

## THE REACTION OF *o*-NITRO- AND *p*-NITRO-PHENYL SELENOCYANATES WITH ARYLTHIOLS

E.R. CLARK and M.A.S. AL-TURAIHI \*

*Department of Chemistry, University of Aston in Birmingham, Gosta Green, Birmingham B4 7ET (Great Britain)*

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### Summary

The interaction of *o*-nitro- and *p*-nitro-phenyl selenocyanate with aromatic thiols *p*-thiocresol, *p*-chlorothiophenol, 4-bromothiophenol, *o*-mercaptobenzoic acid and pentafluorothiophenol in non-aqueous media and under an atmosphere of dry nitrogen has been investigated. The main products are the diselenide or the selenenyl sulphide depending on the reactants. Hydrogen cyanide is given in all cases. The IR and Raman spectra of the diselenides and selenenyl sulphides are considered.

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### Introduction

Although the reactions of organoselenium compounds have received less attention than those of many other organometallic compounds, several reviews have been published [1—5]. Current revival in interest is focussed on biological aspects, viz. the possible use of selenium compounds as chemotherapeutic agents and the role of selenium and its compounds in nature and medicine. Some organoselenium compounds have been subjects of X-ray studies [6,7] but vibrational analysis has been confined to only a few compounds; papers on this subject have been reviewed [8].

Our studies have been concerned with the re-examination of published routes for the synthesis of compounds containing selenium—carbon bonds and the investigation of new synthetic routes [9]. We have also investigated the preparation of compounds containing selenium—sulphur bonds and the stereo-chemistry of the selenium acceptor atom in these compounds [10,11]. We now describe the reactions of *o*-nitro- and *p*-nitro-phenyl selenocyanate with several aromatic thiols and characterisation of the products by chemical analyses and infrared and Raman spectra. Some reactions of this type have been previously reported

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\* On study leave from the National Iraqi Minerals Company, Baghdad (Iraq).

by Nakazaki [12] but no account was given of limitations to the experimental conditions and in particular the importance of the presence of absence of water and/or oxygen was not assessed.

The hydrolysis of aryl selenocyanates gives rise to diaryl diselenides, and since it is believed [13] that a selenol is the initial product which is then oxidized by oxygen to the diselenide it was decided to investigate the interaction of some aryl selenocyanates with some aromatic thiols in scrupulously dry media and under oxygen-free dry nitrogen which would also serve to sweep away gaseous products.

## Experimental

*p*-Thiocresol was obtained from B.D.H. Ltd. Pentafluorothiophenol and *p*-chlorothiophenol were obtained from Koch-Light Laboratories and Aldrich Chemicals Ltd. Benzene and methanol were dried as recommended by Vogel [14].

### *Preparation of o-nitrophenylselenocyanate*

A modification of the method proposed by Bauer [15] was used. *o*-Nitroaniline (13.8 g) was dissolved in a hot mixture of 30 ml of hydrochloric acid and 30 ml of water. The solution was cooled to below 5°C and 7 g of sodium nitrite in 20 ml of water added gradually so that the temperature did not rise above 5°C. (The precipitate of *o*-nitroaniline hydrochloride which appears dissolves at lower temperatures to form a clear reddish liquid.) The solution was filtered because a small quantity of the precipitate remained undissolved. Sodium acetate was then added until Congo Red paper indicated that the solution was neutral. Then a solution of 15 g of potassium selenocyanate in 40 ml of water was added at such rate that the temperature did not rise above 5°C. The yellow *o*-nitrophenyl selenocyanate which separated was filtered off, washed several times with water, and finally recrystallised from ethanol in the presence of animal charcoal. M.p. 140°C (lit. [15] 142°C). Found: C, 37.00; H, 2.00; N, 12.30.  $C_7H_4N_2O_2Se$  calcd.: C, 37.05; H, 1.76; N, 12.32%.

### *Preparation of p-nitrophenyl selenocyanate*

The Sandmeyer-type reaction first proposed by Bauer [15] was used. The diazotisation was carried out as described for preparation of *o*-nitrophenyl selenocyanate. The product was recrystallised twice from ethanol in the presence of charcoal. M.p. 139°C (lit. [15] 135, 138°C). Found: C, 37.15; H, 1.85; N, 12.16; Se, 34.7.  $C_7H_4N_2O_2Se$  calcd.: C, 37.05; H, 1.76; N, 12.32; Se, 34.8%.

### *Reaction of o-nitrophenyl selenocyanate with aromatic thiols*

General procedure: A mixture of the thiol (0.3 mmol) was refluxed for 1 h with *o*-nitrophenyl selenocyanate (0.3 mmol) and 10 ml of dry benzene contained in a three necked flask equipped with a drying tube. Dry nitrogen was passed through the vessel.

