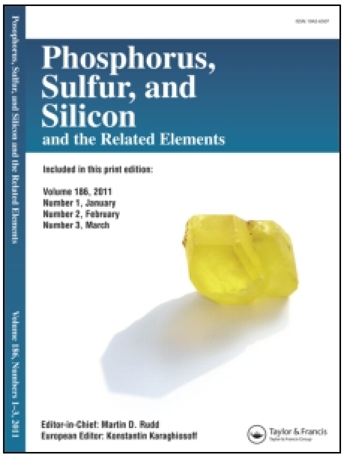

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HYDANTOIN DERIVATIVES. SYNTHESES AND INFRARED SPECTRA OF 5,5-DIMETHYLIMIDAZOLIDINES HAVING O, S OR SE ATOMS AT C-2 AND C-4

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HYDANTOIN DERIVATIVES. SYNTHESES AND INFRARED SPECTRA OF 5,5-DIMETHYLIMIDAZOLIDINES HAVING O, S OR SE ATOMS AT C-2 AND C-4

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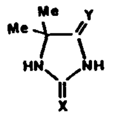
The syntheses of a complete series of 5,5-dimethylimidazolidines 2,4-disubstituted with chalcogen atoms (O, S and Se) are reported. Their infrared spectra (4000–250 cm^{-1}) are discussed on the basis of the selenation effect and the bands arising from —HN—CX—NH—CY— (X, Y = O, S, Se) groups are tentatively assigned.

INTRODUCTION

In the last years, we have been interested in the coordinating properties of the thio- and seleno-amido groups contained in several pentaatomic rings (i.e. pyrrolidine-, oxazolidine-, thiazolidine- and imidazolidine-2-thione or -selenone) towards metal ions[1–3] and molecular iodine.[4] Although the above compounds have various donor atoms, they always use the exo-atom in 2 (i.e. S or Se) to form the coordinative bond.[1–4]

Following our interest in this field, we are now considering the following 5,5-dimethylimidazolidines:



X	Y		X	Y	
O	O	**1**	S	S	**6**
S	O	**2**	Se	S	**7**
O	S	**3**	S	Se	**8**
Se	O	**4**	Se	Se	**9**
O	Se	**5**			

In these molecules, whose skeleton is practically planar,[5,6] the exo-atoms have different donor abilities and will compete in determining the coordinative bond.

Since the comparison of the infrared spectra between the free and bonded ligand is used in recognizing the coordination site, it is essential to have correct assignments of the bands of the groups interested in the coordination.

In this paper we report the infrared spectra of **1**–**9** in order to tentatively locate the bands related to the —HN—CX—NH—CY— groups.

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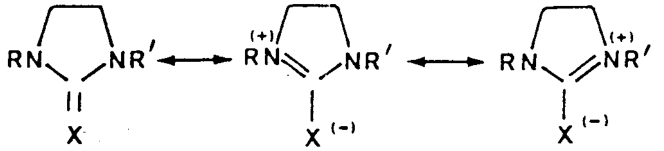
RESULTS AND DISCUSSION

It is well known that the carbonyl stretching vibrations fall in a well-defined range, usually without other vibrations, whereas the absorptions due to ν_{CS} and ν_{CSe} fall in a very wide range in the finger-print region, and couple with many other vibrations. For this reason contrasting assignments on $\rangle\mathrm{C{=}S}$ are often reported in literature for same molecules.

Our procedure[7] in dealing with this difficult problem consists in employing "selenation"[8] as the main tool for locating the $\rangle\mathrm{C{=}S}$ and $\rangle\mathrm{C{=}Se}$ modes. The procedure consists in the superimposition of the infrared spectra of two parent sulphur and selenium compounds. Normally, the spectra are very similar and only a few bands move towards lower wavenumbers in the selenium isologue. Clearly, the contributions of the $\rangle\mathrm{C{=}S}$ and $\rangle\mathrm{C{=}Se}$ modes must be retained by the shifting bands.

