The Synthesis of Heteroaromatic Cations Containing Sulfur or Selenium Atoms

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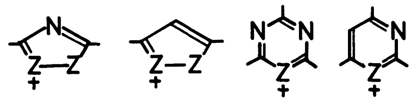
Synopsis. The dialkylamino-substituted heteroaromatic cations, such as 1,2,4-diselenazolium, 1,2-diselenolium, 1,3,5-selenadiazinium, and 1,3-selenazinium cations, were newly synthesized, and their *S*-analogs were also obtained through similar procedures.

Heteroaromatic cations containing sulfur atoms, **1**, **3**, **5**, and **7**, (Fig. 1), have been accessible; they are very reactive toward various nucleophiles to give many kinds of heterocyclic derivatives.[1—5] On the other hand, the synthetic routes of heteroaromatic cation compounds containing selenium atoms, such as **2**, **4**, **6**, and **8**, (Fig. 1), are so far unexplored.

Since it is of interest to examine the reactivities of these seleno-compounds and to compare them with the corresponding *S*- and *Se*-analogs regarding their chemical and physical properties, we attempted to synthesize these seleno-compounds, and have succeeded, as described below.



Z = S : 1 3 5 7
Z = Se: 2 4 6 8

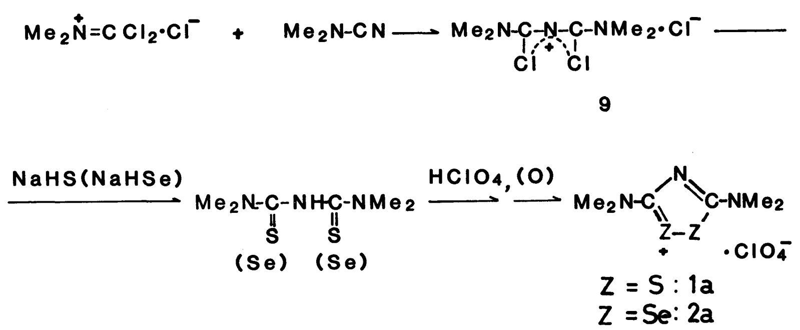
Fig. 1. Heteroaromatic cations containing *S*- or *Se*-atoms.

3,5-Bis(dimethylamino)-1,2,4-dithiazolium perchlorate (**1a**) and the corresponding *Se*-analog (**2a**) were prepared in the manner shown in Scheme 1.

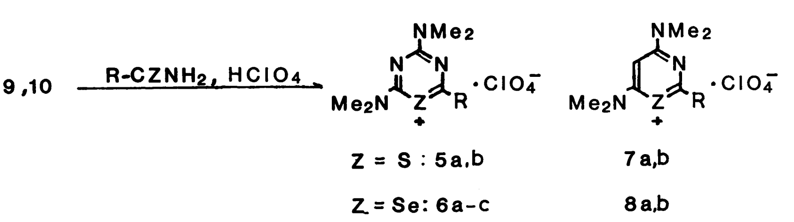
1,3-Bis(dimethylamino)-1,3-dichloro-2-azapropenylium chloride (**9**), obtained by treating (dichloromethylene)dimethylammonium chloride with dimethylcyanamide,[6] afforded tetramethyldithiobiuret by treating it with sodium hydrogensulfide. Then, without separating the biuret, a successive addition of perchloric acid and oxidation by hydrogen peroxide or *m*-chloroperbenzoic acid led to **1a** almost quantitatively. Similarly, the use of sodium hydrogen selenide, instead of sodium hydrogensulfide, gave **2a** as a stable white crystalline salt in 51 % yield. The results of their yields, mps, elemental analyses, and UV spectral data are summarized in Table 1.

3,5-Bis(dimethylamino)-1,2-dithiolium perchlorate (**3a**) and the 1,2-selenolium perchlorate (**4a**) were prepared when 1,3-bis(dimethylamino)-1,3-dichloropropenylium chloride[7] (**10**) was treated in a similar manner as **1a** and **2a**. Their characterization data are collected in Table 1.

As for the six-membered heteroaromatic cations, **5**, **6**, **7**, and **8** (Fig. 1), 2-substituted 4,6-bis(dimethylamino)-1,3,5-thiadiazinium perchlorates (**5a, b**) and the corresponding 1,3,5-selenadiazinium perchlorates (**6a—c**) were prepared by the reaction of **9** with thiocarbamoyl or selenocarbamoyl compounds, respectively (see Scheme 2). Similarly, the 1,3-thiazinium perchlorates (**7a, b**) and the 1,3-selenazinium perchlorates (**8a, b**) were also derived from **10** in good yields.



