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# The Cathodic Cleavage of the S-P Bond. Synthesis and Electrochemical Behaviour of Sulfonamide Phosphorus Analogues

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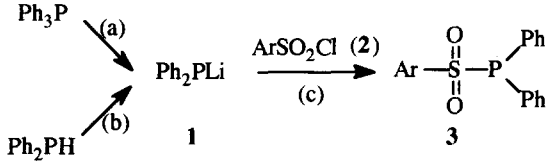
*Abstract:* P-diphenylarylsulfophosphamides can be obtained by condensation of $Ph_2PLi$ on various arylsulfonyl chlorides. These sulfonamide phosphorus analogues exhibit facile cathodic cleavage reaction yielding, after quenching, diphenylphosphinic acid and aryl sulfide. © 1997 Elsevier Science Ltd.

Since the three last decades[1], the electrochemical reduction of sulfonamides has been extensively studied, especially in our laboratory[2], in connection with the selective deprotection of amino groups. Thus the sulfonamide electrochemical cleavage (conducted most of the time at a mercury cathode using dimethylformamide as solvent) was found to be one of the mildest deprotecting method. In connection with this work, we describe here the synthesis and the electrochemical behaviour of P-diphenyl-aryl-sulfophosphamides, a new class of sulfonamide phosphorus analogues.

Sulfonyl chlorides are known to react in solution under quite mild conditions onto amines to afford sulfonamides. An extension of this procedure regarding sulfophosphamides proved to be straightforward. While a number of secondary phosphines are available, this preliminary note remained focused exclusively on the corresponding reaction of arylsulfonyl chlorides with lithium diphenylphosphine 1 [3](Scheme 1):

**Scheme 1**




(a) Li, tBuBr RT 30mn; (b) nBuLi/THF or $Et_2O$ -20°C; (c) $Et_2O$ -10°C

The condensation of the phospha-anion **1** (readily available either from triphenylphosphine or diphenylphosphine) to aryl sulfonylchlorides **2** at -10°C afforded the corresponding P-diphenyl-aryl-sulfophosphamides **3** (Table 1). These new derivatives all exhibit a notable stability toward strong acids and

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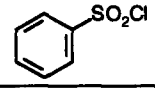
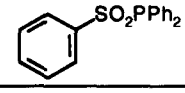
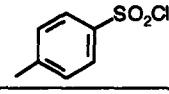
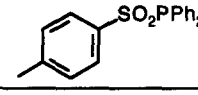
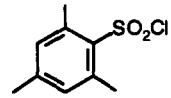
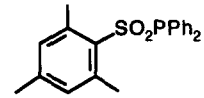
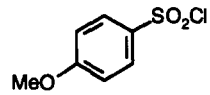
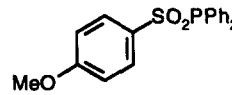
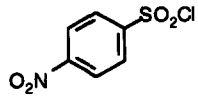
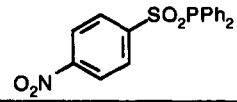
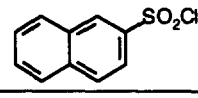
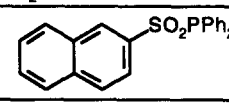
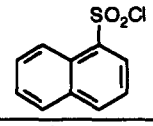
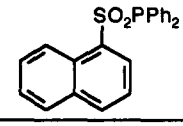
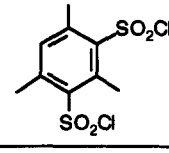
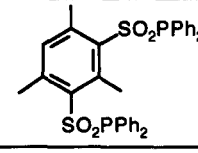
bases. As a matter of fact, no decomposition was found after treatment of **2a** with 1M HCl in THF at room temperature for 24h.

**Table 1**

| Entry | Substrate 2 | Product 3 | yield(1) (%) | mp (°C) | $^{31}$P NMR (ppm)(4) |
|---|---|---|---|---|---|
| **a** |  |  | 71 | 90 | 42,1 |
| **b** |  |  | 75 | 106 | 42,0 |
| **c** |  |  | 66 | 72 | 40,1 |
| **d** |  |  | 79 | 128 | 41,9 |
| **e** |  |  | 68(2) | | 33,2 |
| **f** |  |  | 74 | 92 | 42,3 |
| **g** |  |  | 58 | (3) | 42,1 |
| **h** |  |  | 62(2) | 137 | 40,2 |
| **i** | $H_3C-SO_2Cl$ | $H_3C-SO_2PPh_2$ | 55 | (3) | 45,1 |

(1) isolated yield; (2) crude yield; (3) viscous oil; (4) reference $H_3PO_4$.

