

# Characterization of organic polyselenide ions in *N,N*-dimethylacetamide

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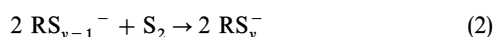
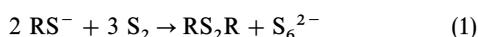
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The reactivity of selenolate ions  $\text{RSe}^-$  [ $\text{R} = \text{Ph}$  (**1**),  $\text{PhCH}_2$  (**2**)] towards solid selenium has been investigated by UV-visible spectrophotometry in *N,N*-dimethylacetamide. After the slow formation of  $\text{RSe}_2^-$ , further addition of Se yielded  $\text{RSe}_3^-$  and  $\text{RSe}_4^-$  species, which partly disproportionated ( $\text{RSe}_3^-$ , 30%;  $\text{RSe}_4^-$ , 50%) into diselenes  $\text{RSe}_2\text{R}$  (**a**) and polyselenide ions  $\text{Se}_4^{2-}$  and  $\text{Se}_6^{2-}$ , respectively. These equilibria were readily attained by the reactions between electrogenerated  $\text{Se}_x^{2-}$  ions ( $x = 4, 6$ ) and substrates **1a** and **2a**. Visible spectra of  $\text{RSe}_3^-$  and  $\text{RSe}_4^-$  ions ( $380 < \lambda < 580 \text{ nm}$ ) were calculated [ $\lambda_{\text{max}} = 420$  (**1**),  $400 \text{ nm}$  (**2**)]. The formation of  $\text{RSe}_2\text{R}$  as major products in the  $\text{RSe}_x\text{R}$  mixtures obtained by the nucleophilic reactions  $\text{Se}_4^{2-} + \text{PhCH}_2\text{Br}$  ( $\bar{z} = 2.17$ ) or  $\text{CH}_3\text{I}$  ( $\bar{z} = 2.48$ ) on a preparative scale agrees with the disproportionation of intermediate  $\text{RSe}_y^-$  ions.

Diselenide ions have been described as being conveniently obtained from the reduction of solid selenium, either by a number of chemical agents<sup>1</sup> or by electrolysis in THF, DMF and acetonitrile.<sup>2</sup> However, relatively little is known about polyselenide ions  $\text{Se}_x^{2-}$  ( $x \geq 3$ ) in aprotic solvents, compared to polysulfide ions  $\text{S}_8^{2-}$ ,  $\text{S}_6^{2-}$  ( $\rightleftharpoons \text{S}_3^{2-}$ ),  $\text{S}_4^{2-}$  and  $\text{S}_3^{2-}$ , which were thoroughly studied in DMF, HMPA, DMSO, acetonitrile, etc., over a period of thirty years.<sup>3</sup>  $\text{Se}_x^{2-}$  species were first characterized by UV-visible spectroscopy in  $\text{NH}_3$  ( $x = 3, 4, 6$ )<sup>4</sup> and in DMF ( $x = 3-6$ ) by  $^{77}\text{Se}$  NMR,<sup>5</sup> and then by our group in *N,N*-dimethylacetamide (DMA) by spectroelectrochemistry ( $x = 4, 6, 8$ ).<sup>6</sup>

Alkyl polysulfide ions  $\text{RS}_y^-$  are stabilized in aprotic media,<sup>7</sup> as are  $\text{Se}_x^{2-}$  ions. The reaction of sulfur with thiolates occurs by two parallel routes:<sup>7</sup> (i) weak oxidation according to eqn. (1) and (ii) preponderant and successive formation [eqn. (2)] of  $\text{RS}_y^-$  ions ( $\text{R} = \text{alkyl}$ ,  $y = 2-5$ ;  $\text{R} = \text{aryl}$ ,  $y = 2-4$ ):



The equilibrium in eqn. (3) was evidenced by the addition of dialkyl disulfides to  $\text{S}^{3-}$  ions ( $\text{S}_6^{2-} \rightleftharpoons \text{S}_3^{2-}$ ):



Prior to this work, we showed that only colored 2-nitrophenyl diselenide ions resulted from the addition of solid selenium to  $2\text{-NO}_2\text{C}_6\text{H}_4\text{Se}^-$  ions,<sup>8</sup> as already observed for the analogous sulfur species  $2\text{-NO}_2\text{C}_6\text{H}_4\text{S}^-$  and  $2\text{-NO}_2\text{C}_6\text{H}_4\text{S}_2^{2-}$ .<sup>7,9</sup> In THF,  $\text{RSe}_2^-$  ions were characterized by  $^{77}\text{Se}$  NMR at the end of  $\text{RLi} + 2 \text{Se}$  reactions ( $\text{R} = \text{Me}$ , *n*-Bu, Ph),<sup>10,11</sup> and alkylation of their solutions yielded diselenes  $\text{RSe}_2\text{R}$  ( $\text{R} = \text{Me}$ , *n*-Bu). However, further addition of selenium to  $\text{RSe}_2^-$  in an attempt to prepare  $\text{RSe}_y^-$  ions "led to complex disproportionation reactions"<sup>12</sup> that were not elucidated. It was therefore of interest to establish whether these species exist.

The present paper reports on the expected stabilization of  $\text{RSe}_y^-$  ions in DMA, based on the study of  $\text{Se} + \text{RSe}^-$  and  $\text{Se}_x^{2-}$  ( $x = 4, 6, 8$ ) +  $\text{RSe}_2\text{R}$  [ $\text{R} = \text{C}_6\text{H}_5$  (**1**),  $\text{C}_6\text{H}_5\text{CH}_2$  (**2**)] reactions by UV-visible spectrophotometry combined with

voltammetry using a rotating gold disc electrode. Our results are then applied to the understanding of the nucleophilic reactivity of the polyselenide ion  $\text{Se}_4^{2-}$  towards alkyl halides.

