUMO (p* level) and the cleavage reaction affords the obtainment of $\mathrm{Ar}^\bullet$ radicals mainly.

Concomitantly, such anion radicals as intermediates may present a certain stability. On the contrary, with donating groups on the Ar group, the life time of anion radicals was found to be much shorter ($k_C^1 < < k_C^2$) and the first charge transfer could generally fit with a p $\rightarrow$ s* like transition. Here the regioselectivity of the observed scission reaction was found to be fundamentally changed and appears to be a source of R$^{\bullet}$ radical. The fate of radicals of both kind, whatever the nature of the cleavage reaction, depends both on the reducing capability of the medium (heterogeneous when k_C^1 or/and k_C^2 are extremely large allowing the formation of radical at the electrode surface or homogeneous when diffusion permits more stable anion radical to cleave in solution) and the H-donor character of the used solvent or electrolyte towards those transient free radicals. The scheme above aims to summarize the mode of cleavage of aryl alkyl sulfones in general which then corresponds to a two electron reaction according to a E-C-Disp mecanism (DISP : like Disproportionation) since the second electron transfer takes place in solution (case where k_C^1 or $k_C^2 << 10^6\ s^{-1}$). Values E° (redox potential of the first charge transfer) and Ep (peak potential in voltammetry for the overall conversion $ArSO_2R \rightarrow RH$ or ArH) may depend on a certain number of parameters especially the energy level of the LUMO and kinetic factors. However, up to now, it can be said that the $ArSO_2$ group is not in very most of the cases a very good "electrophore" (moiety of the molecule which determines in a large extend the level of the relevant LUMO) and accordingly values E° and Ep (of different signification but found to be very near) correspond to that of rather reducing potentials (say within a range of - 2.2 V when Ar = Ph to - 1.8 V when Ar is a polyaromatic system ; potentials are of course refered to the mostly used saturated calomel electrode (SCE)).

CATHODIC CLEAVAGE OF MONOSULFONES

To a matter of fact(3), the following aromatic sulfones :



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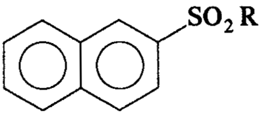

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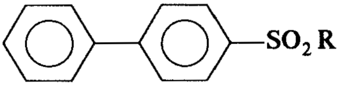

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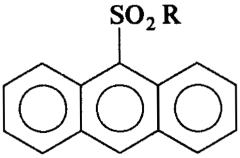


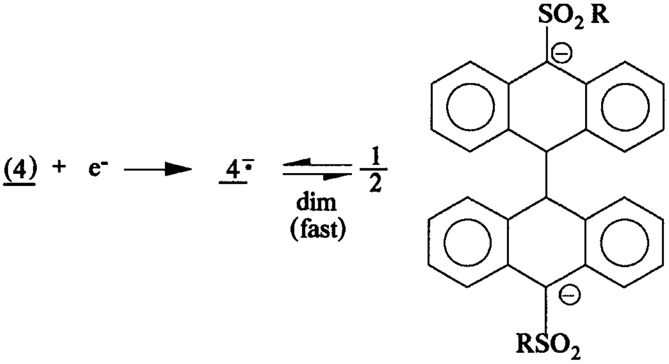
4

exhibit (at least with 1-3) rather or even very stable anion radicals and then the p → p* transition to the LUMO is confirmed. With such systems favoring the cleavage of Ar-S bonds, the scission regioselectivity can be easily checked by the observation of voltammetries in non aqueous media in the presence of weak amounts of proton donor where the two main steps account for :

$$\mathrm{Ar\,SO_2\,R} \xrightarrow[\text{2 H}^+ \text{ (proton source)}]{2\,e^-} \mathrm{Ar\,H} \qquad \text{(irreversible first peak)}$$

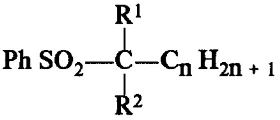
$$\mathrm{Ar\,H} \xrightarrow{e^-} \mathrm{Ar\,H}^{\overset{-}{\bullet}} \qquad \text{(reversible second peak)}$$

However, sulfones 4 (R = Me, alkyl, Ph) behave abnormally owing to the occurrence of a fast reversible dimerization process probably through a radical anion coupling :



The cathodic cleavage of allylic and propargylic aryl sulfones had then demonstrated(2) the ability to form corresponding free radical which can be trapped or which lead to the relevant dimers).