In the reaction involving pentafluorothiophenol, yellow crystals formed at this stage, and these were filtered off from the hot solution and identified as di(*o*-nitrophenyl) diselenide. M.p. 205–206°C (lit. [5] 209°C [5]). For analysis

see Table 1. In all the other cases the selenenyl sulphide was isolated by addition of a few drops of dry methanol. On cooling, yellow crystals formed, and these were filtered off and dried under vacuum. Elemental analysis (Table 1) showed that the reaction products were selenenyl sulphides.

#### Reaction of *p*-nitrophenyl selenocyanate with aromatic thiols

A mixture of the selenocyanate (0.3 mmol) was refluxed for 1 h with 0.3 mmol of the thiophenol in 10 ml dry benzene under dry nitrogen. The yellow crystalline solid which formed on cooling was filtered off, dried and examined by infrared analysis and characterised by its m.p. and chemical analysis to be  $(p\text{-NO}_2\text{C}_6\text{H}_4)_2\text{Se}_2$ . Typical analysis: Found: C, 35.95; H, 2.11; N, 6.83.  $\text{C}_{12}\text{H}_8\text{N}_2\text{O}_4\text{Se}_2$  calcd.: C, 35.83; H, 2.01; N, 6.97%. M.p. 175–176°C (lit. [16] 180°C).

#### Identification of the gaseous products

The gaseous products were collected in an absorption tube cooled at  $-180^\circ\text{C}$ . The liquid collected was then vaporised into an infrared gaseous absorption cell and the spectrum obtained over the ranges 800–670 and 3350–3250  $\text{cm}^{-1}$ . The fundamental bands obtained were compared with published data [17]. Hydrogen cyanide was evolved from all reactions, and there was no evidence for cyanogen.

TABLE 1

PRODUCTS OBTAINED BY THE REACTION OF *o*-NITROPHENYL SELENOCYANATE WITH AROMATIC THIOLS

Reactants: <i>o</i> -nitrophenyl selenocyanate and	Product	Analysis found (calcd.) (%)			
		C	H	N	Se
<i>p</i> -Bromothiophenol		37.75 (37.04)	2.10 (2.07)	3.65 (3.60)	21.01 (20.3)
<i>p</i> -Chlorothiophenol		41.80 (41.82)	2.40 (2.34)	4.40 (4.07)	22.39 (22.92)
<i>p</i> -Thiocresol		48.20 (48.15)	3.40 (3.39)	4.28 (4.32)	24.83 (24.37)
<i>o</i> -Mercaptobenzoic acid		44.40 (44.07)	2.60 (2.56)	4.10 (3.96)	22.21 (22.31)
Pentafluorothiophenol		35.90 (35.82)	2.05 (2.01)	6.75 (6.96)	39.51 (39.23)

### Identification of the products in solution


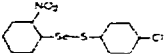
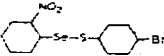
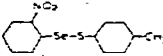
The presence of thiocyanate in the solutions after reaction was tested for by using a modification of the standard qualitative tests using iron(III) and cobalt(II) solutions as recommended by Vogel [18]. Aqueous solutions of these reagents were shaken with the organic solvent in a separating funnel. The colours characteristic of  $\text{CNS}^-$  were not produced.

**IR and Raman spectra.** The spectra of all the compounds were recorded as KBr discs on a Perkin-Elmer 475 IR spectrophotometer over the range  $4000-250\text{ cm}^{-1}$ ; as Nujol mulls on a Perkin-Elmer 225 grating IR spectrophotometer and a Fourier spectrophotometer FS 720 (R.I.I.C) over the range  $400-80\text{ cm}^{-1}$ . Raman spectra were recorded on Cary 81 Laser Raman spectrometer exciting laser line at  $6328\text{ \AA}$ .

**Elemental analysis.** Selenium was determined by decomposition using the oxygen flask technique followed by atomic absorption of the solution produced as described for the analysis of the tellurium content of organotellurium compounds [19].

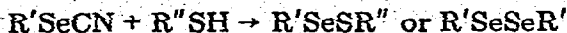
TABLE 2

INFRARED AND RAMAN SPECTRA OF THE SELENOCYANATES AND THE PRODUCTS OF REACTION WITH THIOPHENOLS

							
IR	Raman	IR	Raman	IR	Raman	IR	Raman
120m							
142m		148m		147msh		147m(sh)	144w(sh)
171m(sh)		170s		170ssh		167m(sh)	
185s		182s		183s		182s	176m
		188s				189s	
		218s	211w				
256w	261w			255m	250s		
282m	275m	283m	279w	282m	278m	283m	280w
			293m				
	307w	302w	303m	302m	299w	303w	
315w	315m	311m					
		317m					
		335m		328m	322w	322m	327w
		342m(sh)					
		357s(sh)	351m	350msh	359m		
361m	357w						
						378m	378w
		387m				393m	
393m							

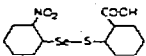
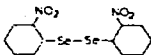

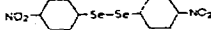
## Results and discussion

It was found that the products of the reactions were either selenenyl sulphides or diselenides depending upon the nature of R' and R'':



*o*-Nitrophenyl selenocyanate reacts with some thiophenols (see Table 1) to form the corresponding selenenyl sulphides. However, when pentafluorothiophenol is used, the main reaction product isolated is di(*o*-nitrophenyl) diselenide. *p*-Nitrophenyl selenocyanate reacts with all the thiophenols to form di(*p*-nitrophenyl) diselenide. All the products were characterised by chemical analysis (Table 1) and by melting points.