## Results and discussion

### Polyselenide and selenolate ions in DMA

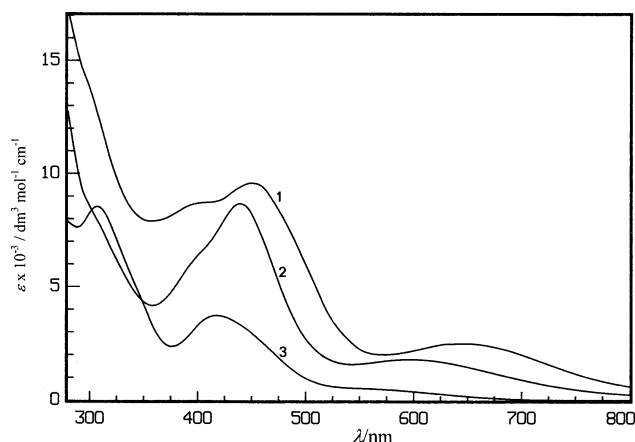
In DMA, the electroreduction of selenium deposited on a large gold grid electrode (see Experimental) was found to occur in four steps ( $\text{R}_1\text{--R}_4$ ), leading successively to colored  $\text{Se}_x^{2-}$  ions<sup>6</sup> that were characterized:<sup>6</sup>  $\text{Se}_8^{2-}$  (dark brown),  $\lambda_{\text{max}} = 648, 453$  and  $398 \text{ nm}$ ,  $E_{1/2}(\text{R}_2) \simeq -0.55 \text{ V vs. reference}$ ;  $\text{Se}_6^{2-}$  (dark green),  $\lambda_{\text{max}} = 598$  and  $440 \text{ nm}$ ,  $E_{1/2}(\text{R}_3) = -0.83 \text{ V}$ ;  $\text{Se}_4^{2-}$  (brown),  $\lambda_{\text{sh}} = 550 \text{ nm}$  and  $\lambda_{\text{max}} = 417 \text{ nm}$ ,  $E_{1/2}(\text{R}_4) \simeq -1.2 \text{ V}$ . The final reduced species ( $\text{Se}_2^{2-}$  ions?) were not produced by the electrolysis because of passivation phenomena at the gold electrode surface.  $\text{Se}_6^{2-}$  and  $\text{Se}_8^{2-}$  oxidize (O) at the same potentials [ $E_{1/2}(\text{O}) \simeq -0.34 \text{ V}$ ]. The limiting currents for reduction (R) of  $\text{Se}_8^{2-}$  and  $\text{Se}_6^{2-}$  ions were small and roughly reproducible in comparison with those of only sulfur species ( $\text{S}_8$ ,  $\text{S}_8^{2-}$ ,  $\text{S}_6^{2-}$ ), but the  $E_{1/2}(\text{R})$  values gave reliable information about the presence of  $\text{Se}_x^{2-}$  ions in the solutions. UV-visible spectra ( $280 < \lambda < 800 \text{ nm}$ ) of the anionic  $\text{Se}_x^{2-}$  species and molar absorptivities for each one at 550, 598, 648 and  $700 \text{ nm}$ <sup>6</sup> used here for quantitative data processing are summarized in Fig. 1 and Table 1.

Selenolate ions ( $\text{RSe}^-$ ) **1b** and **2b** were generated ( $[\text{RSe}^-]_0 \leq 4.0 \times 10^{-3} \text{ mol dm}^{-3}$ ) by exhaustive electrolysis of  $\text{RSe}_2\text{R}$  compounds **1a** and **2a** at a controlled potential

**Table 1** Molar absorptivities  $\epsilon_i$  of  $\text{Se}_x^{2-}$  ions at various wavelengths in dimethylacetamide<sup>6</sup>

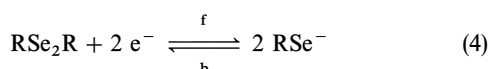
	$\lambda/\text{nm}$			
$\epsilon_i^a$	550	598	648	700
$\text{Se}_8^{2-}$	2200	2150	2500	2000
$\text{Se}_6^{2-}$	1600	1750	1450	900
$\text{Se}_4^{2-}$	500	400	150	—

<sup>a</sup>  $\epsilon_i/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1} \pm 4\%$ .



**Fig. 1** UV-visible absorption spectra of  $\text{Se}_8^{2-}$  (1),  $\text{Se}_6^{2-}$  (2) and  $\text{Se}_4^{2-}$  (3) ions in dimethylacetamide.

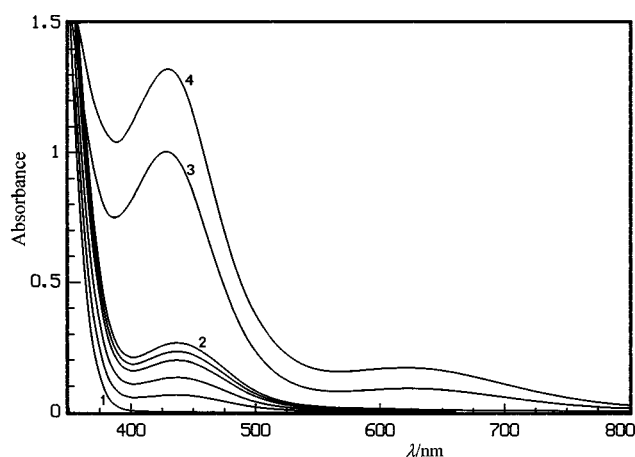
( $E = -1.1$  and  $-1.5$  V *vs.* reference, respectively) on the plateaux of their bielectronic waves [eqn. (4)]:<sup>13</sup>



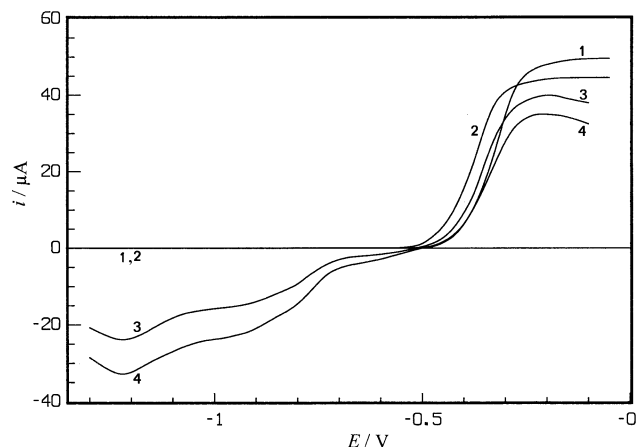
The electrochemical and spectrophotometric characteristics of the **a** and **b** species (Table 2) were obtained from the changes in voltammograms and spectra in the course of the electro-oxidation of selenolate ions on their well-defined anodic wave.

#### Reactivity of selenolate ions with selenium

When Se powder was added to stirred solutions of  $\text{RSe}^-$  ions **1b** and **2b** at successive molar ratios  $n = (\text{Se})_{\text{ad}}/(\text{RSe}^-)_0 = 1, 2, 3, 4$ , the changes in UV-visible spectra and voltammograms were similar in both cases, as illustrated in Fig. 2 and 3. The total consumption of selenium initially required about 2 h ( $n = 1$ ), then *ca.* 3 h ( $n = 2, 3$ ), whereas traces of solid Se

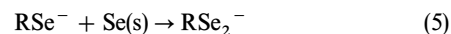


**Fig. 2** Changes in UV-visible spectra with the addition of selenium powder to a  $[\text{PhSe}^-]_0 = 3.9 \times 10^{-3} \text{ mol dm}^{-3}$  solution at ratios  $n = (\text{Se})_{\text{ad}}/(\text{RSe}^-)_0 = 0$  (1), 0.99 (2), 1.99 (3), 2.98 (4); recordings at equilibrium except for (1)  $\rightarrow$  (2),  $A = f(t)$ ,  $0 < t < 145$  min. Thickness of the cell = 0.1 cm; scan rate =  $500 \text{ nm min}^{-1}$ .