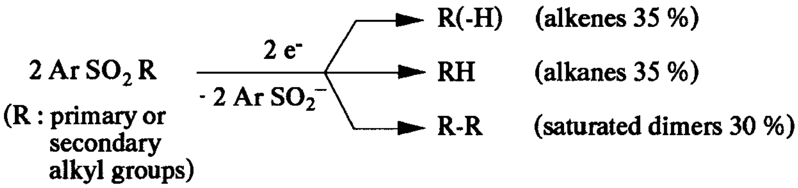
The behaviour of long chain sulfones 5 (n ≥ 7) was also studied(4) :



$$\mathrm{PhSO_2{-}C(R^1)(R^2){-}C_nH_{2n+1}}$$

5

Thus, in media of very low acidity, unexpected coulometric balances demonstrate in those cases a global consumption of one mole of electron per mole of substrate ; two main reasons for that are (i) the occurence of dimerization process (ii) the b-elimination provoked by electrogenerated bases at the cathode interface :



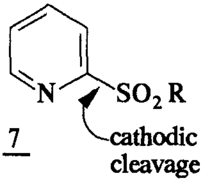
Therefore, the cleavage of the C-S bond has two concomitant sources : the classical electrochemical cleavage producing one equivalent of strong base per each electron pair transfered leading to b-elimination on the non-reduced substrate either in the reaction layer or in the catholyte bulk. Here the specific behaviour of long chain sulfones (formation of dimers R-R) could be due to the amphilic nature of substrates, strongly adsorbed and then possibly cleaved in heterogeneous phase. Nucleophilic displacements by R^- anion onto the starting sulfone as a source of dimer appear unlikely since sulfones possessing secondary R groups lead also to a similar amount of R-R dimers.

Diaromatic sulfones 6 were also studied

$$\mathrm{Ar{-}SO_2{-}Ar'}$$

6

and do exhibit rather stable anion radicals. They can be considered as a good way to produce both $Ar^{\bullet}$ or $Ar'^{\bullet}$ radicals. Another way of producing easily such aryl radicals (for addition to unsaturated systems or to spin markers) was also achieved(5) from the following monosulfones :



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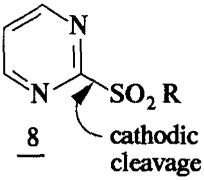

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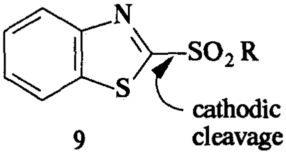
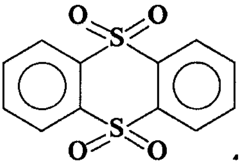


9

The electrochemical method was also reported to be a facile route to alkyl sulfinate specially from 9 (such reaction was experimentally shown to be possible with primary $R=C_8$, C_{10}, C_{12} or C_{18}) the formation of which being considered continuously by means of a selective extraction using a two phase system.

DISULFONES

9,9,10,10-tetraoxide thianthene 10 has been studied electrochemically(6). Thus, 10 may afford a radical anion and a dianion both of them surprisingly stable :



10

The ESR spectrum of 10 anion radical obtained by in situ electrolysis in aprotic dimethylformamide containing tetraalkylammonium salts exhibits (Figure 1) only a quintet easily interpreted by the splitting of protons a. On the contrary, for protons b, the splitting constant is extremely small. Therefore, the antibonding orbital of the anion relative to each aromatic ring corresponds to an antisymmetric one. Moreover, the low coupling constants experimentally found fit very well with a equal delocalisation of the charge between the two aromatic nuclei.

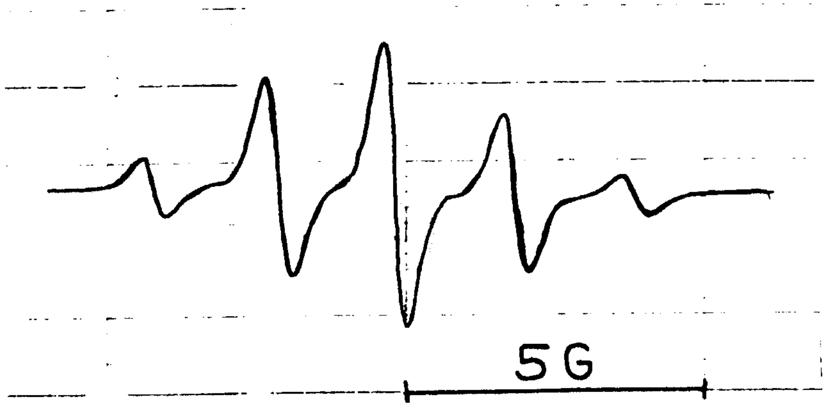


FIGURE 1 : ESR spectrum of 10 anion obtained under electrolysis (DMF - Bu_4NBF_4 0.1 M). Pt grid. Current density 10 µA.cm^{-2}.