This kind of study has been applied to some imidazolidines-2-thione and -2-selenone, variously *N*,*N*′-disubstituted,[9,10] where the typical $\rangle\mathrm{C{=}S}$ and $\rangle\mathrm{C{=}Se}$ modes were located below 650 cm^{-1}. This was interpreted as being due to the prevailing contributions of the zwitterionic forms to the resonance (Scheme 1).



SCHEME 1

The discussion on the infrared spectra of **1**–**9** which follows will consider first the carbonyl stretching vibrations, then the effect of selenation at C-2 and C-4.

Carbonyl Stretching Vibrations

In Figure 1 the spectrum of **1** is reported together with that of imidazolidine-2,4-dione (hydantoin), on which a complete NCT analysis[11] has been carried out. Although the two compounds differ only as far as regards the methyl groups, their infrared spectra are fairly different in the finger-print region, and bands of imidazolidine-2,4-dione attributed to the common groups are absent in **1** (for example see the band at 690 cm^{-1}). Perhaps, it is the steric hindrance of the methyl groups that changes the crystal packing, thus producing strong variations in the infrared spectrum of **1**. As far as the ν_{CO} vibrations are concerned, **1** exhibits three strong bands at 1768, 1736 and 1708 cm^{-1}, whereas imidazolidine-2,4-dione has only two bands at 1775 and 1706 cm^{-1}, although the latter is very broad. The NCT calculation assigned the band at 1775 cm^{-1} to the C-2 carbonyl and that at 1706 to that of C-4. However, we retain that in **1**, the band at higher energy must be due to the C-4 carbonyl, whereas the other two should be attributed to the C-2 carbonyl, probably split by hydrogen bonding interaction. This attribution considers that the ν_{CO}'s for **2** and **4** (carbonyl at C-4) fall at 1742 and 1745 cm^{-1} respectively, while for **3** and **5** (carbonyl at C-2) they fall at 1717 and 1728 cm^{-1}.

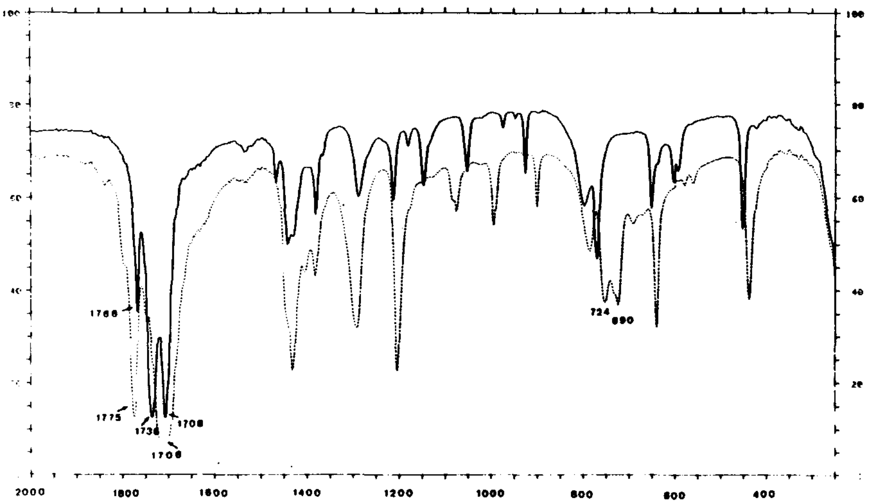


FIGURE 1 Superimposed spectra of imidazolidine-2,4-dione (---) and 5,5-dimethylimidazolidine-2,4-dione (—).

"Selenation" at C-2

In order to point out the effect of selenation at carbon-2, the superimposed spectra of the couples **2–4**, **6–7** and **8–9** having O, S and Se at C-4 respectively, are reported in Figures 2, 3 and 4. This superimposition shows that there is a very close similarity between the spectra of each sulphur compound and the selenium isologue over 600 cm^{-1}, while some differences are found in the low frequency region. All the spectra of each couple of compounds exhibit only a few discrepancies in intensity or in position in the finger print region, due to a secondary effect of selenation.[7] This is