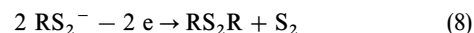
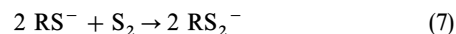
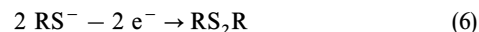


**Fig. 3** Changes in voltammograms with the addition of selenium to a  $[\text{PhSe}^-]_0 = 3.9 \times 10^{-3} \text{ mol dm}^{-3}$  solution. Same conditions as for Fig. 2.  $E$  *vs.* Ag/AgCl, KCl sat. in DMA- $\text{N}(\text{Et})_4\text{ClO}_4$  ( $0.1 \text{ mol dm}^{-3}$ ). Scan rate =  $10 \text{ mV s}^{-1}$ .

remained unreacted for  $n = 4$ . As long as  $n$  remained less than 1 (first addition, Fig. 2, curves 1  $\rightarrow$  2), the absorbance increased *vs.* time at  $\lambda_{\text{max}} = 438 \text{ nm}$ , in agreement with the slow formation of  $\text{RSe}_2^-$  ions:



As soon as solid Se was added, the whole oxidation wave of  $\text{RSe}^-$  began to shift towards less anodic potentials up to  $\Delta E(\text{O}) \simeq -80 \text{ mV}$  (Fig. 3, curve 2), as observed in the course of the reaction  $2\text{-NO}_2\text{PhSe}^- + \text{Se}^8$  and of the homogeneous reactions  $\text{RS}^- + \text{S}_2$ .<sup>7</sup> In the latter case, the sequence of electrocatalytic processes in eqn. (6), (7) and (8) was proven:<sup>9b</sup>



After the fast reaction in eqn. (7), sulfur is released from the electrooxidation of  $\text{RS}_2^-$  into  $\text{RS}_2\text{R}$  [eqn. (8)], which is faster than the electrooxidation of  $\text{RS}^-$  [eqn. (6)] at the gold electrode surface. Here also (conditions of curve 2, Fig. 3) grey selenium was deposited on the gold disc electrode when its potential was kept at  $-0.35 \text{ V}$ . The study of this phenomenon is currently being extended by our group to  $\text{RSe}_2^-$  ions. For  $n$  greater than 1 (Fig. 2 and 3, curves 3 and 4), two absorption bands, at *ca.* 430 and *ca.* 630 nm, increased without showing any constant  $A_{630}/A_{430}$  ratio. At the same time, the weak reduction currents of  $\text{Se}_x^{2-}$  ions ( $x = 8, 6, 4$ ;  $E_{1/2} \simeq -0.55, -0.83, -1.2 \text{ V}$ ) were detected on the voltammograms, with a greater current at potentials close to those of diselenes  $\text{RSe}_2\text{R}$  ( $\text{R} = \text{Ph}$ ,  $E_{1/2} = -0.76 \text{ V}$ ;  $\text{R} = \text{PhCH}_2$ ,  $E_{1/2} \simeq -1.20 \text{ V}$ ). These results are in agreement with the partial oxidation of  $\text{RSe}^- + n \text{ Se}$  solutions ( $n > 1$ ) into  $\text{RSe}_2\text{R} + \text{Se}_x^{2-}$ , but the majority of the absorbance values  $A_{430}$  cannot be attributed to polyselenide ions in terms of their own spectra (Fig. 1). Furthermore, spectra and voltammograms at equilibrium had the same shapes when the following stoichiometries were

**Table 2** Electrochemical and spectrophotometric characteristics of diselenes  $\text{RSe}_2\text{R}$  and selenolate ions  $\text{RSe}^-$  in dimethylacetamide.  $E_{1/2}$  at a rotating gold disc electrode *vs.* reference

R	$\text{RSe}_2\text{R}$			$\text{RSe}^-$		
	$E_{1/2}(\text{R})/\text{V}$	$\lambda_{\text{max}}/\text{nm}$	$\epsilon_{\text{max}}^a$	$E_{1/2}(\text{O})/\text{V}$	$\lambda_{\text{max}}/\text{nm}$	$\epsilon_{\text{max}}^a$
Ph	-0.76	325	1000	-0.36	318	12 700
PhCH <sub>2</sub>	-1.20	300 sh	870	-0.50	288 sh	4600

<sup>a</sup>  $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ .

achieved:  $\text{RSe}^- + 2 \text{Se}$  (Fig. 2 and 3, curve 3) and  $\text{RSe}_2\text{R} + \text{Se}_4^{2-}$ ;  $\text{RSe}^- + 3 \text{Se}$  (curve 4) and  $\text{RSe}_2\text{R} + \text{Se}_6^{2-}$ . The assumed formation of  $\text{RSe}_y^-$  ions during the slow  $\text{RSe}^- + n \text{Se}$  ( $n > 1$ ) reactions was then confirmed by analysis of the spectra evolving in the course of the fast reactions between  $\text{RSe}_2\text{R}$  diselanides and  $\text{Se}_x^{2-}$  polyselenide ions.

#### Reactivity of diselanides $\text{RSe}_2\text{R}$ 1a, 2a with $\text{Se}_x^{2-}$ ions ( $x = 4, 6, 8$ )

The study was carried out in the same way with all the  $\text{Se}_x^{2-}$  ions: spectra and voltammograms were recorded at  $20.0 \pm 0.5^\circ\text{C}$  during the addition of concentrated solutions of  $\text{RSe}_2\text{R}$  1a, 2a in DMA at the ratio  $m = [\text{RSe}_2\text{R}]_{\text{ad}}/[\text{Se}_x^{2-}]_0$ . Absorbances always reached stable values within 20 s. A typical experiment is illustrated in Fig. 4 for the reaction of  $\text{PhCH}_2\text{Se}_2\text{CH}_2\text{Ph}$  added to a solution of  $\text{Se}_6^{2-}$ . The simultaneous presence of  $\text{Se}_6^{2-}$  and  $\text{Se}_8^{2-}$  at a definite value of  $m$  was at the root of the maximum absorbance at wavelengths evolving between 598 and 648 nm;  $[\text{Se}_6^{2-}]$  and  $[\text{Se}_8^{2-}]$  were thus deduced from  $A_{598}$  and  $A_{648}$  measurements and verified ( $\pm 5\%$ ) by comparing calculated  $A_{700}$  values with experimental values ( $\epsilon_i$  in Table 1):

$$A_i = \epsilon_i(\text{Se}_6^{2-})[\text{Se}_6^{2-}] + \epsilon_i(\text{Se}_8^{2-})[\text{Se}_8^{2-}] \quad (9)$$