The capability of 10 dianion to be used as reducing species was demonstrated(4) in cyclic voltammetry in the presence of aromatic halides ArX. Kinetic data concerning k constants values at room temperature are available.

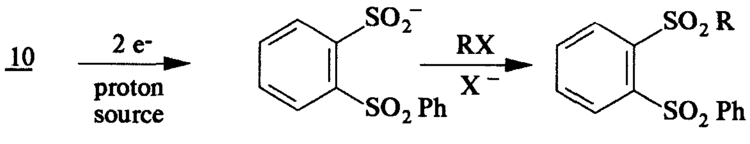
$$\underline{10} \overset{e^-}{\rightleftharpoons} \underline{10}^{\bullet -} \overset{e^-}{\rightleftharpoons} \underline{10}^{=}$$

$$\underline{10}^{=} + ArX \underset{k_{-1}}{\overset{k}{\rightleftharpoons}} \underline{10}^{\bullet -} + ArX^{\bullet -}$$

$$ArX^{\bullet -} \xrightarrow{k_c} Ar^{\bullet} + X^{-}$$

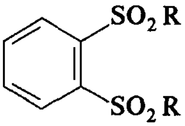
A comparison of the reducing power for both anion radicals and dianions of same redox potentials was made. Electron exchange kinetic values from 10 dianion was found to be of the order of 10 times lower than corresponding anion radicals can be explained by an increase of the reorganization energy in the course of the homogeneous electron transfer.

The cleavage reaction of 10 under cathodic means was also studied(7). The formation of an opened sulfinate was demonstrated. The addition of primary aliphatic halides RX at the end of the electrolysis allows the easy obtainment in high yield of a new series of sulfones 11 :

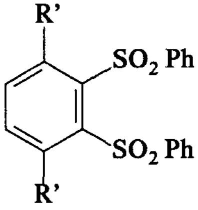


11

The behaviour of ortho-bis (alkyl sulfonyl) and (aryl sulfonyl) benzenes 12 appears probably worthwhile to be described here in a few details.

