

Preliminary communication

SYNTHESIS OF ARYLPHENYL SELENIDES BY THE  $S_{RN}1$  MECHANISM

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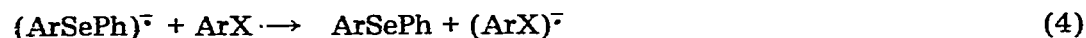
Summary

Haloarenes react with phenyl selenide ion in liquid ammonia under irradiation by Pyrex-filtered light to form arylphenyl selenides in good yields when the aromatic moiety is phenanthrene, naphthalene and biphenyl, probably by the  $S_{RN}1$  mechanism.

The recently recognized  $S_{RN}1$  mechanism of aromatic substitution [1] is operative in many nucleophilic substitution reactions of simple appropriately substituted arenes and heteroarenes [2,3]. Heretofore the  $S_{RN}1$  mechanism has been observed with amides ( $NH_2^-$  and  $C_6H_5NH^-$ ) [1,4], carbanionic nucleophiles [5], dialkyl phosphites [6], mercaptides and thiophenoxides [7]. We have found that phenyl selenide ion also reacts with aromatic halides, probably by the  $S_{RN}1$  mechanism.

When a solution of a haloarene and phenyl selenide ion in refluxing liquid ammonia (under nitrogen) was irradiated with Pyrex-filtered 350 nm UV light, a reaction occurred to form the arylphenyl selenide. Under the same experimental conditions there is no dark reaction. The presumed mechanism is indicated in Scheme 1 [8]. This is the standard photostimulated  $S_{RN}1$  aromatic substitution mechanism as adapted to the present case.

SCHEME 1



In this mechanism photons probably induce electron transfer from the phenyl selenide ion to the haloarene and thus are involved in the initiation of

TABLE 1

## PHOTOSTIMULATED REACTION OF HALOARENES WITH PHENYL SELENIDE IONS IN LIQUID AMMONIA

Experiment	ArX	M	PhSe <sup>-</sup> M	Method <sup>a</sup>	Time <sup>b</sup> (Min.)	Yield (%) <sup>c</sup>	
						X <sup>-</sup>	ArSePh
1	Chlorobenzene	0.053	0.053	A	180	< 1	<i>d</i>
2	Bromobenzene	0.045	0.045	A	120	5	<i>d</i>
3	1-Chloronaphthalene	0.038	0.038	B	120 <sup>e</sup>	< 1	0 <sup>f</sup>
4	1-Chloronaphthalene	0.050	0.050	A	290	80	69
5	1-Chloronaphthalene	0.016	0.034	B	170	88	73
6	4-Chlorobiphenyl	0.027	0.027	B	240	59	37 (52) <sup>g</sup>
7	9-Bromophenanthrene	0.019	0.020	B	220	85	72

<sup>a</sup>Method A: PhSe<sup>-</sup> was prepared by the reaction of Na or K t-butoxide with PhSeH; Method B: the nucleophile was prepared from diphenyl diselenide and two equivalents of sodium metal. <sup>b</sup>Irradiated in a reactor equipped with two 250 W high-pressure UV lamps (Philips Model HTP) refrigerated with water. <sup>c</sup>X<sup>-</sup> determined potentiometrically and the yields of ArSePh represent isolated material. Pure samples were obtained and their spectral properties agreed with the structure proposed. <sup>d</sup>Not determined. <sup>e</sup>Dark reaction, wrapped with aluminium foil. <sup>f</sup>Determined by TLC. <sup>g</sup>Determined by GLC.

a chain mechanism (step 1). In principle the formation of PhSe<sup>•</sup> could be demonstrated if PhSeSePh was isolated as reaction product. However, as PhSe<sup>-</sup> is easily oxidized to PhSeSePh by air during the work-up, we have made no efforts in isolating this compound from our reaction mixtures.

The radical anion thus formed then cleaves to form an aryl radical (step 2), which reacts with phenyl selenide ion to form a new radical anion (step 3), which transfers its extra electron to give the substitution product (step 4).

The phenyl selenide ion was generated by the reaction of benzeneselenol with sodium or potassium t-butoxide, prepared in situ in liquid ammonia, or by the reaction of diphenyl diselenide with two equivalents of metallic sodium in liquid ammonia.

From the results in Table 1 we can see that the reactivity of the aromatic moiety is naphthalene > biphenyl >> benzene, the order of the ease of reduction of the arene, which is in line with the electron transfer reaction of step 1. 9-Bromophenanthrene appears to be as reactive as 1-chloronaphthalene, but the leaving group is different and the compound is slightly soluble in liquid ammonia, so a comparison is not valid. Similar reactions of other mono- or di-substituted haloarenes and heteroarenes are under investigation.

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