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ATTEMPT TO SYNTHESIZE SELENIUM AND TELLURIUM ANALOGS  
OF 1,5-BIS(ARYL)-2,4-DIAZA-1,3,5-TRITHIA-2,3-PENTADIENES

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UDC 542.91:547.318:546.23

Acyclic azathienes have been thoroughly studied and have found wide use in organic synthesis. The study of acyclic azaselenes and azatellurenes has only begun [1]. The purpose of the present work was to attempt the synthesis of the Se and Te analogs of 1,5-bis(aryl)-2,4-diaza-1,3,5-trithia-2,3-pentadienes.

According to the data of [2], a convenient synthesis of 1,5-bis(aryl)-2,4-diaza-1,3,5-trithia-2,3-pentadienes would be the reaction of aromatic sulfenyl chlorides with 1,3-bis(trimethylsilyl)-1,3-diaza-2-thiaallene (I). Actually, compound (I) reacts readily with phenyl- and pentafluorophenylsulfenyl chlorides to form 1,5-bis(phenyl)- and 1,5-bis(pentafluorophenyl)-2,4-diaza-1,3,5-trithia-2,3-pentadienes (II) and (III), which were previously synthesized by other methods [1]. But while (I) and phenylselenenyl chloride react under mild conditions to form 1,5-bis(phenyl)-2,4-diaza-3-thia-1,5-diselena-2,3-pentadiene (IV) in high yield, the only identifiable product of the reaction of (I) with pentafluorophenylselenenyl chloride is decafluorodiphenyl diselenide. The reaction of (I) with phenyltellurenyl bromide (the chloride is not described) gives a product of empirical formula  $C_6H_5BrN_2S_2 \cdot Te$  (V), probably with a heterocyclic structure.

A general approach to the synthesis of 1,5-bis(aryl)-2,4-diaza-1,3,5-trithia-2,3-pentadienes and their selenium and tellurium analogs might be the reaction of N-arylchalcogenylhexamethyldisilazanes with chalcogen tetrahalide. From lithium N,N-bis(trimethylsilyl)amide and arylchalcogenyl halides, N-phenylsulfenyl-, N-pentafluorophenylsulfenyl-, N-phenylselenenyl-, and N-pentafluorophenylselenenylhexamethyldisilazanes (VI)-(IX) were synthesized ((VI) and (VII) have been described previously [3-5]). N-Phenyltellurenyl hexamethyldisilazane could not be synthesized by this method. Nor was it possible to cleave the Te-Te bond of diphenyl ditelluride by the action of sodium N,N-bis(trimethylsilyl)amide in boiling benzene (in contrast to the S-S bond of diphenyl disulfide [3]).

The reaction of (VIII) with  $SeCl_4$  gives two products: diphenyl diselenide and an unidentified material that decomposes explosively when separated from the reaction mixture. In this connection other reactions of (VI)-(IX) with selenium and tellurium tetrahalides were not carried out.

Compound (VII) does not react with  $SF_4$  in THF at  $-20^\circ$ . According to [6], under similar conditions  $SF_4$  can be replaced by  $SCl_2$  or  $S_2Cl_2$ . But the reactions of compounds (VII)-(IX) with  $SCl_2$  give cyclotetraazathiene  $(SN)_4$  and diaryl dichalcogenides.

From the UV spectra of (II) and (IV) it follows that replacement of S by Se at positions 1 and 5 of the azathiene chain of (II) increases the energy of transition to the first excited state;  $\lambda_{max}$  of the longwave band shifts from 460 to 392 nm. A similar hypsochromic shift takes place when H is replaced by F in (II); in the spectrum of (III) the long-wave absorption maximum appears at 402 nm.