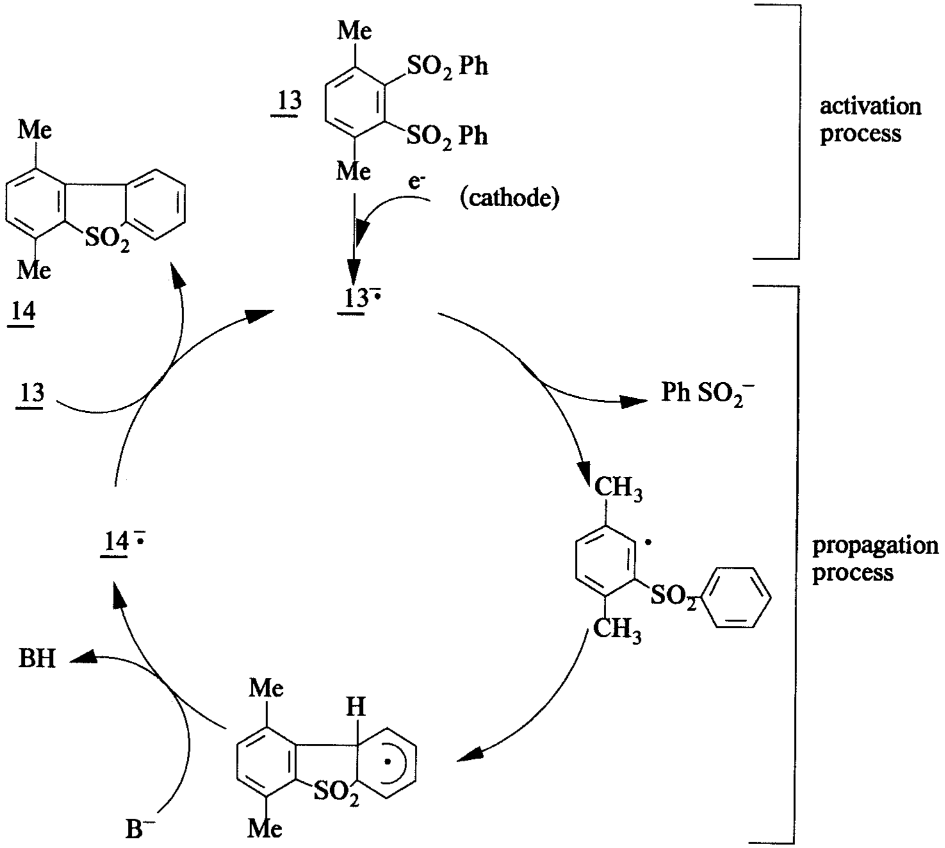


12

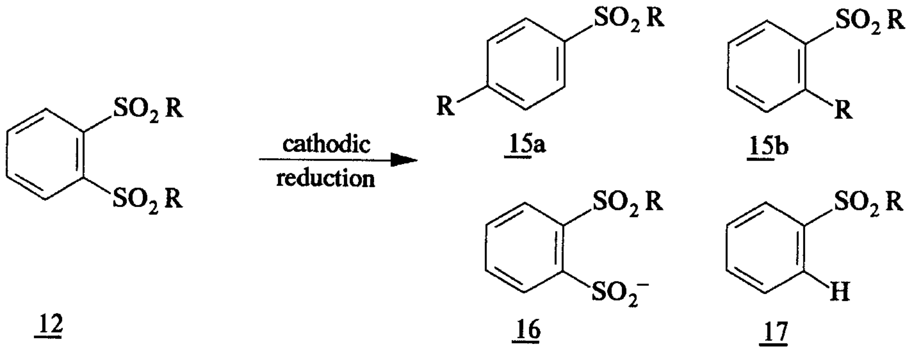


13

First of all, let us describe the nice electrocatalytic reaction found by Novi(8) with 13 where R′ = Me, in weakly H-donor solvent (e.g. dimethysulfoxide) and in the presence of a strong base in the considered medium : (B$^-$ = tetrabutylammonium acetate). The reactivity of 13 was fully explained by the catalytic cycle given below after only an activation electron transfer taking place at the cathode. When side reactions (reduction of the free radical, transfer of hydrogen atom) weakly occur, the overall electricity consumption necessary to the formation of the monosulfone 14 is very low (0.14 mole of electron per mole of 13).



Differences in the cathodic behaviour between series 12 (R = Ph) and series 12 (R = alkyl group) are totally dramatic. The latter, when reduced in aprotic solvent for a wide palette of primary R substituents affords(9) the following product distribution :



The total yield experimentally reported for 15a + 15b was found to be equal to that of 16. The disappearance of 12 anion radical was shown to correspond to a bimolecular reaction (kinetics studied by UV, ESR or voltammetry), except with R = Me and or secondary alkyl groups for which classical monomolecular type cleavages were found. Accordingly, the latters afford high yields in 16 (see table below).

Substrate 12 with R =	Fixed potential E(V)	Electricity consumption (F. mole^{-1})	Experimental conditions	Isolated products (%)			
				15a	15b	16	17
Me	- 1.32	1.42	aprotic medium	traces	0	75	10
Et	- 1.18	1.34	aprotic medium	33	2	30	13
		1.12	presence of $PhSNBu_4$$^{(a)}$	42	traces	-	0
		1.45	presence of phénol$^{(b)}$	22	2	28	28
n-Bu	- 1.21	1.31	aprotic medium	32	2	34	11
		1.10	presence of $AcONBu_4$$^{(c)}$	44	traces	-	0
n-Oct	- 1.22	1.44	aprotic medium	30	0	35	18
i-Pr	- 1.25	1.48	aprotic medium	17	traces	53	12

