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1,4-Bis(alkylsulfonyl)benzenes. A new and unexpected cathodic cleavage leading to the corresponding phenoxy ions

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Abstract

1,4-Bis(alkylsulfonyl)benzenes **2** exhibit the formation of a fairly stable anion radical under cathodic electron transfer. Its fragmentation leads both to 1-alkylsulfonyl-4-alkyl benzenes (*ipso* substitution) and 4-alkylsulfonylphenoxy ions, the presence of the latter suggesting a new mode of cleavage for strongly activated sulfones. © 2000 Published by Elsevier Science Ltd. All rights reserved.

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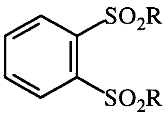
It now appears that attempts to classify and normalize to a certain extent the modes (and mechanisms) of reduction of monoalkyl sulfonyl and poly(alkylsulfonyl) benzenes is a difficult task. In fact, reactions involving 1,3,5-tris and 1,2,4,5-tetraalkyl (and aryl) sulfonyl benzenes showed complex mechanisms but, in most cases, coupling of radical anions to strongly stabilized dianions could be considered as the main primary pathway.[1] Coupling reactions were not found to occur for more substituted benzenes, and hexa(alkylsulfonyl)benzenes, for example, exhibited conformational changes at the stage of the radical anion owing to the strong crowding and mutual interactions of sulfonyl groups.[2] Concerning disulfones **1** (R=alkyl group), the two-electron reduction in aprotic solvents mainly afforded substitution compounds **1a** (mixture of ortho — minor — and meta — major — alkylated derivatives) and sulfinates **1b**.[3] The ratios **1a**/**1b** were found to be roughly equal to 1. Under such conditions, it was strongly expected that the title compounds **2** would follow a very similar course and a study of their cathodic reduction was, for some time, postponed owing to its assumed lack of originality.



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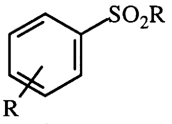
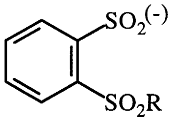


1a



1b

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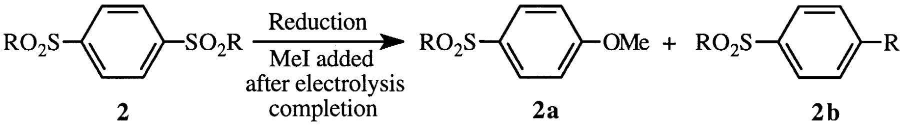
This short preliminary note aims to show that the behaviour of compounds **2** could not be easily foreseen. The cleavage reaction of $\mathbf{2}^{\cdot-}$ (a first order reaction within a concentration range between 10^{-4} to 3×10^{-3} mol L^{-1}) was found to be solvent-independent. Thus, dimethylformamide (DMF), dimethylsulfoxide (DMSO) and acetonitrile were successfully used and all permit phenoxy ion formation. Electrolyses were performed on a mercury pool or amalgamated copper grid, a platinum sheet as well as a glassy carbon electrode. Electrolytes were in all cases tetraalkylammonium salts, mainly tetrafluoroborates. Thus, a certain number of disulfones **2** were reduced and Table 1 shows the principal preliminary data. It is worth noting that after total completion of electrolyses (about 2 mol of electron per mol of **2**), an electrophile such as methyl iodide was added in the cathodic compartment before work-up and contact with air. It must also be pointed out that all electrolyses were achieved under an inert argon atmosphere and in very dry solvents by treatment of the solution with activated neutral alumina (heated to 350°C for several hours under vacuum).

Table 1
Fixed potential electrolyses of **2** (1 mmol) at Cu/Hg electrode (area: 15 cm^2) in DMF+$n$$Bu_4NBF_4$ 0.1 mol L^{-1}



R (E° in V)	Electricity consumed (Fxmole^{-1})	Isolated compounds Yield (%) **2a**	 **2 b**	^{1}H NMR δ in ppm (*J in Hertz*)
Me (-1.21)	1.92	70	0	**2a** : 7.8 (2H, d, *9*); 7 (2H, d, *9*); 3.9 (3H, s); 3.1 (3H, s)
Et (-1.16)	1.97	65	0	**2a** : 7.75 (2H, d, *9*), 6.95 (2H, d,*9*); 3.8 (3H, s); 3 (2H, q, *7.5*); 1.2 (3H, t, *7.5*)
iPr (-1.18)	2.08	40	20	**2a** : 7.7 (2H, d, *9*); 6.95 (2H, d, *9*); 3.8 (3H, s); 3.1 (1H, sept, *7*); 1.2 (6H, d, *7*) **2b** : 7.8 (2H, d, *8.5*); 7,4 (2H, d, *8.5*); 3.2 (1H, sept, *7*); 3 (1H, sept, *7*); 1.31 (6H, d, *7*); 1.27 (6H, d, 7)
tBu (-1.21)	2.05	25	48	**2a** : 7.8 (2H, d, *9*); 6.95 (2H, d, *9*); 3.85 (3H, s); 1.4 (9H, s) **2b** : 7.7 (2H, d, *8.5*); 7.45 (2H, d, *8.5*); 1.27 (9H, s); 1.26 (9H, s)
nPent (-1.21)	2.06	60	5	**2a** : 7.75 (2H, d, *9*); 6.95 (2H, d, *9*); 3.85 (3H, s); 3 (2H, m); 1.65 (2H, m); 1.25 (4H, m); 0.8 (3H, m) **2b** : 7.7 (2H, d, *8.5*); 7 (2H, d, *8.5*); 3.1 (2H, t, *8*); 3 (2H, t, *8*); 1.9-1.7 (4H, m); 1.4-1.2 (8H, m); 0.9 (6H, m)
nOct (-1.19)	2.11	70	2	**2a** : 7.7 (2H, d, *9*); 6.95 (2H, d, *9*); 3.8 (3H, s); 3.05 (2H, m); 1.65 (2H, m); 1.35-1.15 (10H, m); 0.8 (3H, t, *7*) **2b** : 7.8 (2H, d, *8.5*); 7 (2H, d, *8.5*); 3.05 (4H, m); 1.65 (4H, m); 1.3 (20H, m); 0.85 (6H, m)

Anode: carbon rod. Volume of catholyte: 100 ml (area: 20 cm^2). Applied potential: that of E° (standard potential of the first peak) obtained by voltammetry. Reference electrode: $Ag/AgI/I^-$ 0.1 mol L^{-1} in DMF.

The concomitant obtention of compounds **2a** and **2b** appears surprising. It strongly depends both on the relative stability of $R^{\cdot}$, possibly produced during the reduction process, and on substrate concentration. Compound **2b** would come from an *ipso* substitution explained by a radical coupling of $\mathbf{2}^{\cdot-}$ and $R^{\cdot}$ normally issued by the cleavage of $\mathbf{2}^{\cdot-}$ in the bulk (the transient anion would suffer an elimination leading to the loss of RSO_2^-). However, the formation of **2a** is more intriguing since it is strongly expected that the oxygen atom can come neither from dioxygen nor from solvent moisture. Disulfones were also shown to be totally unreactive in the presence of strong bases like Bu_4NOH and, therefore, an aromatic substitution process cannot be considered. A new mode of fragmentation involving a radical anion possessing a sulfonyl group should then occur.

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