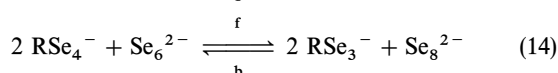
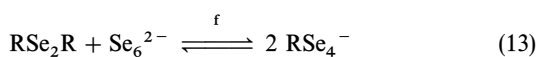
All the concentrations of the species in equilibrium and the average number  $\bar{y}$  of Se atoms in  $\text{RSe}_y^-$  chains could then be obtained by solving the set of conservation equations [eqn. (10)–(12)]:

$$2 [\text{RSe}_2\text{R}]_{\text{ad}} = 2 [\text{RSe}_2\text{R}] + [\text{RSe}_y^-] \quad (10)$$

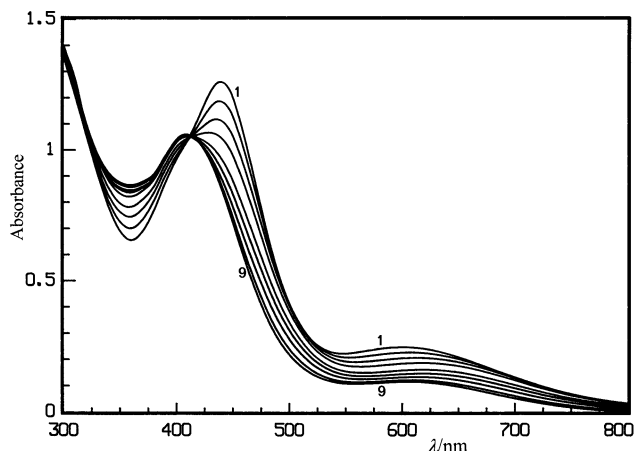
$$2 [\text{RSe}_2\text{R}]_{\text{ad}} + 6 [\text{Se}_6^{2-}]_0 = 2 [\text{RSe}_2\text{R}] + 6 [\text{Se}_6^{2-}] + 8 [\text{Se}_8^{2-}] + \bar{y} [\text{RSe}_y^-] \quad (11)$$

$$2 [\text{Se}_6^{2-}]_0 = 2 [\text{Se}_6^{2-}] + 2 [\text{Se}_8^{2-}] + [\text{RSe}_y^-] \quad (12)$$

During the initial consumption of  $\text{Se}_6^{2-}$  ( $0 < m \leq 0.5$ ; Fig. 4, curves 1–5), absorption  $A_{440}$  decreased, to the benefit of  $A_{406}$  (isosbestic point at  $\lambda_{\text{is}} = 412 \text{ nm}$ ), with partial formation of  $\text{Se}_8^{2-}$  giving the shift  $A_{598} \rightarrow A_{618}$ . Recovery of a proportion of the  $\text{Se}_6^{2-}$  ions was then revealed ( $0.5 < m \leq 1.01$ ) by the backward displacement  $A_{618} \rightarrow A_{602}$  (curves 5–9). These results agree with both eqn. (13) and (14):



Reaction (13), leading to  $\text{RSe}_4^-$  ions, is analogous to that observed with sulfur species [eqn. (3)].<sup>7</sup> In the presence of



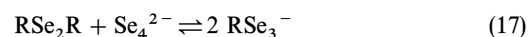
**Fig. 4** Absorption spectral changes observed on the addition of dibenzyl diselenide to a  $[\text{Se}_6^{2-}]_0 = 1.38 \times 10^{-3} \text{ mol dm}^{-3}$  solution:  $m = [\text{RSe}_2\text{R}]_{\text{ad}}/[\text{Se}_6^{2-}]_0 = 0$  (1), 0.11 (2), 0.22 (3), 0.33 (4), 0.50 (5), 0.61 (6), 0.72 (7), 0.88 (8), 1.01 (9).

excess amounts of  $\text{Se}_6^{2-}$  ions ( $0 < m < 0.5$ ), the “Se-exchange reaction” [eqn. (14f)], which can be viewed as a redox process, occurs in accordance with the overall eqn. (15) [=eqn. (13) + eqn. (14)] for  $m = 0.5$ :

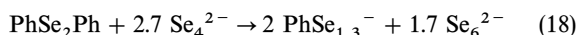


Further addition of  $\text{RSe}_2\text{R}$  resulted in the progressive displacement of eqn. (14b) until only the equilibrium in eqn. (13) remained for  $m = 1$ .

With the reaction  $\text{PhCH}_2\text{Se}_2\text{CH}_2\text{Ph} + \text{Se}_4^{2-}$ , two steps were again observed from the successive shifts: (i) for  $0 < m < 0.65$ ,  $A_{417} \rightarrow A_{430}$  and  $A_{550} \rightarrow A_{570}$  ( $\text{Se}_4^{2-} \rightleftharpoons \text{Se}_6^{2-}$ ); (ii) for  $0.65 < m < 1.01$ ,  $A_{570} \rightarrow A_{555}$  ( $\text{Se}_6^{2-} \rightarrow \text{Se}_4^{2-}$ ) and  $A_{430} \rightarrow A_{402}$  ( $\text{Se}_6^{2-} \rightarrow \text{RSe}_3^-$ ,  $\lambda_{\text{is}} = 426 \text{ nm}$ ). The treatment of  $A_{550}$  and  $A_{598}$  for  $[\text{Se}_4^{2-}]_0 = 1.75 \times 10^{-3} \text{ mol dm}^{-3}$  led to  $[\text{Se}_4^{2-}]$  and  $[\text{Se}_6^{2-}]$  concentrations as a function of  $m$ , and to the overall equations in eqn. (16) and (17) at ratios of  $m \approx 0.65$  and 1, respectively:



With the more oxidizing substrate  $\text{PhSe}_2\text{Ph}$ , the first stage looked like a nearly quantitative redox process [eqn. (18)]:

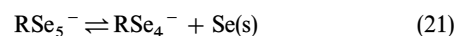


It was followed by the reaction of  $\text{Se}_6^{2-}$  ions, increasing the Se content of  $\text{RSe}_y^-$  ions up to  $y \approx 2.5$ , and the appearance of  $\text{Se}_8^{2-}$  ions.

