Unexpected Single Electron Transfer Catalysed Cyclisation of Prenyl Sulphone Dimer. Evidence for Radical Anion Coupling in the Outer-sphere Oxidation of Prenyl Sulphone Carbanion

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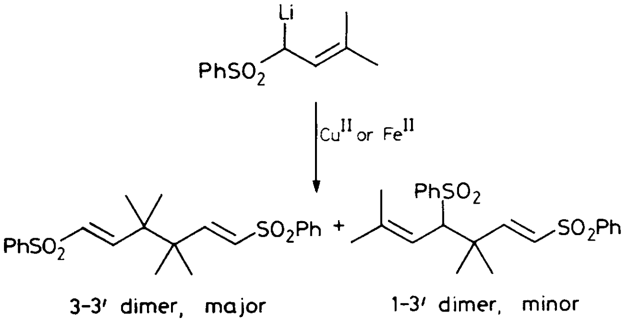
Preparative electrochemical oxidation of metallated phenyl prenyl sulphone leads to a previously unknown cyclic dimer, the formation of which has been rationalized, providing strong evidence for a radical-anion coupling mechanism in outer-sphere oxidative dimerization of α-sulphonyl carbanions.

Lithiated allylic sulphones, as other α-sulphonyl carbanions, can be oxidized by various reagents. α-Halogenation,[1] and a few reactions with oxygen or peroxides leading to conjugated aldehydes or ketones[2] *via* sulphinate elimination from the α-hydroxysulphone derivative, are known. However most oxidation reactions involve transition metal salt catalysis. Functionalization, *viz.* halogen or oxygen transfer, can then take place on C-3.[3,4]

When the metal salt itself acts as the oxidant (Cu^{II}, Fe^{III}), dimerization is often observed;[5] coupling can take place on C-1 or -3 for each molecule. Three dimers are then expected. In the case of γ-disubstituted allylic sulphones, only two are actually formed, the 3—3′ being the major dimer (Scheme 1). On the other hand, in the nickel(II) catalysed reaction of the lithium or magnesium derivative of phenyl prenyl sulphone, formation of 2,7-dimethylocta-2,4,6-triene in high yield proceeds in an overall 1–1′ coupling.[6]

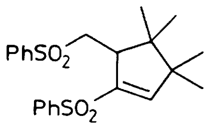
In order to get a better understanding of the role of the transition metal salt, we tried to dissociate artificially its 'pure oxidative' properties (outer-sphere oxidation) from those related to the specific environment in its co-ordination shell (inner-sphere). For this reason, electrochemical oxidation (which is by its nature of pure outer-sphere character) of lithiated phenyl prenyl sulphone has been investigated. Cyclic voltammetry (C.V.) at 2 V/s of a 2×10^{-3} M solution of this lithiated anion in tetrahydrofuran (THF) with $Bu^n_4NBF_4$ (0.3 M), showed a one-electron oxidation wave at E_p −0.53 V *vs.* saturated calomel electrode (SCE). A high scan rate C.V. (1000 V/s) allowed a determination of E_0 as −0.52 V *vs.* SCE.[7]

Preparative scale electrolysis was performed in a divided cell; oxidation of the lithiated sulphone (5.7 mmol) in THF (80 ml) with $Bu^n_4NBF_4$ (0.3 M) took place on a gold grid, the potential of which was −0.40 V. After consumption of about 500 C (90% for a one-electron process), the current decreased to less than 10% of its initial value. Electrolysis was also carried out in liquid ammonia, with potassium bromide as supporting electrolyte; the starting sulphone (2.5 mmol) was



Scheme 1

Table 1. Electrochemical oxidative coupling of phenyl prenyl sulphone anion (**1**).



dimer C

Solvent	Recovered (**1**)	Dimer 1–3′	Dimer 3–3′	Dimer C
THF	13%	6% (8)[a]	4% (6)[a]	62% (86)[a]
NH_3	19%	16% (22)[a]	—	55% (78)[a]

[a] Ratio of the particular dimer among the three dimers.