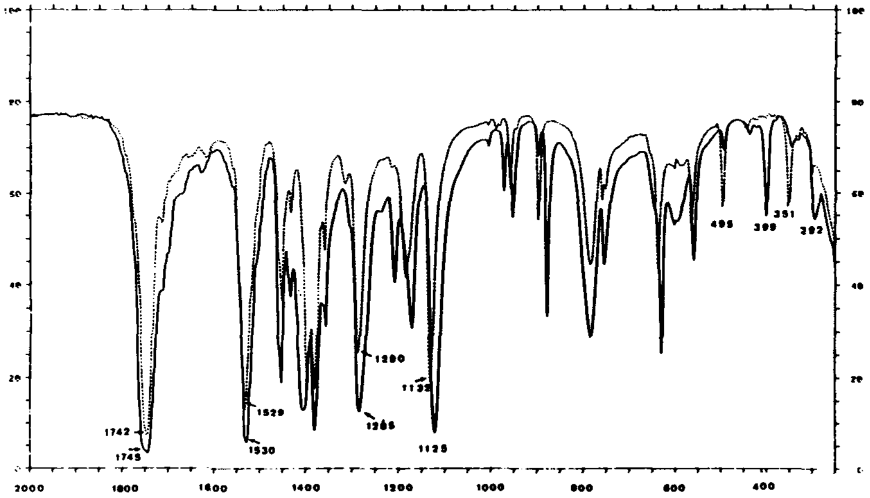


FIGURE 2 Superimposed spectra of **2** (---) and **4** (—).

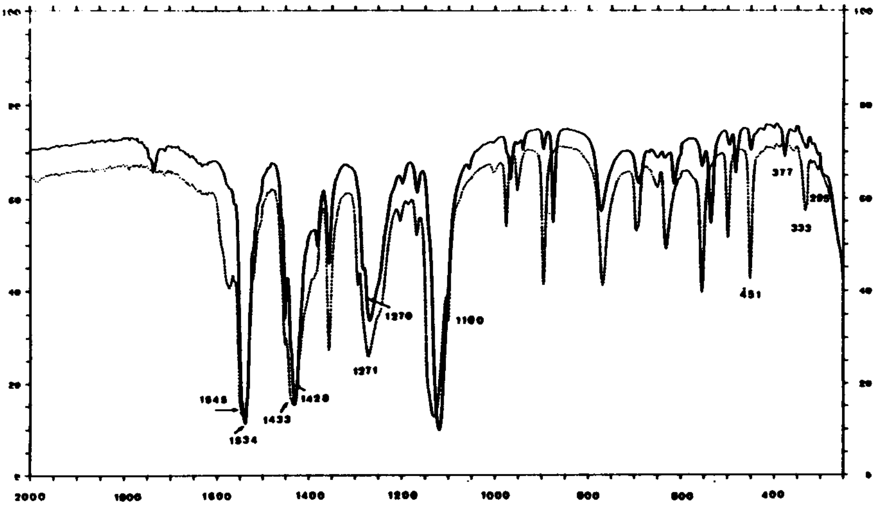


FIGURE 3 Superimposed spectra of **6** (---) and **7** (—).

not surprising since the simple substitution of NH with ND, promotes comparable shifts also in bands which do not have any contribution from the NH modes.[11,12] A further interesting observation could be made in examining Figures 3 and 4; in fact, the spectra of the four compounds are still very similar in the finger print region, except for the band at 1100 cm^{-1} in **6** and the bands at 1058 and 1057 cm^{-1} in **8** and **9** respectively. However, since selenation on carbon-2 does not move these bands, they can not be originated from the $\rangle C{=}S$ and $\rangle C{=}Se$ vibrations of carbon-2.