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TABLE 1.  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{19}\text{F}$ ,  $^{29}\text{Si}$ , and  $^{77}\text{Se}$  NMR Spectra of Synthesized Compounds\*

| Com-<br>pound | NMR spectrum, $\delta$ , ppm |      |                 |       |       |                 |     |      |                  |                  |               |        |      | $\sigma_I^\dagger$ | $\sigma_R^\ddagger$ |  |
|---------------|------------------------------|------|-----------------|-------|-------|-----------------|-----|------|------------------|------------------|---------------|--------|------|--------------------|---------------------|--|
|               | $^1\text{H}$                 |      | $^{13}\text{C}$ |       |       | $^{19}\text{F}$ |     |      | $^{29}\text{Si}$ | $^{77}\text{Se}$ | $\Delta_{43}$ |        |      |                    |                     |  |
|               | Ph $\dagger$                 | Me   | o-              | m-    | Me    | hypso           | o-  | m-   |                  |                  |               | p-     |      |                    |                     |  |
| (I)           |                              | 0,21 |                 |       |       |                 |     |      |                  |                  |               |        |      |                    |                     |  |
| (II)          | 7,37                         |      | 124,5           | 129,5 | 127,2 | 138,0           |     | 30,3 | 2,2              | 13,8             |               |        | -2,3 |                    |                     |  |
| (III)         |                              |      | 146,3           | 138,0 | 143,7 | 108,5           |     |      |                  |                  |               |        | 4,5  | 0,25               | 0,01                |  |
| (IV)          | 7,37                         |      | 127,2           | 129,6 | 129,0 | 138,8           |     |      |                  |                  |               | 984 ** |      |                    |                     |  |
| (V)           | 7,06                         | 0,19 | 120,8           | 127,8 | 123,6 | 144,7           | 4,5 |      |                  |                  |               |        | -4,2 |                    |                     |  |
| (VI)          |                              | 0,33 | 143,9           | 137,4 | 139,3 | 118,4           | 0,8 | 23,5 | 0,0              | 4,9              |               |        | -2,3 | 0,14               | -0,13               |  |
| (VIII)        | 7,33                         | 0,34 | 125,1           | 128,1 | 127,4 | 131,7           | 1,9 |      |                  |                  |               | 684    | -0,7 |                    |                     |  |
| (IX)          |                              | 0,27 | 145,0           | 137,5 | 140,3 | 110,0           | 4,8 | 31,4 | 0,9              | 7,5              |               |        | -1,4 | 0,26               | -0,12               |  |

\*Conditions for recording spectra -  $^1\text{H}$ : compounds (I), (VI), (IX), solution in  $\text{CCl}_4$ ;  $^{13}\text{C}$ : (VI)-(IX), pure liquid; (II)-(IV), solution in  $\text{CHCl}_3$ ;  $^{19}\text{F}$ : (VII), (IX), pure liquid; (III), solution in  $\text{CCl}_4$ ;  $^{29}\text{Si}$ : (VI)-(IX), pure liquid;  $^{77}\text{Se}$ : (VIII), (IX), pure liquid; (IV), solution in  $\text{CHCl}_3$ .

†Location of center of multiplet.

‡Taft constants of substituents in aromatic rings calculated from XC of  $^{19}\text{F}$  NMR according to [14].

\*\*Signal width of ~4 kHz at half-height is apparently evidence for isomer mixture in solution, e.g., with cis-, trans-, and trans-trans disposition of phenylselenenyl groups with respect to NSN groups.

TABLE 2. Properties of Synthesized Compounds

| Com-<br>pound | Yield, % | M.p. or b.p.,<br>$^\circ\text{C}$ (p, mm<br>Hg) | Found, % |      |      |       |        |   |   | Calculated, % |       |        |      |       |  |       |
|---------------|----------|---|----------|------|------|-------|--------|---|---|---------------|-------|--------|------|-------|--|-------|
|               |          |   | C        |      |      | H     |        | N |   | S             |       | F (Br) |      |       |  |       |
|               |          |   | C        | H    | N    | S     | F (Br) | C | H | N             | S     | F (Br) |      |       |  |       |
| (IV)          | 80       | 73-74   | 38,43    | 3,22 | 7,45 | 8,21  |        |   |   |               | 38,71 | 2,89   | 7,35 | 8,60  |  |       |
| (V)           |          | 201-202   | 18,59    | 4,46 | 7,02 | 18,32 |        |   |   |               | 19,12 | 4,33   | 7,43 | 16,99 |  |       |
| (VIII)        | 67       | 90-91(1)  | 45,31    | 7,39 | 4,52 |       |        |   |   |               | 45,57 | 7,28   | 4,43 |       |  |       |
| (IX)          | 73       | 82-83(1)  | 35,23    | 4,12 | 3,11 |       |        |   |   |               | 35,47 | 4,43   | 3,45 |       |  | 23,40 |