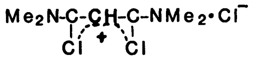
Scheme 1.



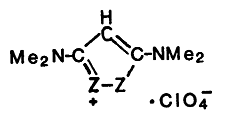
Scheme 2.

Table 1. Preparation of Dimethylamino-Substituted Heteroaromatic Cations, **1a**—**8b**

Compd	R-	Z	Mp θ_m/°C	Yield/%	λ_{max}/nm (ε)	Found (Calcd)/% C	H	N
1a		*S*	210	95	266 (25000)	24.62 (24.87)	4.07 (4.17)	14.53 (14.50)
2a		*Se*	239	51	275 (22900)	18.78 (18.79)	3.15 (3.15)	10.96 (10.96)
3a		*S*	260	78	312 (33000)	29.09 (29.12)	4.47 (4.54)	9.67 (9.70)
4a		*Se*	212	43	322 (32000)	21.72 (21.98)	3.30 (3.42)	7.26 (7.32)
5a	$(CH_3)_2N$-	*S*	>300	73	275 (22500)	32.39 (32.98)	5.52 (5.53)	21.44 (21.36)
5b	Ph-	*S*	286	47		43.21 (43.28)	4.72 (4.75)	15.62 (15.53)
6a	$(CH_3)_2N$-	*Se*	>300	63	285 (24900)	32.26 (32.14)	5.19 (5.12)	14.95 (14.99)
6b	Ph-	*Se*	281	44		38.25 (38.30)	4.17 (4.20)	13.85 (13.74)
6c	$(CH_2)_4N$-	*Se*	294	53		32.95 (32.97)	5.06 (5.03)	17.47 (17.48)
7a	$(CH_3)_2N$-	*S*	>300	55	332 (19400)	36.79 (36.75)	5.84 (5.86)	17.24 (17.15)
7b	Ph-	*S*	303	64		46.73 (46.73)	4.97 (5.04)	11.58 (11.68)
8a	$(CH_3)_2N$-	*Se*	>300	51	341 (20100)	31.96 (32.14)	5.06 (5.12)	14.80 (14.99)
8b	$(CH_2)_4N$-	*Se*	>300	60		36.12 (36.02)	5.23 (5.30)	14.03 (14.02)



10



Z = S : 3a
Z = Se : 4a

The synthetic methods of heteroaromatic cations containing selenium atoms, as well as sulfur atoms, have thus been developed systematically, and their procedures could be performed at room temperature.

The results (summarized in Table 1) show that all *S*-analogs have better yields than the corresponding *Se*-analogs, and that, in many cases, they have a higher melting point. These facts suggested that the *S*-analogs are more stable than the corresponding *Se*-analogs.

Giving attention to the spectral data of dimethylamino-substituted cations, **1a**—**8a**, we found several interesting points to be noted. Namely, the IR spectra of **1a** and its *Se*-analog, **2a**, were almost the same, (Fig. 2); these phenomena were also observed between the other *S* and *Se*-analogs: (**3a**, **4a**), (**5a**, **6a**), and (**7a**, **8a**), respectively. In their UV spectra, the *Se*-analogs (**2a**, **4a**, **6a**, and **8a**), have their absorption maxima shifted to about 10 nm longer than that of the corresponding *S*-analogs. In the ^{1}H NMR spectra of **1a** and **2a**, the signals assignable to the dimethylamino group appear as two peaks in the range δ=3.281—3.407 at room temperature. This fact indicates that the rotation of their dimethylamino groups around the C(3)-N bond is restricted or stopped. Similar phenomena were also observed among **5a**—**8a**. A NMR study of these phenomena will be further discussed in our next report.

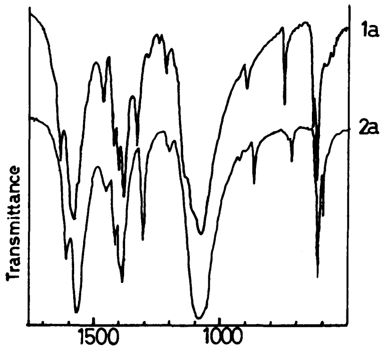


Fig. 2. IR spectra of **1a** and **2a**.

Experimental

All melting points are uncorrected. The IR spectra were recorded on a JASCO A-302 spectrometer using KBr disks. The UV spectra were taken in ethanol solutions using a Hitachi 200-10 spectrometer. The ^{1}H NMR spectra were measured on JEOL GX400 (399.65 MHz) spectrometer; solvent: DMSO-d_6, ca 7 mM (1 M=1 mol dm^{-3}), δ: ppm from TMS.