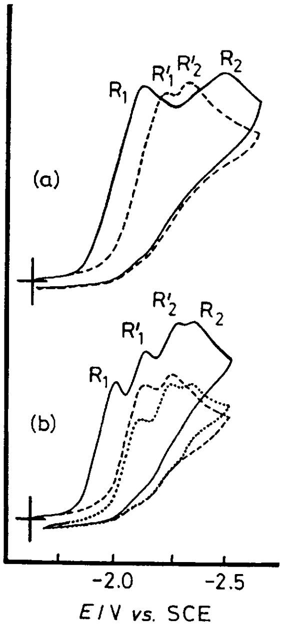
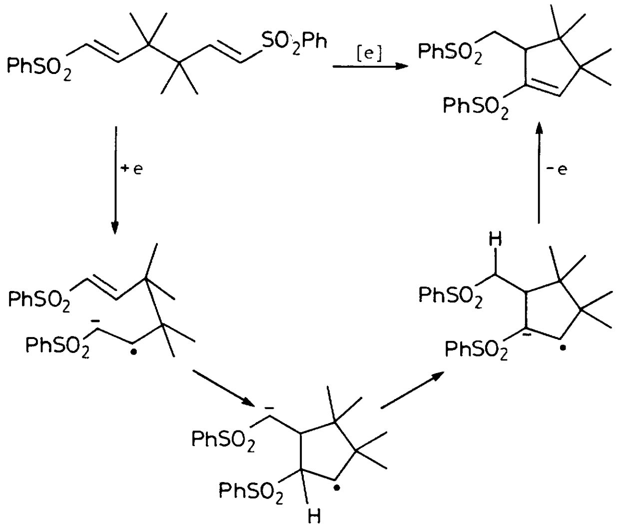


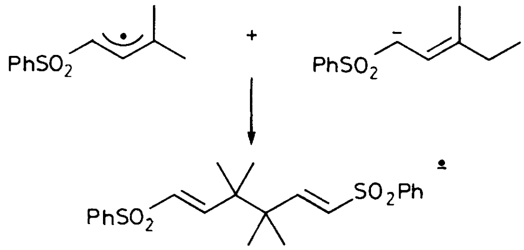
Figure 1. Cyclic voltammetry of dimers 3–3′ (2×10^{-3} M) in THF, 0.3 M $Bu^n_4NBF_4$ (20 °C): (a) scan rate 5 V s^{-1}, (b) scan rate 0.5 V s^{-1}; first scan (—), second scan (...). The cyclic voltammetry of dimer C, under identical conditions, is superimposed as the dashed curve (____) on (a) and (b).

deprotonated by potassium t-butoxide. The cathodic reaction was reduction of a lead rod to anionic amino complexes.[8] After 150 C (62%) had been passed, electrolysis was stopped. Results of both experiments are given in Table 1.

Besides the two dimers which are formed in the transition metal salt oxidation, a new compound† is obtained as the major product. This cyclic dimer C had never been described before and it was important to know more about the mechanism of its formation. One-electron electrochemical oxidation affords the α-sulphonyl radical from the parent anion; however it has been shown that homocoupling of this free radical generated by tributyltin hydride reduction of α-chloro prenyl sulphone leads to dimers 1—3′ and 3—3′ only.[9]



Scheme 2



Scheme 3

An explanation of the puzzling formation of dimer C was provided by cyclic voltammetry. Figure 1 shows the voltammograms corresponding to reduction of dimer 3—3′ at different scan rates. At 5 V/s (Figure 1a) the C.V. exhibits two main waves: R_1 at E_p −2.13 V (followed by a very small wave) and a broad wave R_2 at about −2.47 V. At lower scan rate (Figure 1b) the C.V. is more complicated: wave R_1 is now smaller and what was a nearly invisible wave has now grown to become wave R_1'. Similarly, wave R_2 has decayed to the benefit of a new wave R_2'. A second and immediate scan showed the complete disappearance of wave R_1, the C.V. being now quite similar to what is obtained at the same scan rate for dimer C (Figure 1b, dashed curve). This behaviour clearly shows that dimer 3–3′ is isomerized into dimer C by a single electron transfer catalysed reaction. At a high scan rate, reduction of dimer 3–3′ is observed (wave R_1) whereas at lower scan rates, the catalytic process which started on the foot of wave R_1 rapidly converts dimer 3–3′ into dimer C, leading to a decrease of wave R_1 and appearance of wave R_1' assigned to reduction of dimer C. No dimer 3–3′ is left upon a second scan at 500 mV/s. The reaction process can be described as in Scheme 2.