The compositions of solutions at equilibrium for known initial conditions  $[\text{RSe}^-]_0 + n(\text{Se})_{\text{ad}}$  ( $n = 2, 3$ ) and  $[\text{RSe}_2\text{R}]_0 = [\text{Se}_x^{2-}]_0$  ( $x = 4, 6$ ), which were obtained from equations such as eqn. (10)–(12) are reported in Table 3. The concentrations evaluated and values of  $\bar{y}$  confirm the identities of the solutions  $\text{RSe} + 2 \text{Se} \equiv \text{RSe}_2\text{R} + \text{Se}_4^{2-}$  and  $\text{RSe} + 3 \text{Se} \equiv \text{RSe}_2\text{R} + \text{Se}_6^{2-}$ , with the formation of mixtures  $\text{RSe}_2^-/\text{RSe}_3^-$  [ $\bar{y} \approx 2.5$  (1); 2.8 (2)] and  $\text{RSe}_3^-/\text{RSe}_4^-$  [ $\bar{y} \approx 3.7$  (1); 3.9 (2)]. Comparisons between  $[\text{RSe}_2\text{R}]_0$  and  $[\text{RSe}_2\text{R}]_{\text{eq}}$  for solutions  $[\text{RSe}_2\text{R}]_0 = [\text{Se}_x^{2-}]_0$  imply the following disproportionation levels for  $\text{RSe}_y^-$  ions:  $y = 3$ , ca. 25 (1) and ca. 35% (2);  $y = 4$ , ca. 45 (1) and 50% (2), with an assessable constant  $K$  (293 K) in the last case ( $\text{R} = \text{PhCH}_2$ ) for eqn. (13b):

$$K = [\text{RSe}_2\text{R}][\text{Se}_6^{2-}][\text{RSe}_4^-]^{-2} = 0.22 \pm 0.04 \quad (19)$$

With the addition of diselanides 1a and 2a,  $\text{Se}_8^{2-}$  ions readily reacted at first, with a decrease in absorbance at 453 and 648 nm; the latter shifted to  $A_{625}$ , corresponding to the partial generation of  $\text{Se}_6^{2-}$  ions. However, no quantitative calculations could be performed because of the appearance of solid selenium within the solutions, as previously shown in the “equivalent mixtures”  $(\text{RSe}^-)_0 + 4 (\text{Se})_{\text{ad}}$ . It can only be suggested that the ions containing the highest number of Se atoms  $\text{RSe}_5^-$ , resulting from eqn. (20) dissociate into  $\text{RSe}_4^-$  species [eqn. (21)] with subsequent disproportionation, as in eqn. (13b):



The spectra of  $\text{RSe}_y^-$  ions ( $\bar{y}$  values and conditions of Table 3) were calculated between 380 and 580 nm: the absorbances of  $\text{Se}_x^{2-}$  ions estimated from their concentrations and spectrophotometric data (Fig. 1) were subtracted from the experimental  $A$  values. Therefore, supposing that  $2 < \bar{y} < 3$  and  $3 < \bar{y} < 4$  correspond to mixtures  $\text{RSe}_2^-/\text{RSe}_3^-$  and  $\text{RSe}_3^-/\text{RSe}_4^-$  of definite compositions (e.g.,  $\bar{y} = 3.7$  gives 30%  $\text{RSe}_3^-$  and 70%  $\text{RSe}_4^-$ ), the use of the known  $\text{RSe}_2^-$  spectra (Fig. 2,  $\text{PhSe}^- + 1 \text{Se}$ ) led to  $\text{RSe}_y^-$  spectra ( $y = 3$  and 4). The calculated ( $\pm 15\%$ ) spectra of  $\text{PhSe}_y^-$  ions are reported in Fig.

**Table 3** Calculated compositions of solutions at equilibrium for the reactions  $\text{RSe}_2\text{R} + \text{Se}_x^{2-}$  ( $x = 4, 6$ ) and  $\text{RSe}^- + n \text{Se}$  ( $n = 2, 3$ ) depending on initial conditions<sup>a</sup>

Initial cond.	$[\text{Se}_4^{2-}]$	$[\text{Se}_6^{2-}]$	$[\text{Se}_8^{2-}]$	$[(\text{RSe})_2]$	$[(\text{RSe}_y)^-]$	$\bar{y}$
$[(\text{PhSe})_2]_0 = 2.46$	—	0.31	0.29	0.58	3.77	2.5
$+ [\text{Se}_4^{2-}]_0 = 2.48$	—	0.22	0.18	0.40	2.02	2.54
$[\text{PhSe}^-]_0 = 2.82$	—	0.38	0.23	0.60	1.32	3.65
$+ [\text{Se}]_0 = 5.87$	—	0.27	0.21	0.48	1.43	3.7
$[(\text{PhSe})_2]_0 = 1.26$	—	0.22	—	0.59	2.16	2.8
$+ [\text{Se}_6^{2-}]_0 = 1.28$	0.35	0.22	—	0.55	2.1	2.7
$[\text{PhSe}^-]_0 = 2.4$	0.31	0.24	—	0.69	1.35	3.94
$+ [\text{Se}]_0 = 7.14$	—	0.59	(0.04)	0.67	1.78	3.8
$[(\text{PhCH}_2\text{Se})_2]_0 = 1.67$	—	0.60	(0.07)			
$+ [\text{Se}_4^{2-}]_0 = 1.65$						
$[\text{PhCH}_2\text{Se}^-]_0 = 3.2$						
$+ [\text{Se}]_0 = 6.16$						
$[(\text{PhCH}_2\text{Se})_2]_0 = 1.36$						
$+ [\text{Se}_6^{2-}]_0 = 1.3$						
$[\text{PhCH}_2\text{Se}^-]_0 = 3.12$						
$+ [\text{Se}]_0 = 9.18$						

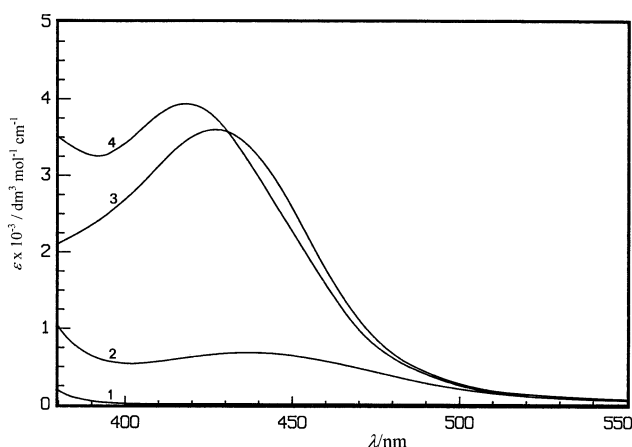
<sup>a</sup> All concentrations are in  $\text{mmol dm}^{-3}$ .

5, and Table 4 summarizes the  $\lambda_{\text{max}}$  and  $\epsilon_{\text{max}}$  values ( $\text{R} = \text{Ph}, \text{PhCH}_2$ ).

These results were applied to the understanding of the nucleophilic substitution of  $\text{Se}_4^{2-}$  ions on benzyl bromide.

#### Reactivity of $\text{Se}_4^{2-}$ ions towards benzyl bromide and methyl iodide

Fig. 6 shows the spectral changes when  $\text{PhCH}_2\text{Br}$  was added to a solution of  $\text{Se}_4^{2-}$  in the proportion  $m = [\text{RBr}]_{\text{ad}}/[\text{Se}_4^{2-}]_0$ . As long as  $m$  remained less than 0.5 (curves 1 → 2) the continuous variations  $A_{417} \rightarrow A_{435}$  and



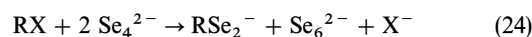
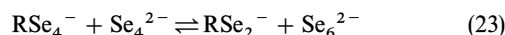
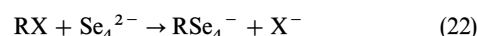
**Fig. 5** Calculated visible spectra ( $\epsilon_i/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1} \pm 15\%$ ) of  $\text{PhSe}_y^-$  ions. The curves are numbered according to the  $y$ -values for each.

