

UNSYMMETRICAL BIARYLS FROM ARYLOXIDE ANIONS  
AND ARYLAZO PHENYL SULFIDES IN DMSO.

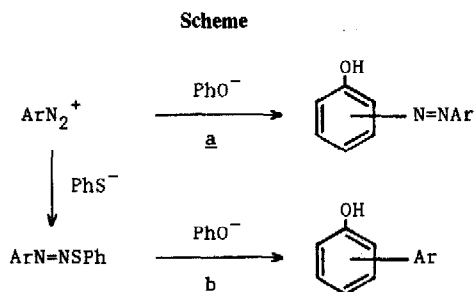
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*Summary* - Carbon-arylation of phenoxide and naphthoxide anions by arylazo phenyl sulfides represents a convenient synthesis of unsymmetrically substituted hydroxybiaryls.

Arenediazonium salts classically react with aryloxide anions to eventually furnish azo compounds via N-C bond formation (Scheme, path a).

Within the context of our recent efforts<sup>1</sup> to provide new synthetic approaches from arenediazonium tetrafluoroborates or their covalent derivatives, we herein report preliminary results on the reaction of arylazo phenyl sulfides (ArN=NSPh) with aryloxide anions, which effectively leads to biaryls via C-C coupling (Scheme, path b). It is worth recalling that C-C bond-forming processes are in general of primary importance in

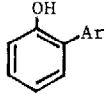
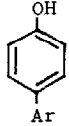
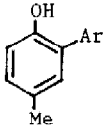
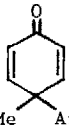
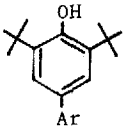
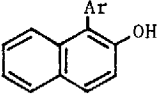


preparative chemistry and much interest has been recently attached in particular to the synthesis of hydroxybiaryls,<sup>2</sup> especially when containing electron-withdrawing groups, because of the ensuing optical properties.<sup>2b</sup>

Herein experiments were typically run under argon at room temperature by addition of a DMSO substrate solution to the aryloxide dissolved in a double volume of the same solvent. The reaction progress was followed by TLC analysis of sample aliquots, the final point being roughly judged through both TLC disappearance of substrate and ceasing of nitrogen evolution. After quenching with 3% HCl, usual work-up<sup>1</sup> followed by column chromatography (silica gel/petroleum ether - dichloromethane mixtures) yielded pure compounds. Further details are reported in the Table. As far as regiochemistry is concerned, while *meta*-substitution products were never observed, *ortho*-arylation seems favoured over *para*-arylation well beyond the statistical factor when both such ring positions are unsubstituted (entry 1) but any competition is strongly reduced when either is alkylated (entries 2-4); it is noteworthy, though, that some C-arylation at substituted ring positions does actually occur, leading to semiquinone derivatives (entries 2 and 3). With the 2-naphthoxide ion, arylation at the 1-position exclusively occurs, leaving little room for any negative steric effect by the *peri*-hydrogen atom.

Scope and limitations of the process are under investigation and will be reported in a forthcoming paper together with mechanistic details.

**Table.** Arylation of aryloxyde anions ( $\text{Ar}'\text{O}^-$ ) by cyanophenylazo phenyl sulfides ( $\text{ArN}=\text{NSPh}$ ) in DMSO.<sup>a</sup>

Entry	Ar	Ar'	Time (min)	Yield (%) <sup>b</sup>	
				<i>o</i> -C arylation	<i>p</i> -C arylation
1	4-CNC <sub>6</sub> H <sub>4</sub>	Ph	120	 : 46	 : 14
2	"	4-MeC <sub>6</sub> H <sub>4</sub>	90	 : 69	 : 4
3	3-CNC <sub>6</sub> H <sub>4</sub>	"	45	" : 62	" : 11
4	4-CNC <sub>6</sub> H <sub>4</sub>	2,6-Bu <sup>t</sup> <sub>2</sub> C <sub>6</sub> H <sub>3</sub> <sup>c</sup>	360		 : 58
5	"	2-naphthyl	120	 : 68	

<sup>a</sup>[ArN=NSPh] = 0.09 M if not otherwise stated; [Ar'O<sup>-</sup>]/[substrate] = 10; Bu<sup>n</sup><sub>4</sub>N<sup>+</sup> as the counterion of the aryloxyde, if not otherwise stated; unknown compounds gave correct microanalytical data. <sup>b</sup>Isolated yield. <sup>c</sup>[ArN=NSPh] = 0.065 M; K<sup>+</sup> as the counterion.

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