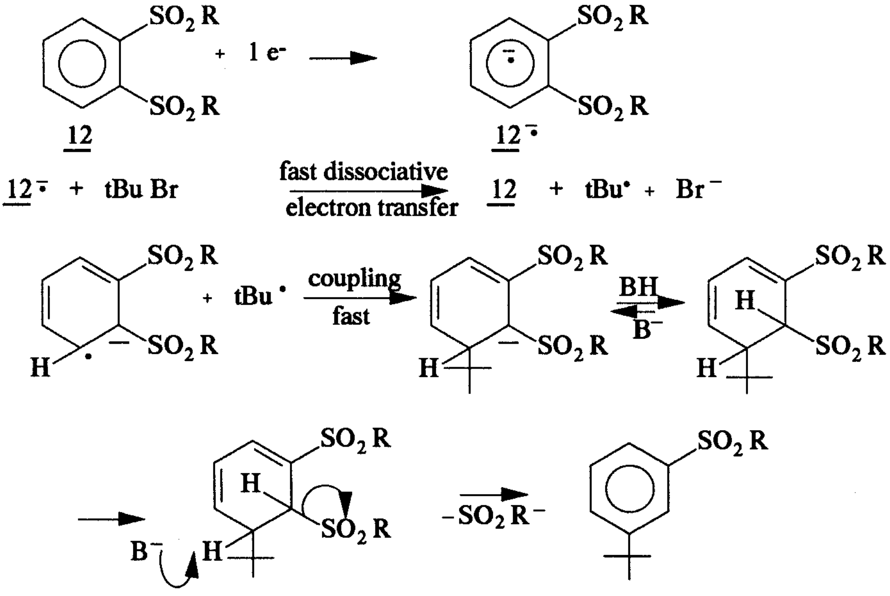
Table 1 : Potentiostatic electrolyses for compounds 12. Solvant : DMF. Electrolyte : NBu_4BF_4 0.1 M of area of 10 cm^2. Cathode : stirred mercury pool. Divided cell. Reference system : Ag/AgI/I$^-$ 0.1 M.

(a) excess of nucleophile : 20 times. (b) excess of proton donor : 4 molar equivalents.

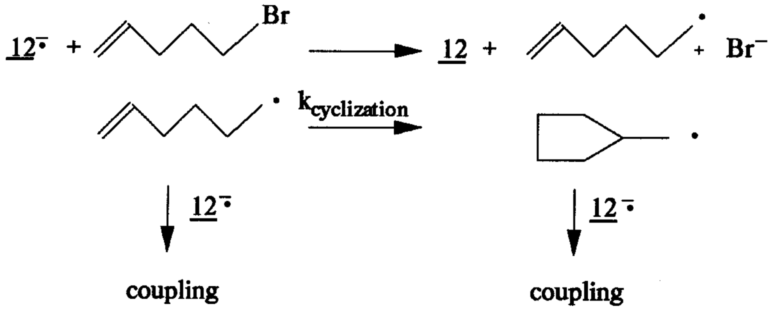
(c) excess of base : 6 molar equivalent.

It was established that the reactivity of 12 anion radical should fit with a S_N2 like reaction between this species and the substrate. Kinetic constants for bimolecular reactions were found to be of the order of 50.M^{-1}.s^{-1} (e.g. R = n-Bu) while cleavage of the anion radical is about 0.4 s^{-1} (case where R = Me). Ratio between those two kinetic constants consequently imply that substrate concentration may strongly monitor the overall rate and therefore the nature of the reaction.

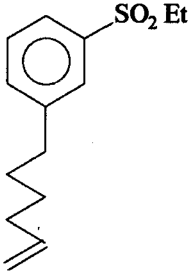
Similarly, disulfones 12 were also reduced in the presence of electrophiles other than the starting substrate. With primary alkyl halides RX in excess (and especially when X = I or Br), very high yields of substituted compounds 15 were obtained. On the contrary, secondary and tertiary RX change dramatically the regioselectivity of the alkylation. The following mecanism may account for the alkylated compound formation, supposed "*a priori*" to be based on a coupling reaction :



But, surprisingly(11) the use of radical chemical scavengers does not decrease the yield of alkylated compound. Moreover, when RX is now a radical probe such as hexenyl bromide, one should expect the competition in attachment of two radicals :



since $k_{cyclization}$ is known to be very high. As a matter of fact, the mixed reduction of 12 (R = Et) and hexenyl bromide in twenty fold concentration excess leads to :



18

with an isolated yield of 60 %. It was definitively not found in product distribution any formed compound possessing a cyclopentenyl moiety. Consequently, it can be expected that alkylation should instead occur fast inside a solvent cage :

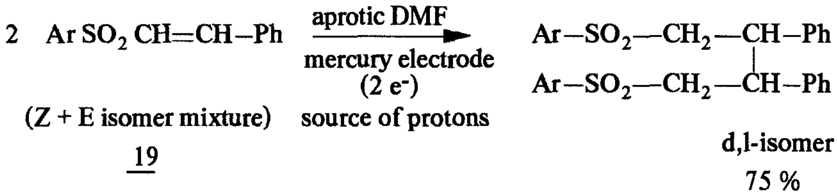
$$\underline{12}^{\cdot -} + RX \longrightarrow [\underline{12}, R^{\cdot}, X^{-}]_{sc} \longrightarrow [\underline{12}\text{—}R]^{\cdot} + X^{-}$$

$$\xrightarrow{-H^{\cdot}} \underline{18}$$

a, b-ETHYLENIC SULFONES

The electrochemical behaviour of olefines activated by a sulfonyl group is totally different of that already broadly emphasized e. g. with a,b-ethylenic ketones or nitriles. With the present series there is practically no case of dimerization or saturation probably for structural reasons but also, as already evoked here, the reduction of most sulfones cannot be completed in aqueous and worse in acidic media.