The radical anion of dimer C formed by proton migration in the intermediate Michael adduct can easily transfer an electron to a neutral molecule of dimer 3–3′ and then allow the catalytic cycle to propagate.

Feasability of this reaction on a preparative scale has been demonstrated by the quasi-quantitative transformation of 0.5 mmol of dimer 3–3′ into dimer C by a slow addition of a catalytic amount of a THF solution of sodium anthracene. The best results were obtained when the reductant was added in several portions, with a few hours between each addition (a typical procedure consisted of five additions of 0.02 mmol of sodium anthracene each, in an overall period of 36 h).

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† Spectroscopic data for dimer C: m.p. 123 °C; ^1H n.m.r. (250 MHz, $CDCl_3$): δ 0.80 (s, 3H), 0.95 (s, 3H), 0.99 (s, 3H), 1.06 (s, 3H), 2.96 (dd, J 8 and 1.7 Hz, 1H), 3.41 (dd, J 15 and 8 Hz, 1H), 3.99 (dd, J 15 and 1.7 Hz, 1H), 6.77 (s, 1H), 7.5—8.1 (m, 10H); ^{13}C n.m.r.: 18.50 (CH_3), 20.79 (CH_3), 25.40 (CH_3), 26.21 (CH_3), 46.98 (C), 47.48 (CH), 48.58 (C), 55.12 (CH_2), 127.71 (2CH), 127.92 (2CH), 129.00 (2CH), 129.14 (2CH), 133.39 (CH), 133.58 (CH), 138.54 (C), 139.62 (C), 140.46 (C), 154.40 (CH); m/z 419 (M + H), 277 ($M - PhSO_2$), 197, 135, 125; satisfactory elemental analysis.

Formation of dimer C during the oxidative electrolysis of phenyl prenyl sulphone anion cannot be explained by this reductively promoted isomerisation. Consequently, it is good evidence for formation of the radical anion of dimer 3–3′ as an intermediate in the electrolysis,‡ which must in turn derive from the coupling of one radical with the parent anion (Scheme 3). Cyclisation of this radical anion must take place before its oxidation at the electrode. Such a situation is not met during oxidation of this carbanion by high oxidation level transition metal salts.

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7 Although of practical interest, the peak potential E_p must not be confused with E_0, the latter being the thermodynamic value whereas the former includes kinetic contributions; see for instance J. O. Howell, J. M. Goncalves, C. Amatore, L. Klasinc, R. M. Wightman, and J. K. Kochi, *J. Am. Chem. Soc.*, 1984, **106**, 3968. A detailed cyclic voltammetry study of the oxidation of α-sulphonyl carbanions, including kinetics, will be reported elsewhere.

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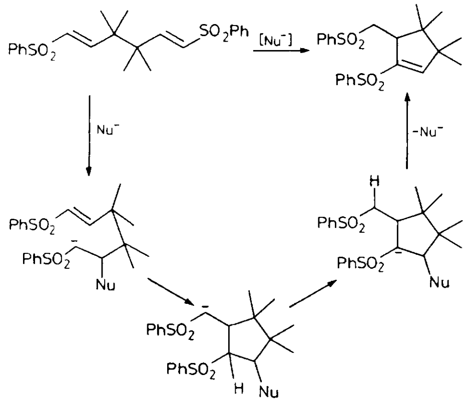
‡ A referee suggested an alternative mechanism for the formation of the cyclic dimer, involving a two-electron process induced by addition of a nucleophile to the neutral species (Scheme 4). Since the electrolysis was conducted in a two-compartment cell, no nucleophile generated at the cathode should be present in the anolyte. Therefore, the only possible nucleophile present in the anolyte is the sulphonyl anion itself; the fact that cyclic dimers are not obtained in the chemical oxidations[5] [which involve the simultaneous presence of sulphonyl anions (reactant) and 3–3′ dimers (product)] makes this hypothesis rather unlikely.



Scheme 4