**Table 4** Spectrophotometric characteristics of  $\text{RSe}_y^-$  ions ( $y = 2-4$ ) in dimethylacetamide

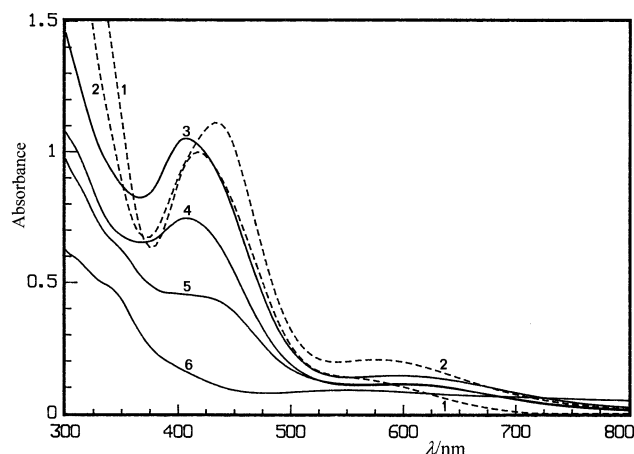
R		$\text{RSe}_2^-$	$\text{RSe}_3^-$	$\text{RSe}_4^-$
Ph	$\lambda_{\text{max}}^a/\text{nm}$	438	425	420
	$\epsilon_{\text{max}}^b$	685	3600 <sup>c</sup>	3900 <sup>c</sup>
$\text{PhCH}_2$	$\lambda_{\text{max}}^a/\text{nm}$	462	400	405
	$\epsilon_{\text{max}}^b$	450	4100 <sup>c</sup>	4700 <sup>c</sup>

<sup>a</sup>  $\lambda_{\text{max}}$  ( $y = 3, 4$ )  $\pm 4 \text{ nm}$ . <sup>b</sup>  $\epsilon_i/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ . <sup>c</sup>  $\epsilon_i \pm 15\%$ .

$A_{550} \rightarrow A_{590}$  were in agreement with the overall eqn. (24) [=eqn. (22) + eqn. (23)]:



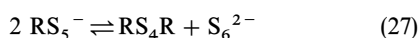
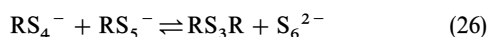
The excess reducing ions displace Se from  $\text{RSe}_4^-$  ions [eqn. (23)] resulting from the initial substitution in eqn. (22). Absorption spectra obtained were those of  $\text{Se}_4^{2-}/\text{Se}_6^{2-}$  mixtures without a significant contribution from  $\text{RSe}_2^-$  ions, the absorption of which is very weak (Table 4). For  $0.5 < m \leq 1.0$  (curves 2 → 3) the consumption of the most reactive  $\text{Se}_4^{2-}$  ions with respect to  $\text{Se}_6^{2-}$  shifted the equilibrium in eqn. (23) to the left with an increase in the average Se content  $\bar{y}$  up to  $\text{RSe}_4^-$  (growths of  $A_{\sim 400}$ ,  $\lambda_{\text{is}} \simeq 415 \text{ nm}$ ). For  $m = 1$  (curve 3), the calculated concentrations of species in equilibrium are as follows:  $[\text{RSe}_2\text{R}] = 0.59 \times 10^{-3}$ ,  $[\text{Se}_6^{2-}] = 0.54 \times 10^{-3}$ ,  $[\text{Se}_8^{2-}] \simeq 0.05 \times 10^{-3}$  and  $[\text{RSe}_{3.9}^-] = 1.33 \times 10^{-3} \text{ mol dm}^{-3}$ . The spectra of the mixtures 1  $\text{RX} + 1 \text{Se}_4^{2-}$ , 1  $\text{RSe}^- + 3 \text{Se}$  and 1  $\text{RSe}_2\text{R} + 1 \text{Se}_6^{2-}$  were the same, showing partly disproportionated  $\text{RSe}_4^-$  ions [eqn. (13)] with the presence of  $\text{Se}_6^{2-}$  ions ( $\lambda_{\text{max}} = 598 \text{ nm}$ ). With further addition of  $\text{RBr}$  ( $1.0 < m \leq 2$ ), Se was released in the course of the reaction of  $\text{RSe}_4^-$  and/or  $\text{Se}_6^{2-}$  ions; this initially entails the partial formation of  $\text{Se}_8^{2-}$  ions ( $A_{598} \rightarrow A_{617}$ ) before the appearance of colloidal selenium within the solutions, giving



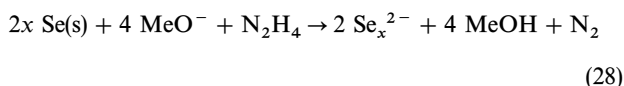
**Fig. 6** Changes in UV-visible spectra during the addition of benzyl bromide to a  $[\text{Se}_4^{2-}]_0 = 2.70 \times 10^{-3} \text{ mol dm}^{-3}$  solution:  $m = [\text{RBr}]_{\text{ad}}/[\text{Se}_4^{2-}]_0 = 0$  (1), 0.50 (2), 1.0 (3), 1.38 (4), 1.63 (5), 2.04 (6).

unexploitable UV-visible spectra: the last spectrum (curve 6,  $400 < \lambda < 700$  nm) was similar to those recorded after the chemical formation of colloidal Se dispersions in aqueous media (particle diameters  $< 200$  nm).<sup>14</sup>

Mixtures of polysulfanes  $RS_zR$  ( $z = 2-5$ ) were synthesized in aprotic media (DMF, DMA) by substitution reaction of polysulfide ions  $S_x^{2-}$  ( $x = 4, 6, 8$ ) with alkyl halides ( $m = [RX]_{ad}/[S_x^{2-}]_0 = 2$ ),<sup>15</sup> with predominant formation of tri- and tetrasulfanes in DMA.<sup>15b</sup> For example, the stoichiometric addition of  $PhCH_2Br$  to  $S_6^{2-}$  ions led to the following molar composition:  $z = 2$ , 8%;  $z = 3$ , 37%;  $z = 4$ , 30%;  $z = 5$ , 25%.<sup>15b</sup> This was explained by the enhanced nucleophilic character for intermediate  $RS_y^-$  ions ( $m = 1$ ) as  $y$  decreases ( $RS_3^- > RS_4^- > RS_5^-$ ), and by disproportionations in eqn. (25) and (26) proven by direct addition of  $RS_2R$  or  $RS_3R$  species ( $R = \text{alkyl, benzyl}$ ) to  $S_6^{2-}$  ( $\rightleftharpoons S_3^{2-}$  ions):  $RS_4^- \simeq 25\%$ ,  $RS_4^-/RS_5^- \simeq 15\%$  [ $(RS_4^-) = (RS_5^-)$ ], and presumed for  $RS_5^-$  [eqn. (27)]:<sup>7</sup>