The example given below remains up to now very exceptionnal$^{(10)}$. Aromatic ethylenic sulfones 19 (with Ar = Ph or $pMeC_6H_4$) were found to lead rather selectively (yield 75 %) to the corresponding d,l d-disulfones.

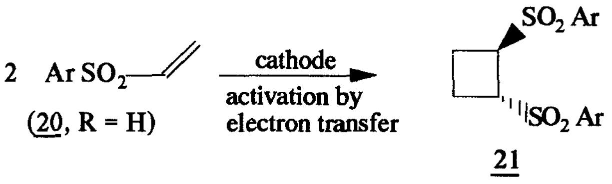


But in an unexpected manner, the cathodic reactivity of other ethylenic sulfones 20 (R = H or alkyl)

$$Ar\,SO_2\,CH{=}CH{-}R$$

20

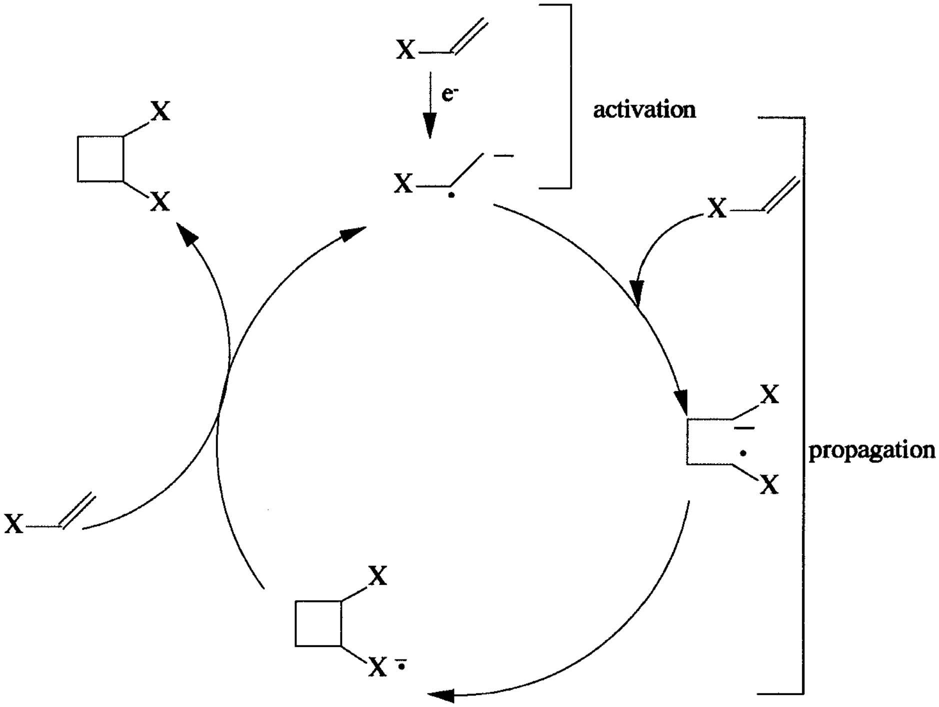
still studied in aprotic organic solvents, revealed the existence of electrocatalytic cyclodimerizations or additions. Thus, with R = H, sulfones 20 afford$^{(10)}$ the formation often in fairly high yield of the corresponding cyclodimers.



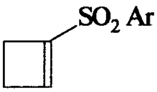
21

trans isomer
(55-95 %)

Cyclodimers 21 were not described so far. Their formation by electron transfer activation at the mercury or platinum cathode requires a very low electricity consumption (0.1 to 0.2 mole of electron per mole of 20). Attempts to produce cyclodimers 21 by chemical reducing reagents acting by electron transfer (e. g. dissolved metal in THF) have failed so far. The formation of 21 can be understood through a catalytic cycle (X represents the arylsulfonyl moiety) based on the thermodynamic unequality $E^o_{20} > E^o_{21}$ which appears likely with voltammetric data.