Empirical formula  
 $\text{C}_{12}\text{H}_{10}\text{N}_2\text{SSe}_2$   
 $\text{C}_6\text{H}_6\text{BrN}_2\text{S}_2\text{Te}$   
 $\text{C}_{12}\text{H}_{23}\text{NSeSi}_2$   
 $\text{C}_{12}\text{H}_{18}\text{F}_5\text{NSeSi}_2$

From the  $^{13}\text{C}$  NMR data (Table 1), using the  $\Delta_{43}$  criterion, it follows that, in the compounds studied, except for (III), the chalcogen-nitrogen groups are weak  $\pi$ -donors with respect to the aromatic ring. Replacement of S by Se decreases the absolute value of  $\Delta_{43}$ , while replacement of H by F in (II) changes the direction of the mesomeric effect; in (III) the azathiene grouping, judging from  $\Delta_{43}$ , shows weak  $\pi$ -acceptor properties or, as follows from the value of the  $\sigma_{\text{R}}^0$  constant (see Table 1), essentially does not interact with the pentafluorophenyl ring by a mesomeric mechanism.

#### EXPERIMENTAL

NMR spectra were recorded as follows:  $^1\text{H}$  and  $^{19}\text{F}$  on a Varian A56/60A spectrometer (60 and 56.4 MHz, respectively);  $^{13}\text{C}$  on a Bruker CXP-200 pulsed spectrometer (50.323 MHz);  $^{29}\text{Si}$  and  $^{77}\text{Se}$  on a Bruker CXP-300 pulsed spectrometer (59.618 and 57.265 MHz, respectively); relaxant, chromium acetylacetonate added to solutions. Standards: internal, TMS ( $^1\text{H}$ ,  $^{13}\text{C}$ ) and  $\text{C}_6\text{F}_6$  ( $^{19}\text{F}$ ); external, TMS ( $^{29}\text{Si}$ ) and dimethyl selenide ( $^{77}\text{Se}$ ). UV spectra were recorded with a Beckman DU-8 spectrophotometer in  $\text{CHCl}_3$ .

Syntheses were carried out in absolute solvents in an argon atmosphere. Properties of synthesized compounds are shown in Table 2, NMR spectral data in Table 1. Diaryl dichalcogenides were purified by recrystallization and identified by melting point and IR spectrum (cf. [8-10]).

1,3-Bis(trimethylsilyl)-1,3-diaza-2-thiaallene (I) was synthesized according to [11], but instead of  $\text{NaN}(\text{SiMe}_3)_2$  the lithium derivative was used; yield 63%.

1,5-Bis(phenyl)-2,4-diaza-3-thia-1,5-diselena-2,3-pentadiene (IV). To a stirred solution of 1.03 g (5 mmole) of (I) in 10 ml of  $\text{CH}_2\text{Cl}_2$  at  $-30^\circ\text{C}$  was added dropwise a solution of 1.93 g (10 mmole) of phenylselenenyl chloride in 15 ml of  $\text{CH}_2\text{Cl}_2$ . Cooling was removed and stirring was continued for 1 h. The solvent was distilled off at reduced pressure, and the residue was recrystallized from 6:1 hexane- $\text{CH}_2\text{Cl}_2$ . Compound (IV), lustrous orange-yellow scales.

1,5-Bis(phenyl)-2,4-diaza-1,3,5-trithia-2,3-pentadiene (II) and 1,5-bis(pentafluorophenyl)-2,4-diaza-1,3,5-trithia-2,3-pentadiene (III) were synthesized similarly; yields 84 and 81%, respectively. Under the same conditions, (I) and pentafluorophenylselenenyl chloride gave decafluorodiphenyl diselenide; yield 75%.