By comparison with sulfonamides, it was found that sulfophosphamides **3** exhibit a similar reactivity toward electrochemical reduction. However, the cathodic cleavage of derivatives **3a-i** leads, under mild conditions to the selective formation of the surprising diphenylphosphinic acid **7** and the arene sulfide ion **8** (Table 2). This reaction is expected to proceed by a two-electron process via the *diphenylphosphinyl* radical **5** whom formation was demonstrated by using *in situ* tertiobutylphenylnitrone as spin marker.

Surprisingly, diphenylphosphinic acid (protonation of **7** during the work-up) was generated by oxygen migration between the diphenylphosphine anion **6** and the sulfinate **4** (Scheme 2), phosphorus derivatives being

well-known reducing reagents of sulfur compounds[4]. Additionnally it has been checked under our experimental conditions that sodium sulfinate in the presence of diphenylphosphine in basic media leads to anions **7** and **8**.

**Scheme 2**

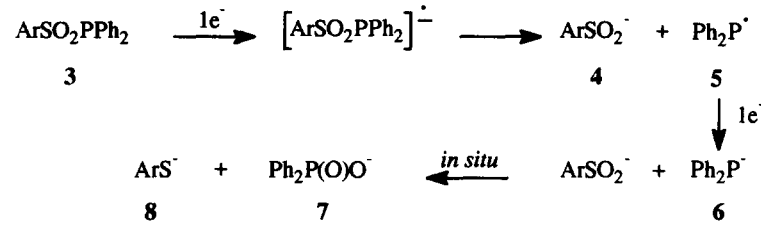
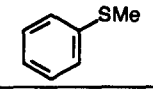
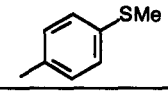
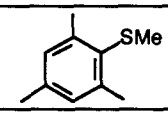
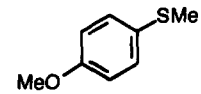
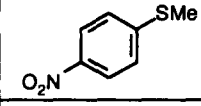
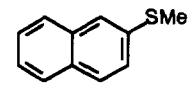
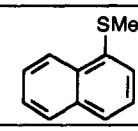



**Table 2**

| sulfo-phosphamides **3** | Voltam-metric peak potential (V) | Applied potential (V) | n (F * mole) | arylmethylsulfide (methylation of **8** by means of MeI) | isolated yield (%) |
|---|---|---|---|---|---|
| **3a** | -1,70 | -1,70 | 1,93 |  | 93 |
| **3b** | -1,72 | -1,75 | 1,95 |  | 88 |
| **3c** | -1,68 | -1,70 | 2,18 |  | 98 |
| **3d** | -1,75 | -1,75 | 2,14 |  | 82 |
| **3e** | -0,35 | -0.40 | 2.11 |  | 85 |
| **3f** | -1,49 | -1,55 | 2,09 |  | 92 |
| **3g** | -1,52 | -1,60 | 2,11 |  | 90 |
| **3i** | -1.89 | -1.90 | 2.07 | - | - |

As expected[5], electron-donating groups (table 2) (entries **3d, 3i**) shifted the cleavage to more negative potential values and thereby render the global cathodic reaction more difficult. On the contrary (entries **3f, g**

and **3e**), an electron-withdrawing group had a reverse effect. In other respects, the two-electron reduction of **3h**, involving the selective cleavage of only one S-P bond in absence of proton-donor species can be explained by the produced sulfide anion deactivating effect. Moreover, the successful cleavage of **3i** tended to show that, for energetic reasons, the electron in the intermediate radical-anion is, in most cases (**3a-d**, **3f-i**), preferentially localized on the phosphorus atom. Finally, the use of a platinum cathode as working electrode was found to be the best compromise since an insertion of Hg in the S-P bond has been observed when using a mercury cathode[6].

**General cleavage method** :

Potentiostatic macroelectrolyses of sulfophosphamides were achieved on 0.4 mmole of substrate reduced at a platinum cathode (area: 10 $cm^2$). Reference: Ag/AgI/$I^-$ 0,1M in DMF. Electrolyte : aprotic dimethylformamide + 0,1M $Bu_4NBF_4$. Potential scan rate: 100mV/s. An H-shaped two compartment cell (volume of the cathodic compartment: 30ml) with a porous separator was used. After total depletion of electrolysis current, catholyte solution was treated with an excess methyl iodide.

**References and notes**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6. Pilard, J.F.; Simonet, J., unpublished results.


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