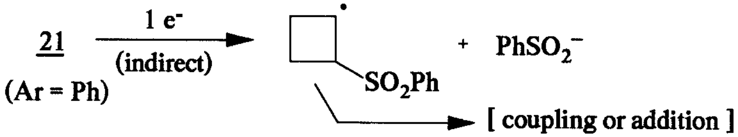


Best yields were obtained when activation reaction is conducted in an indirect manner (e. g. by means of an organic mediator anion radical electrochemically produced). It is worthnoting that 21 is strongly sensitive to the medium basicity and therefore small amounts of 22 can be isolated.

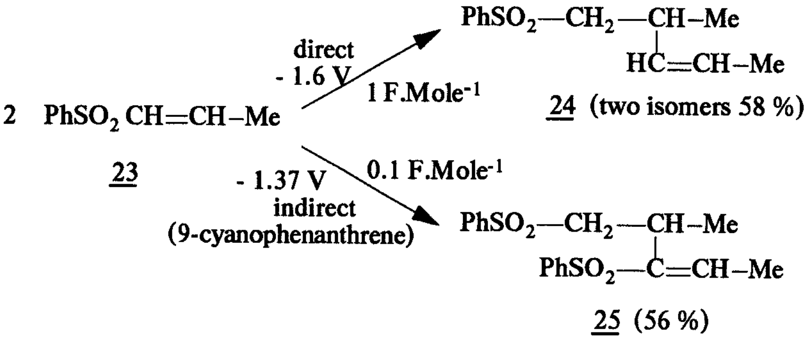


22

Cyclodimers 21 (Ar = Ph) can be considered as good synthons(10) in the cyclobutane chemistry since cleavage may provide the corresponding free radical easily trapped or coupled.

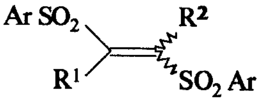


However until now, cyclodimerization reaction could only be achieved in vinylic series. If making R ≠ H, the reactivity is differently oriented. Addition is still electrocatalytic but product distribution depends on the electroactivity of the adduct. In the example below, 25 readily reduced is protected when indirect activation is achieved. Difference in electricity consumption lies only in the cathodic cleavage of one of its C-S bonds.



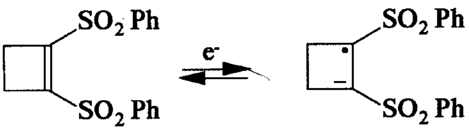
ETHYLENIC DISULFONES

Sulfones possessing the general structure :



26

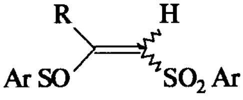
exhibit fairly stable anion radicals. For example, the half life time of the anion radical of 27 :



27

is surprisingly long and the reactivity of the double bond (except the observed saturation in presence of efficient proton donor) toward alkylhalides and other electrophiles was found(3) to be very low.

Attempts for isomerization of geometrical isomers of 26 series by cathodic induction were also achieved(12). This reaction is of interest since the synthesis of Z and E isomers may proceed according quite different procedures. Below is exemplified the Z ⟶ E conversion by cathodic means of structure 28 and 29 conveniently performed in aprotic media in order to prevent protonation of transient anion radicals.



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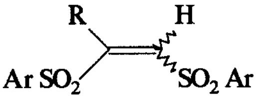
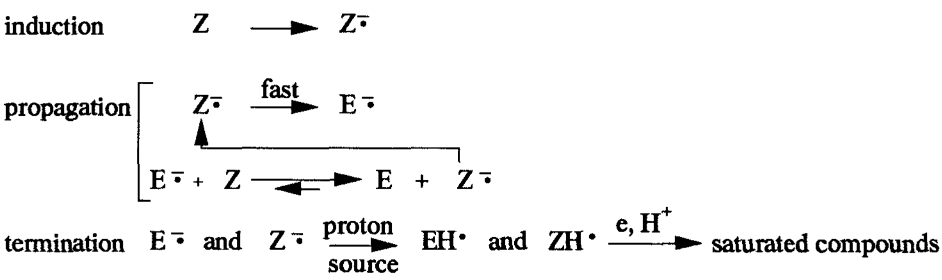


29

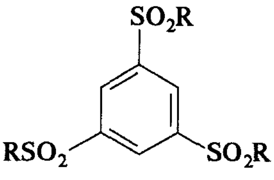
In the described series, Z isomers are less stable and thermodynamic unequality $E^o_Z > E^o_E$ renders possible the isomerization with very high indeed quatitative (case where R = Ph). The occurence of such Z ⟶ E transformation can be easily detected in voltammetry (characteristic feature in the course of the first and the second sweep as exhibited in Figure 2). The Z anion radical reduced first is transformed fast into E anion radical making feasible a chain reaction starting and propagating from the cathode interface.