Reaction of (I) with Phenyltellurenyl Bromide. To a stirred solution of 0.51 g (2.5 mmole) of (I) in 15 ml of THF at  $0^\circ\text{C}$  was added dropwise a solution of 1.42 g (5 mmole) of phenyltellurenyl bromide in THF (prepared according to [12]). Cooling was removed and the solution was heated for 1 h at  $50^\circ$ . Then the solvent was distilled off at reduced pressure and the residue was extracted with 5:1 hexane- $\text{CH}_2\text{Cl}_2$  and 4:3 benzene-THF. When the latter extract was cooled, a fine crystalline orange-brown material precipitated (V), yield 0.2 g.

N-Phenylselenenyl Hexamethyldisilazane (VIII). To a stirred suspension of 3.34 g (20 mmole) of  $\text{LiN}(\text{SiMe}_3)_2$  in 20 ml of THF at  $-35^\circ\text{C}$  was added dropwise a solution of 4.72 g (20 mmole) of phenylselenenyl bromide (obtained according to [9]). After 1 h, the cooling was removed, and the solution was filtered and evaporated to one-third its volume. Then 75 ml of hexane was added, the solution was filtered, the solvent was distilled off at reduced pressure, and the residue was vacuum distilled. N-Phenylselenenyl hexamethyldisilazane, yellow liquid.

N-Pentafluorophenylselenenyl Hexamethyldisilazane (IX). To a stirred suspension of 5.51 g (33 mmole) of  $\text{LiN}(\text{SiMe}_3)_2$  in 60 ml of ether at  $-30^\circ\text{C}$  was added dropwise a solution of 9.29 g (33 mmole) of pentafluorophenylselenenyl chloride in 15 ml of ether. After 1 h, the cooling was removed, and stirring was continued for another hour. The solution was filtered, the solvent was distilled off at atmospheric pressure, and the residue was vacuum distilled twice. N-Pentafluorophenylselenenyl hexamethyldisilazane, yellow liquid.

N-Phenylsulfenyl hexamethyldisilazane (VI) and N-pentafluorophenylsulfenyl hexamethyldisilazane (VII) were synthesized similarly; yields 78 and 60%, respectively.

Reaction of (VIII) with Selenium Tetrachloride. To a stirred solution of 3.16 g (10 mmole) of (VIII) in 7 ml of glyme (glycol dimethyl ether) at  $0^\circ\text{C}$  was added dropwise a solution of 1.11 g (5 mmole) of  $\text{SeCl}_4$  in 13 ml of glyme. After 0.5 h, the cooling was removed and stirring was continued for 2 h. The precipitate was filtered off; when an attempt was made to remove it from the filter, it decomposed explosively. The filtrate was evaporated to dryness; the residue was diphenyl diselenide, yield 1.30 g (83%).

Reaction of Compounds (VII)-(IX) with SCl<sub>2</sub>. To a stirred solution of 10 mmoles of (VII), (VIII), or (IX) in 20 ml of THF at -50°C was added dropwise a solution of 1.03 g (10 mmole) of SCl<sub>2</sub> in 10 ml of THF. After 2 h the cooling was removed, the solvent was distilled off at reduced pressure, and the residue was extracted with hot hexane. The insoluble material was cyclotetraazathiene, which was purified and identified as described previously [13]; yield 0.30-0.33 g (65-72%). The residue after evaporation of the hexane extract contained the corresponding diaryl dichalcogenides, yield 79-83%.

#### CONCLUSIONS

1. 1,5-Bis(phenyl)-2,4-diaza-3-thia-1,5-diselena-2,3-pentadiene has been synthesized. It is the first representative of the acyclic azachalcogenes, containing sulfur and selenium simultaneously.

2. The electronic effects of several chalcogen-nitrogen groups on the aromatic ring were studied by NMR.

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