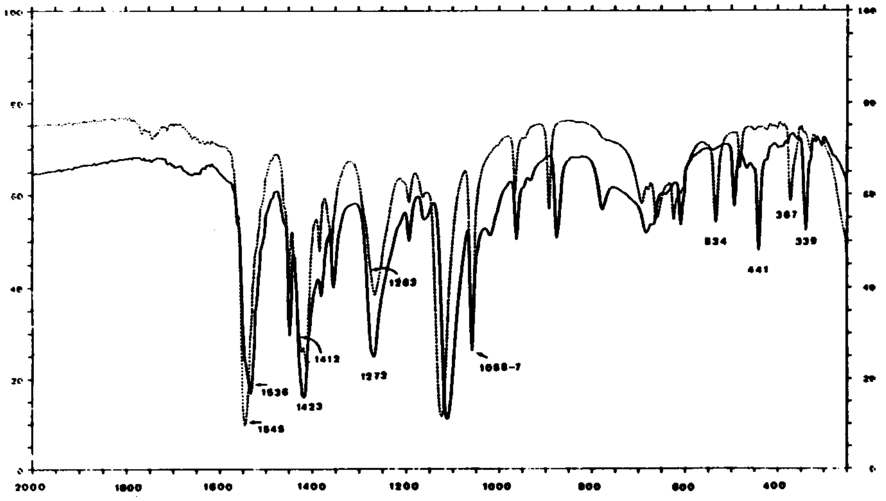
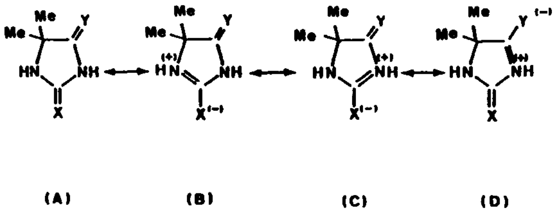


FIGURE 4 Superimposed spectra of **8** (---) and **9** (—).

Since the present interest is focused on the identification of the bands due to those groups involved in the coordination bond, we will restrict our discussion to some bands related to the —NH—CX—NH—CY— groups.

A typical infrared band of the amido, thio- and seleno-amido groups is that due to the C$\overset{\cdots}{-}$N bond, which is often coupled with the δ_{NH} deformation. Its position in the spectrum depends on the double bond character and therefore on its neighbouring atoms. In the previously studied pentaatomic rings, the position of this band has been proved to depend on the contribution to the resonance of the zwitterionic forms, as reported for the imidazolidine series (Scheme 1). The behaviour of this band under coordination is useful in assigning the coordination *via* X.[1-3] In Scheme 2, we report all the important resonance forms for the title compounds:



SCHEME 2

We can see three different C$\overset{\cdots}{-}$N bonds, to which three ν_{CN} absorptions should correspond. In particular, the C(2)–N(1) bond would have higher double bond character, as a consequence of the fact that the electron-releasing of N-1 occurs only towards C-2, whereas that of N-3 is direct towards C-2 and C-4. On the other hand, this agrees with the structural data for 2-thiohydantoin[5] and 5,5-diphenylhydantoin,[6] where the CN bond distances increase in the order N(1)–C(2), N(3)–C(4) and C(2)–N(3). We believe that the band at ~ 1540 cm^{-1} present in the three considered couples can be attributed to a prevailing $\nu_{N(1)-C(2)}$ contribution.[13] The assignment of the other two vibrations is difficult, because they fall in a frequency region which is very rich in bands. However, we hypothesize that they may contribute to the bands at 1433 and 1271 cm^{-1} for **6** and at 1428 and 1270 cm^{-1} for **7** (see Figure 3), at 1412 and 1263 cm^{-1} for **8** and at 1423 and 1273 cm^{-1} for **9** (see Figure 4). In the same frequency range, **2** and **4** show several bands, some of which must be attributed to the C$\overset{\cdots}{-}$N vibrations. Very probably, the bands at 1132 and 1290 cm^{-1} in the spectrum of **2** and at 1121 and 1285 cm^{-1} in that of **4** may retain some ν_{CN} contributions.