The vibrational spectra of some diselenides [20–22] and some selenocyanates [23,24] have been published but the data for the *o*- and *p*-nitro substituted derivatives of these two classes of compounds has not been previously reported. The assignments for *o*- and *p*-nitrophenyl selenocyanate and di(*o*-nitrophenyl) diselenide

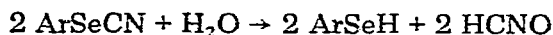
								Assignment
IR	Raman	IR	Raman	IR	IR	Raman		
146m(sh)		142m		117m		110s(h)		
170s(sh)		168m(sh)	172w			158s(sh)	} Substituent-sensitive vibration x	
182s(sh)		181s		186s		194(sh)		
203vs						234m	} Substituent-sensitive vibration u	
224w(sh)	226w			235s	237m	266s		
				263s	266s	272m	} Vibration associated with NO <sub>2</sub> group	
		269m(sh)	265vs		266s	273m		
		281s			273m	272m	} ν(Se-Se)	
281m	279m				286w	288s		
				301s		305s	} Substituent-sensitive vibration t	
314m		318w			320w	329w		
334s	331m						} ν(Se-S)	
346m								
	368m			353s			} Out-of-plane Se-C≡N band	
				400w				
							} Vibration associated with NO <sub>2</sub> group or in-plane Se-C≡N band	

nide and di(*p*-nitrophenyl) diselenide (see Table 2) are made by comparison with previously published data for phenyl selenocyanate [23] and diphenylselenide [22]. The more important bands between 100–400  $\text{cm}^{-1}$  are the substituent  $x$ ,  $u$  and  $t$  vibrations [25];  $\nu(\text{Se}-\text{Se})$  which is found at 265–288  $\text{cm}^{-1}$  (compare 317  $\text{cm}^{-1}$  for elemental bromine) and the in-plane and out-of-plane vibrations of the SeCN group of the selenocyanates.

The infrared and Raman spectra of selenenyl sulphides (also shown in Table 2) have not been published previously. As expected there are many bands in common with the corresponding selenocyanates and diselenides, but the new bands between 322–370  $\text{cm}^{-1}$  may be assigned to the selenium–sulphur stretching vibration,  $\nu(\text{Se}-\text{S})$ . Bands in this region have been previously reported and have been assigned to the Se–S stretching mode [10,11]. A deformation mode,  $\delta(\text{Se}-\text{S})$  may be expected to give rise to a band at lower wavenumbers but this may possibly be hidden by the substituent-sensitive  $x$  and  $u$  vibrations.

Since care was taken to exclude water and oxygen from all the reactions described in this paper it is strange that there should be two kinds of products, selenenyl sulphides and diselenides. The differences could arise from the inductive effects of the substituents in one or both of the reacting species but any differences due to the *ortho* or *para* nitro groups of the selenocyanate is unusual since these  $\text{NO}_2$  groups usually have similar effects.

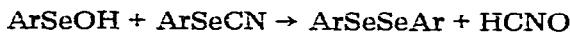
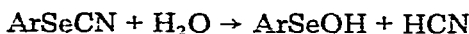
The formation of a diselenide from a selenocyanate is easily understood if water and oxygen are present. No clear-cut mechanism has been proposed for the reaction, but Challenger et al. [13] believe that a selenol is the initial hydrolysis product:



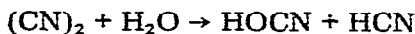
followed by oxidation:



Rheinbolt [26] suggests that the water gives selenic acid as an intermediate:



If care is taken to minimize exposure of the hydrolysis products to atmospheric oxygen, arylselenols may be isolated [27–29]. Behagel and Seibert [30] suggested the formation of  $(\text{CN})_2$  as a by-product, with subsequent formation of HCN and HCNO:



If the thiophenols examined here reacted with the selenocyanates by an analogous reaction, the presence of thiocyanate in the final solution should be detectable. If the mechanism follows a similar course to that proposed by Challenger [13] or Rheinbolt [26] for the hydrolysis by water, thiocyanate should also be formed. However, we could not detect the presence of thiocyanate in the products or evolution of cyanogen during the reaction.

The reactions thus appear to be either the simple elimination of HCN when selenenyl sulphides are formed or may possibly proceed by a disproportionation reaction analogous to that proposed for the reactive acyclic selenenyl sulphides [31] when diselenides (and disulphides) are the major products.

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