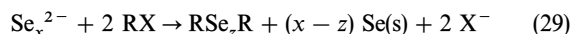


There is only one report on the analogous reactions of polyselenide ions towards alkyl halides in DMF or DMSO;<sup>16</sup>  $Se_x^{2-}$  ions ( $3 \leq \bar{x} \leq 7$ ) were the assumed products of the reduction [eqn. (28)] of elemental selenium by hydrazine and sodium methanolate:

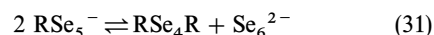
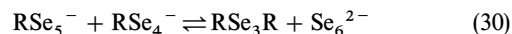


Alkylation of these anions, which proceeded with loss of selenium, yielded mixtures of  $RSe_zR$  polyselanes. Their composition ( $2.25 \leq \bar{z} \leq 2.50$ ) was accurately determined by means of the  $^{77}Se$  NMR spectra for a wide variety of alkyl group structures (typical examples  $R = \text{octyl, benzyl}$  in Table 5). These results were verified in DMA with the addition on a preparative scale of  $CH_3I$  and  $PhCH_2Br$  to the  $Se_4^{2-}$  ions expected from eqn. (28); the UV-visible spectra of the dilute solutions of  $Se_x^{2-}$  were consistent with  $\bar{x} \simeq 4.2$  (90%  $Se_4^{2-}$ , 10%  $Se_6^{2-}$ ). The distributions of  $RSe_zR$  products (mol%) listed in Table 5, which were obtained by  $^1H$  NMR, agreed with the previous distributions from  $2 RX + Se_4^{2-}$  reactions in DMF (Table 5),<sup>16</sup> or  $n-BuLi + n Se$  ( $n = 3, 5, 10$ ) +  $n-BuBr$  in THF ( $2.0 \leq \bar{z} \leq 2.2$ ).<sup>11</sup> As shown by our spectroelectrochemical study, the first substitution step of the  $RX + Se_4^{2-}$  reactions yields  $RSe_4^-$  ions ( $m = 1$ ). Disproportionations [eqn. (13b)] of  $RSe_4^-$  species ( $\simeq 50\%$ ), in greater amounts than for  $RS_4^-$  ( $\simeq 25\%$ ), provide the predomi-

nant source of  $RSe_zR$  compounds in the overall process [eqn. (29)]:



It can be assumed that the greater nucleophilic reactivity of  $Se_6^{2-}$  with respect to  $RSe_4^-$  shifts the equilibrium in eqn. (13) to the right ( $m > 1$ ): the appearance of colloidal selenium might then be attributable to the formation of species containing the greatest numbers of Se atoms ( $RSe_4^- > RSe_5^-$ ), with side equilibria such as in eqn. (30) and (31):



## Conclusions

Stabilization of  $RSe_y^-$  ions ( $y = 2-4$ ), which is analogous to that of  $RS_y^-$  ( $y = 2-5$ ), has been demonstrated for the first time in this study. The slow addition of elemental selenium to selenolate ions agrees with the generation of  $RSe_2^-$  ions whereas  $RSe_3^-$  and  $RSe_4^-$  largely disproportionate into diselanes  $RSe_2R$  and polyselenide ions  $Se_x^{2-}$  ( $x = 4, 6$ ). The reactions between both these species readily yield  $RSe_y^-$  ions ( $y = 3, 4$ ). In the course of the substitution of  $Se_x^{2-}$  ions ( $x = 4, 6$ ) on alkyl halides, the shift of such intermediate equilibria probably explains the significant presence of  $RSe_zR$  in the mixtures of  $RSe_zR$  products ( $z = 2-4$ ). The most frequently used method for preparation of organic diselenides is based on the reaction of  $Se_2^{2-}$  ions with various nucleophiles.<sup>1</sup> However the reduction of selenium to diselenide ions occurs under rather harsh conditions<sup>1</sup> and  $Se_2^{2-}$  ions have been suspected to largely disproportionate into  $Se_3^{2-}$  and  $Se^{2-}$  ions.<sup>4,5</sup> The alkylation of  $Se_x^{2-}$  ions ( $x \geq 4$ ) under mild reaction conditions appears to be an efficient route to the diselanes  $RSe_2R$ .

## Experimental

### Materials and equipment

Distilled *N,N*-dimethylacetamide (Aldrich, HPLC grade) was stored over molecular sieves (4 Å) after addition of  $NEt_4ClO_4$  (Fluka, 0.1 mol  $dm^{-3}$ ) as supporting electrolyte. Selenium in its powdered grey form (100 mesh, 99.999%), hydrazine in THF (1 mol  $dm^{-3}$ ) and sodium methoxide in methanol (31 wt% from titration by picric acid) were obtained from Aldrich. Dibenzyl diselenide (99%) and diphenyl diselenide (99%) were purchased from Acros Organics and used as received. Benzyl bromide and methyl iodide (Aldrich) were distilled just before use. All experiments were performed under a dry nitrogen atmosphere. The thermostatted ( $20.0 \pm 0.5^\circ C$ ) flow-through cell (usable volume = 50  $cm^3$ ) has been described elsewhere.<sup>17</sup> Voltammograms at a rotating gold disc electrode (diameter 2 mm, 1000 rev  $min^{-1}$ ) were obtained by using a EGG-PAR 273 unit. Electroreduction of  $Ar_2Se_2$  compounds **1a**, **2a** and of selenium was carried out on a large gold grid electrode. The counter-electrode was a gold wire in a separate compartment. All the potentials are referenced to  $Ag/AgCl$ , saturated  $KCl$  solution in  $DMA-NEt_4ClO_4$  (0.1 mol  $dm^{-3}$ ) electrode. UV-visible spectra were recorded with a Kontron Uvikon 930 spectrophotometer (pathlength of the cell = 0.1 cm). The mixtures of dialkyl polyselanes were analyzed by  $^1H$  NMR spectroscopy (200.132 MHz, Bruker AC 200) with  $CDCl_3$  as the solvent (internal standard  $Me_4Si$ ), and GC-MS (Hewlett-Packard 5989A, EI 70 eV).