Since no appreciable variations are present in the examined isologues up to 600 cm^{-1}, the characteristic vibrations of $>$C=S and $>$C=Se at carbon-2 must be located below this frequency. An inspection of Figure 2 shows that the bands at 495 and 351 cm^{-1} in the spectrum of **2** strongly decrease in intensity in **4**, whereas new bands at 399 and 292 cm^{-1} appear in the latter. Clearly, these bands are mainly originated from the stretchings and deformations of $>$C=S and $>$C=Se. Analogous attributions can be made for the bands at 451 and 333 cm^{-1} in **6**, shifted to 377

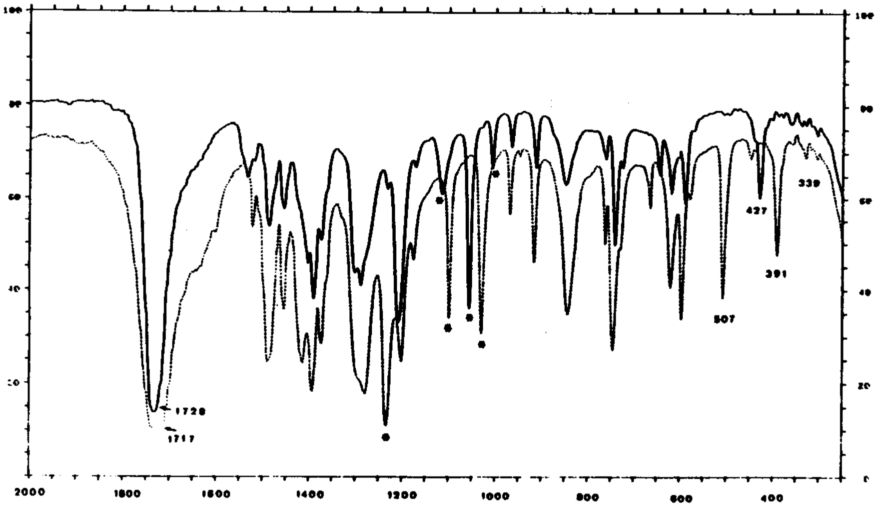


FIGURE 5 Superimposed spectra of **3** (---) and **5** (—).

and 295 cm^{-1} in **7** (see Figure 3), and for the bands at 534 and 367 cm^{-1} in **8** which appear at 441 and 339 cm^{-1} in **9** (see Figure 4).

"Selenation" at C-4

The superimposed spectra of **3**, **6**, and **7** together with their parent selenium compounds **5**, **8** and **9**, having a selenium instead of a sulphur atom at C-4, are reported in Figures 5, 6 and 7.

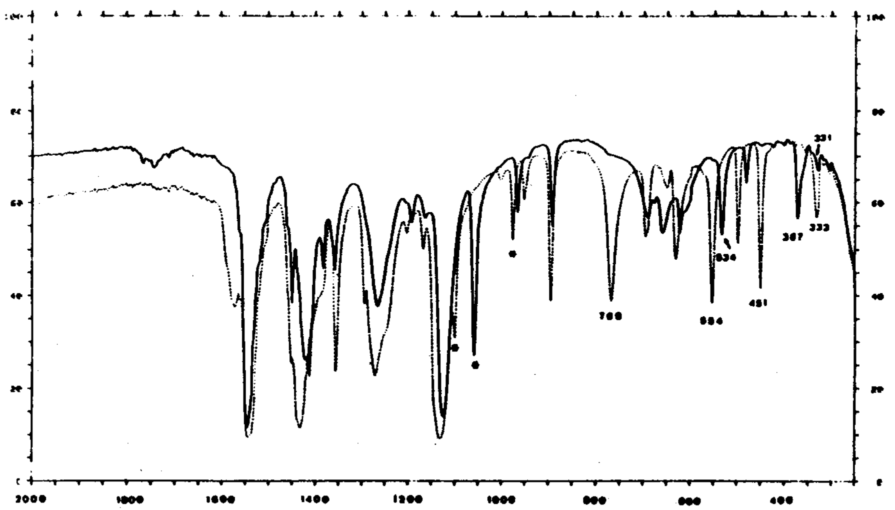


FIGURE 6 Superimposed spectra of **6** (---) and **8** (—).