3,5-Bis(dimethylamino)-1,2,4-dithiazolium Perchlorate (1a) and the 1,2,4-Diselenazolium Perchlorate (2a). A solution of 1,3-bis(dimethylamino)-1,3-dichloro-2-azapropenylium chloride (**9**) in dichloromethane (20 ml) was previously prepared by mixing dimethylcyanamide (0.70 g, 0.01 mol) and (dichloromethylene)dimethylammonium chloride (1.63 g, 0.01 mol).[6)] Then, the solution of **9** was added to a solution of sodium hydrogensulfide (1.70 g, 0.03 mol) in ethanol (20 ml) drop by drop for 1 h with stirring; successively, 70% perchloric acid (2 ml) and 30% hydrogen peroxide (1 ml) or *m*-chloroperbenzoic acid (1.73 g, 0.01 mol) were added to it at room temperature. After the solvent was distilled away under reduced pressure, the residue was dissolved in hot acetonitrile (20 ml), and filtered in order to remove any insoluble substances. White crystals of **1a** were obtained from the mixed solution of the acetonitrile filtrate and the same volume of ethyl acetate after cooling overnight at 0—5 °C. Its *Se*-analog, **2a**, was obtained by a similar manner as follows. The solution of **9** was slowly added to a solution of sodium hydrogenselenide, which was obtained by the reaction of selenium powder (2.40 g, 0.03 mol) with sodium boron tetrahydride (1.15 g, 0.03 mol) in absolute ethanol (70 ml) under an argon atomosphere;[8] then, the reaction mixture was treated in the same procedure as described in **1a**. Their yields, mps, UV data, and elemental analyses results are listed in Table 1, and their IR spectra are shown in Fig. 2.

^{1}H NMR, **1a**: $\delta=3.281$ and 3.395; **2a**: $\delta=3.286$ and 3.407.[9)]

3,5-Bis(dimethylamino)-1,2-dithiolium Perchlorate (3a) and the 1,2-Diselenolium Perchlorate (4a). The solution of 1,3-bis(dimethylamino)-1,3-dichloropropenylium chloride[7)] (**10**) (2.32 g, 0.01 mol) in dichloromethane (20 ml) was treated with sodium hydrogensulfide or sodium hydrogenselenide using similar procedures as in the cases of **1a** and **2a**. Their characterization data are shown in Table 1.

3a IR: 3100, 1558, 1413, 1276, 1064, and 617 cm^{-1};
^{1}H NMR: $\delta=3.264$ and 6.176.
4a IR: 3080, 1551, 1411, 1290, 1085, and 619 cm^{-1};
^{1}H NMR: $\delta=3.269$ and 6.637.

2-Substituted 4,6-Bis(dimethylamino)-1,3,5-thiadiazinium Perchlorates (5a, b) and the 1,3,5-Selenadiazinium Perchlorates (6a—c). To the solution of **9** (0.01 mol) in dichloromethane (20 ml) was added 0.01 mol of thiocarbamoyl or selenocarbamoyl compounds with stirring at room temperature for 1 h; 70% perchloric acid (1 ml) was added to it. The resulting mixture was evaporated and recrystallized from ethanol to give **5a, b** and **6a—c**, respectively.

5a IR: 1603, 1577, 1551, 1413, 1176, 1091, and 619 cm^{-1};
^{1}H NMR: $\delta=3.279$, 3.285, and 3.332.
6a, IR: 1621, 1580, 1545, 1411, 1197, 1091, and 619 cm^{-1};
^{1}H NMR: $\delta=3.332$ and other very broad signals.

2-Substituted 4,6-Bis(dimethylamino)-1,3-thiazinium Perchlorates (7a, b) and the 1,3-Selenazinium Perchlorates (8a, b). The solution of **10** (0.01 mol) in dichloromethane (20 ml) was treated with 0.01 mol of thiocarbamoyl or selenocarbamoyl compounds and perchloric acid (as mentioned above). The resulting mixtures were recrystallized from ethanol to afford **7a, b**, and **8a, b**. Their characterization data are shown in Table 1.

7a, IR: 1613, 1577, 1545, 1414, 1317, 1089, and 617 cm^{-1};
^{1}H NMR: $\delta=3.285$, 3.323, 3.352, and 3.368.
8a, IR: 1603, 1558, 1536, 1409, 1315, 1088, and 615 cm^{-1};
^{1}H NMR: $\delta=3.234$, 3.285, and 3.338.

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9) The results of the NMR spectra analyses of these dimethylamino signals will be submitted somewhere soon.