### Generation of $Se_x^{2-}$ ions ( $x = 4, 6, 8$ )

Concentrated solutions of diselanes  $Ar_2Se_2$  **1a**, **2a** in DMA were added ( $v_{max} = 4$   $cm^3$ ) to  $Se_x^{2-}$  ions ( $x = 4, 6, 8$ ;  $v_0 = 40$   $cm^3$ ). The latter were obtained by a recently described

**Table 5** Chemical shifts  $\delta_H$  (vs. TMS) and molar composition (%) of synthesized  $RSe_zR$  mixtures in DMA compared with previous results in DMF<sup>16</sup>

R		z				$\bar{z}^a$
		2	3	4	5	
CH <sub>3</sub>	$\delta_H$ (6H)	2.53	2.67 <sub>5</sub>	2.75	2.79 <sub>5</sub>	2.48
	%	63	28	7	2	
PhCH <sub>2</sub>	$\delta_H$ (4H)	3.79 <sub>7</sub>	4.22 <sub>5</sub>	4.36	—	
	%	87	9	4	—	2.17
PhCH <sub>2</sub>	% <sup>b</sup>	75	17	6	2	2.35
C <sub>8</sub> H <sub>17</sub>	% <sup>b</sup>	64	26	7	2	2.44

<sup>a</sup>  $\pm 0.1$  from % values. <sup>b</sup> Products from  $RBr + Se_4^{2-}$ .<sup>16</sup>

method:<sup>6</sup>  $\text{Se}_x^{2-}$  solutions ( $\bar{x} \approx 6$ ) were initially chemically prepared according to eqn. (28) by mixing the reagents in 50  $\text{cm}^3$  of DMA at room temperature: sodium methoxide (100  $\mu\text{L}$ , 0.50 mmol); hydrazine (140  $\mu\text{L}$ , 0.140 mmol); powdered selenium (115 mg, 1.46 mmol). After the rapid evolution of nitrogen (10 min) the exhaustive electrooxidation of polyselenide ions was performed at controlled potentials of the large gold electrode, ranging between  $-0.2$  and  $+0.1$  V (initial intensity  $i \approx 120$   $\mu\text{A}$ ). This led to the appearance of colloidal selenium in the solution, with simultaneous deposition on the electrode surface (25–30%, 32 mg in a typical example).  $\text{Se}_x^{2-}$  ions were then accurately generated under cathodic polarization of the Se-coated grid ( $x = 8$ ,  $E = -0.5$  V;  $x = 6$ ,  $E = -0.8$  V;  $x = 4$ ,  $E = -1.2$  V), until the characteristic spectra of the required species were observed (Fig. 1).

### Syntheses of polyselanes

Mixtures of polyselanes  $\text{CH}_3\text{Se}_z\text{CH}_3$  and  $\text{PhCH}_2\text{Se}_z\text{CH}_2\text{Ph}$  were prepared by the reaction of  $\text{Se}_4^{2-}$  ions with methyl iodide and benzyl bromide.  $\text{Se}_4^{2-}$  ions were obtained in DMA (50  $\text{cm}^3$ ) by the hydrazine reduction of selenium [eqn. (28)].<sup>16</sup> RX substrates in 15  $\text{cm}^3$  of DMA were then added dropwise (30 min) at room temperature. The red color that transiently developed could be due to the formation of unstable monoclinic selenium.<sup>10</sup> The mixtures were stirred for 40 min at 80 °C. After filtration (0 °C) of the precipitated selenium and addition of water (150  $\text{cm}^3$ ), the  $\text{RSe}_z\text{R}$  products were extracted with diethyl ether and the organic phase thoroughly washed and then dried over  $\text{MgSO}_4$ . The extract was evaporated *in vacuo*. In both cases the residue was filtered through silica gel (petroleum ether–methylene chloride 2 : 1 as the eluent) without attempting to separate the individual compounds, which usually evolve with selenium extrusion.<sup>16,18</sup>

**$\text{CH}_3\text{Se}_z\text{CH}_3$ .** MeONa (4  $\text{cm}^3$ , 20 mmol),  $\text{N}_2\text{H}_4$  (5.5  $\text{cm}^3$ , 5.5 mmol), Se (3.16 g, 40 mmol),  $\text{CH}_3\text{I}$  (1.5  $\text{cm}^3$ , 24 mmol). Four products were identified from  $\delta_{\text{H}}$  (6 H, s) values listed in Table 5, yield 1.08 g (48% with respect to  $\bar{z} = 2.48$ ).  $\delta_{\text{H}}$  of the major product (63%) was the same as for a commercial sample of  $\text{CH}_3\text{Se}_2\text{CH}_3$ .  $\text{CH}_3\text{Se}_z\text{CH}_3$  ( $z = 2, 3$ ) were identified by GC-MS, this method being unsuccessful for higher polyselanes because of their decomposition. The two minor products (7, 2%) were believed to be  $\text{CH}_3\text{Se}_4\text{CH}_3$  and  $\text{CH}_3\text{Se}_5\text{CH}_3$  on the basis of their detection by  $^{77}\text{Se}$  NMR in  $\text{RSe}_z\text{R}$  mixtures ( $z = 2$ –5, R = octyl).<sup>16</sup> For  $z = 2$ ,  $m/z$  190 ( $^{80}\text{Se}$ ,  $\text{M}^+$ , 100%) and for  $z = 3$ ,  $m/z$  270 ( $^{80}\text{Se}$ ,  $\text{M}^+$ , 100%).

**$\text{PhCH}_2\text{Se}_z\text{CH}_2\text{Ph}$ .** MeONa (4  $\text{cm}^3$ , 20 mmol),  $\text{N}_2\text{H}_4$  (5.4  $\text{cm}^3$ , 5.4 mmol), Se (3.19 g, 40.4 mmol),  $\text{PhCH}_2\text{Br}$  (2.4  $\text{cm}^3$ , 19.8 mmol). Three products were identified from  $\delta_{\text{H}}$  (4 H, s)

values listed in Table 5, yield 2.72 g (78% with respect to  $\bar{z} = 2.17$ ).  $\text{PhCH}_2\text{Se}_2\text{CH}_2\text{Ph}$  (87%) was identified ( $^1\text{H}$  NMR and GC-MS) by comparison with a commercial sample. The tri- and tetraselanes can be proposed for the minor species (9, 4%) from previous  $^{77}\text{Se}$  NMR results.<sup>16</sup> The composition ( $\bar{z} = 2.17$ ) agrees with the elemental analysis of the mixture (C 48.10, H 3.79%) giving  $\text{PhCH}_2\text{Se}_{2.12}\text{CH}_2\text{Ph}$ . Although no specific  $\text{PhCH}_2\text{SeCH}_2\text{Ph}$   $^1\text{H}$  NMR signal was seen in the synthetic mixtures or  $\text{PhCH}_2\text{Se}_2\text{CH}_2\text{Ph}$  samples, this species was detected in both cases in the mass spectra, presumably arising as a result of selenium extrusion from benzylic di- (or poly-) selenides under thermal conditions.<sup>18</sup> For  $z = 1$ ,  $m/z$  262 ( $^{80}\text{Se}$ ,  $\text{M}^+$ , 10%), 91 (100) and 65 (15), for  $z = 2$ ,  $m/z$  342 ( $^{80}\text{Se}$ ,  $\text{M}^+$ , <2%), 91 (100) and 65 (20).

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