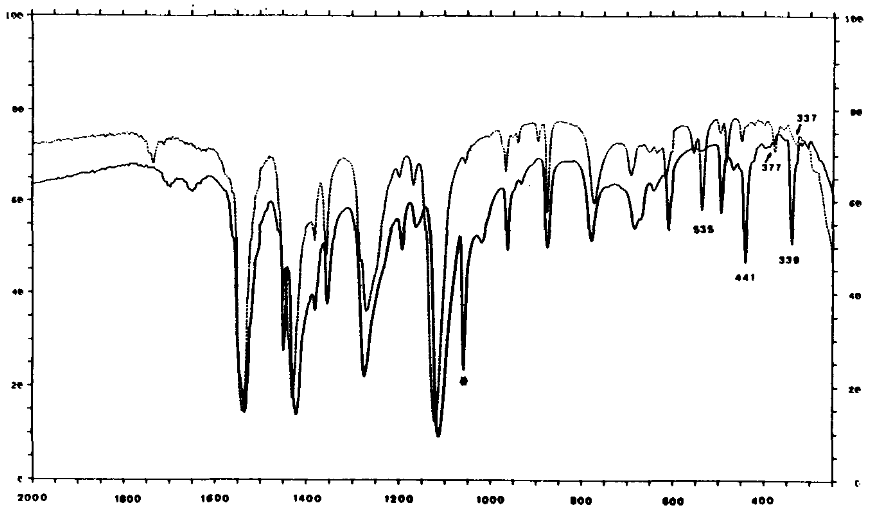


FIGURE 7 Superimposed spectra of **7** (---) and **9** (—).

In contrast with the finding for the selenation at C-2, in the finger-print region the spectra of the isologue couples differ in one band for the couple 7–9 in three bands for **6–8** and in several bands for **3–5** (labelled bands). Very probably all these absorptions retain contributions of the >C=S and >C=Se modes, with the exception of the band at 768 cm^{-1} of **6**, which is absent in **8** (see Figure 6) and disappears in the N-d$_2$ derivative. Hence, this clearly shows that it must be classified as a Δ_{NH} out-of-plane deformation. The analogous absorption of **8** should be overlapped with the bands falling within 600–700 cm^{-1}.

However, the selenation at C-4 is better shown in the low frequency region, where appreciable shifts occur in the selenium derivatives. As shown in Figure 5, the >C=S modes originate the bands at 507 and 391 cm^{-1} of **3** and the corresponding >C=Se modes fall at 427 and 339 cm^{-1} in **5**.

An inspection of Figure 6 shows that the band at 451 cm^{-1}, previously attributed to the >C=S modes (see Selenation at C-2) in **6**, falls at 367 cm^{-1} in **8**, thus confirming that the assignment is correct. The band in **6** at 333 cm^{-1}, previously attributed to >C=S, is still present in **8** as a weak band at 331 cm^{-1}. This is justified because **8** also retains a >C=S bond. Moreover, since the bands at 554 and 534 cm^{-1} in **6** and **8** respectively are absent in **9**, they must be attributed to the >C=S vibrations. A further confirmation of this is found in **7**, where an analogous band at 535 cm^{-1} is present (see Figure 7). From this figure, we must attribute the bands at 441 and 339 cm^{-1} to the >C=Se modes, since at the same frequencies compound **7** has bands of very low intensities.

On the other hand, the comparison of **6** and **9**, where a double selenation has been made, shows that the bands at 441 and 339 cm^{-1} in **9** come from 554 and 451 cm^{-1} in **6**. All the assignments, together with all the other bands falling within 600–250 cm^{-1}, are collected in Table I.

TABLE I

Infrared bands within 600–250 cm^{-1} (solid phase) and >C=S and >C=Se mode assignments

Compound	X	Y	>C=S	>C=Se	Other vibrations
2	S	O	495ms, 351ms		586w, 563ms, 444w, 300w, 282w
3	O	S	507m, 391mw		597m, 580sh, 450sh, 437w, 330mw
4	Se	O		399m, 292w	600w, 558m, 492vw, 435vw, 344vw
5	O	Se		427m, 339w	588m, 568sh, 491vw, 430sh, 363w
6	S	S	554m, 451m, 333mw		499mw
7	Se	S	535ms, 439vw, 337vw	377m, 295w	482m
8	S	Se	534m, 331w	367m	481mw
9	Se	Se		441mw, 339m	494w