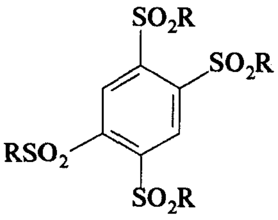
Similar transformations were also attempted on simpler <u>28</u> and <u>29</u> Z isomers (e. g. R = H). However, transient anion radicals involved in the isomerization process are obviously less stable. Consequently, a drop of transformation yields was observed (experimentally found to be of the order of 40 %). The other compounds are cleavage products as expected with this kind of substrates for which p → s* like transition is more expectable.

OTHER AROMATIC POLY SULFONES

The cathodic reduction of trisulfones and tetrasulfones <u>30</u> and <u>31</u> respectively

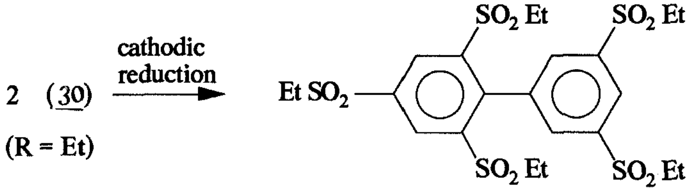


<u>30</u>



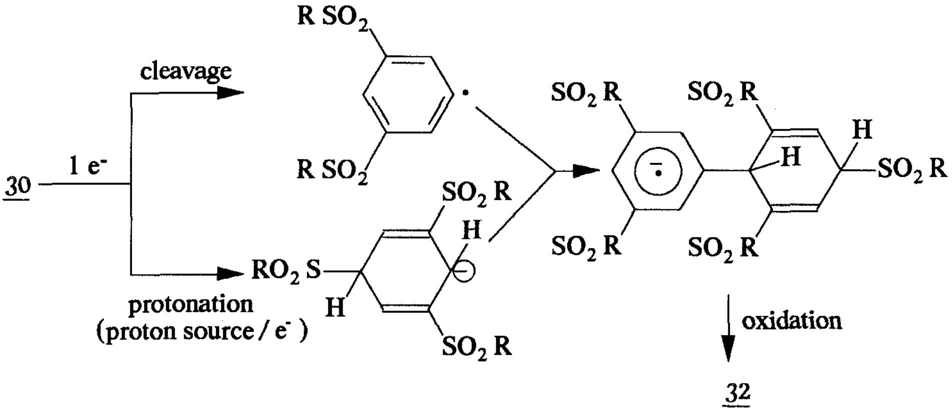
<u>31</u>

were also approachied. However, their respective behaviours are quite different : thus, <u>30</u> (R = Et) was found$^{(13)}$ to be reduced in aprotic medium with a major formation of the unexpected dimer <u>32</u> :

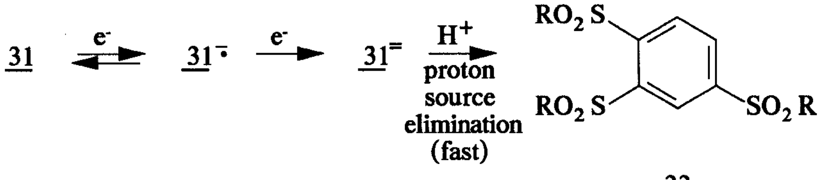


32

It seems (but not yet fully demonstrated) that the obtainment of 32 would be provoked by the concomitant formation of both s aryl radical from 30 and the nucleophile issued from the dihydro reduction of the phenyl ring leading to a $S_{RN}1$ type reaction. The nature of the associated and mandatory oxidation processes and their location cannot be, for the moment, completely precised. Other sulfones 32 (R = CF_3) were also studied(13) and the formation of dimers just evoked.



The formation of dihydro compounds from tetrasulfones 31 and their elimination into the corresponding trisulfone can be demonstrated in an elegant way manner by cyclic voltammetry. The standard potential value for 31 series is extremely high, especially in the case where R = Ph. Therefore polysulfones 31 are among the most easily compounds to be cathodically reduced(11). Anions radicals as excepted are extremely stable and one has to reach the potential corresponding to the formation of the dianion to get the cleaved form.



33

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