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PhSeCl AS A CHLORINATING AGENT FOR ACTIVATED BENZENE DERIVATIVES

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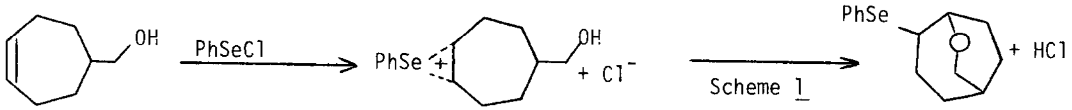
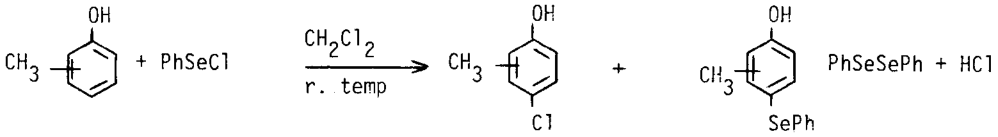
Abstract: Regiospecific chlorination of some aromatic compounds using benzeneselenyl chloride are reported.

Many recent studies have demonstrated the use of benzeneselenyl chloride as a selenylation agent (scheme 1).[1]

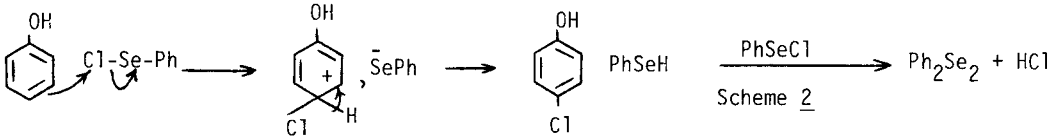


Scheme 1

This communication reports the chlorination of activated benzene derivatives using same reagent (scheme 2).[2]

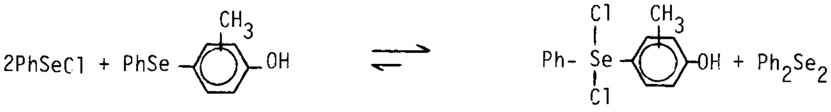


Probable Mechanism



Scheme 2

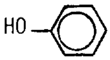
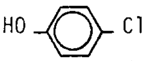
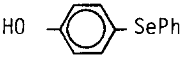
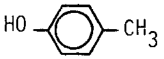
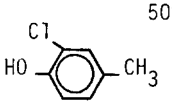
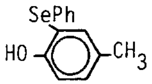
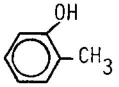
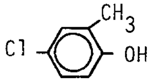
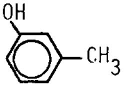
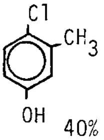
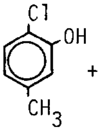
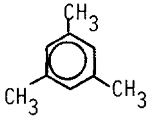
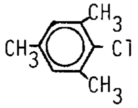
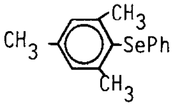
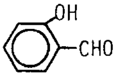
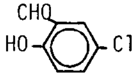
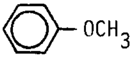
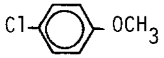
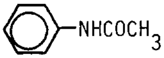
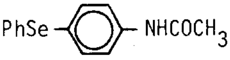
However, we cannot discount the possibility of an intermediate selenide dichloride such as 1 acting as the chlorinating agent.[3]



1

As shown on Table 1, whenever chlorination occurs, the position para to the hydroxyl function is preferred (entries 3 and 4). The following is a typical experimental condition: To 0.5g of reactant dissolved in 10ml of methylene chloride is added a slight excess of benzeneselenyl chloride (molar ratio: 1.0/1.2). The solution is stirred at room temperature for two to twenty-four hours. After evaporating the solvent, the crude mixture is fractionally distilled (~ 1mm Hg) to afford the chlorinated compounds.

Table 1

Entry	Reactant	% Completion	% Product*	
1		70%	 50%	
2		70%	 60%	
3		60%	 40%	+ ortho-, para-selenides
4		50%	 40%	 5% + ortho-, para-selenides
5		60%	 60%	
6	m-Xylene	-	No Reaction	
7		5%		
8		80%	 10%	+ ortho-, para-selenides
9		80%	 100%	

*Percentages are based on gc-trace. The product were identified by comparison of mass-spectral data and gc retention time with those of authentic samples.[4,5]

In conclusion, some of these reactions represent new methodologies for regiospecific chlorination of phenols. They also indicate the potential of benzeneselenyl chloride as a chlorinating agent toward nucleophiles.

REFERENCES AND NOTES

1. K. C. Nicolaou and Z. Lysenko, Tet. Lett., 1257 (1977).
2. PhSeCl sample, with chlorine content analysis ≃ 100%, was obtained from Aldrich Chemical Co., Milwaukee, Wisconsin 53201.
3. H. J. Reich and J. E. Trend, Can. J. Chem. 53, 1922 (1975).
4. A Finnigan 3200E computerized gas chromatograph-mass spectrometer utilizing a 1.6m 3% OV-17 on Supelcoport 60/80 column, temperature programmed from 60 to 300°C at 12°/min, was used. All starting materials and chlorinated products are commercially available.
5. The author wishes to thank Professor James Wheeler of Howard University, without whom this project would not be possible.

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