EXPERIMENTAL

5,5-Dimethylimidazolidine-2,4-dione (**1**), -2-thione-4-one (**2**) and -2,4-dithione (**6**) have been prepared and purified according to literature.[14–16]

5,5-dimethylimidazolidin-2-one-4-thione (**3**) was prepared by refluxing 4.7 g of **1** (0.037 moles) with 3.3 g of P_2S_5 (0.015 moles) in 50 ml of dioxane for 1 hour. After complete distillation of the solvent, the residue was crystallised from ethanol. The white crystalline **3**, reported in ref. 17 as patent, has m.p. 237°C. Anal. Calcd. for $C_5H_8N_2OS$: C, 41.6; H, 5.6; N, 19.4; Found: C, 41.7; H. 5.6; N, 19.4.

5,5-Dimethylimidazolidine-2-selenone-4-one (**4**) was prepared by refluxing 1.1 g of **2** (0.0074 moles) with 0.46 ml of methyl iodide (0.0074 moles) in 30 ml of methanol for 1 hour. After cooling, the *S*-methiodide of **2** was precipitated and then dried. To a solution containing 0.96 g of the methiodide (0.0033 moles) in 20 ml of methanol, a solution of sodium hydrogen selenide (0.0066 moles) in absolute ethanol was added.[18] After a night at room temperature, the solution was acidified with 0.2 ml of acetic acid (0.0033 moles) added to 20 ml of water and distilled up to removal of the alcohol. The aqueous solution was filtered on paper to eliminate the grey selenium and then extracted with chloroform, from which **4** was precipitated by adding petroleum ether 40–60°. M.p. 213°C. Anal. Calcd. for $C_5H_8N_2OSe$: C, 31.4; H, 4.2; N, 14.7. Found: C, 31.5; H, 4.5; N, 14.6.

5,5-Dimethylimidazolidine-2-one-4-selenone (**5**) was prepared by hydrolizing the *Se*-methiodide of **9** by adding 10 ml of water with a few drops of acetic acid. After distillation,[19] the aqueous solution was extracted with chloroform, from which **5** was obtained as **4**; m.p. 245°C. Anal. Calcd. for $C_5H_8N_2OSe$: C, 31.4; H, 4.2; N, 14.7. Found: C, 31.6; H, 4.5; N, 14.7.

5,5-Dimethylimidazolidine-2-selenone-4-thione (**7**) was obtained as **4**. Analysis of **7**. Calcd. for $C_5H_8N_2SSe$: C, 29.0; H, 3.9; N, 13.5. Found: C, 29.1; H, 4.0; N, 13.6. M.p. 165°C.

5,5-Dimethylimidazolidine-2-thione-4-selenone (**8**) was prepared by bubbling H_2Se in a suspension of 1 g of 5,5-dimethylimidazolidine-2-thione-4-imino (0.007 moles), obtained as ref. 15. After distillation, **8** was obtained by treating the residue with chloroform and petroleum ether 40–60°. M.p. 137–8°C. Anal. Calcd. for $C_5H_8N_2SSe$: C, 29.0; H, 3.9; N, 13.5. Found: C, 29.0; H, 3.9; N, 13.8.

5,5-Dimethylimidazolidine-2,4-diselenone (**9**) was prepared by refluxing 1.7 g of carbon diselenide (0.01 moles) in 30 ml of methylene chloride and 0.84 g of α-aminoisobutyronitril (0.01 moles) for 24 hours. After concentration of the solution, **9** was precipitated by adding petroleum ether 40–60°. M.p. 160°C dec. Anal. Calcd. for $C_5H_8N_2Se_2$: C, 23.6; H, 3.2; N, 11.0. Found: C, 24.0; H, 3.3; N, 11.3.

The infrared spectra were recorded as KBr discs or Nujol mulls between CsI pellets on a Perkin Elmer 983 instruments.

ACKNOWLEDGMENTS

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