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Synthesis of Substituted Tetraselenafulvalenes from Dimethylphosgene Iminium Chloride

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SYNTHESIS OF SUBSTITUTED TETRASELENAFULVALENES FROM DIMETHYLPHOSGENE IMINIUM CHLORIDE*

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Tetramethyltetraselenafulvalene (TMTSF) and hexamethylenetetraselenafulvalene (HMTSF) can be conveniently synthesized using dimethylphosgene iminium chloride as a starting material. The method and detailed experimental conditions are described.

Preliminary reports on the synthesis of tetramethyltetraselenafulvalene (TMTSF) and hexamethylenetetraselenafulvalene (HMTSF) starting from dimethylphosgene iminium chloride and the piperidinium salt of hydrogen selenide have recently been presented.[1] The detailed synthetic method and experimental conditions are reported in this paper.

Diselenocarbamates 2, 6, 12 and 17 are key intermediates in the synthesis of TMTSF and HMTSF. In the earlier syntheses of TMTSF and HMTSF, these intermediates were derived from carbon diselenide or selenourea as described in Scheme 1.[2,3] However, both of these approaches have certain limitations.

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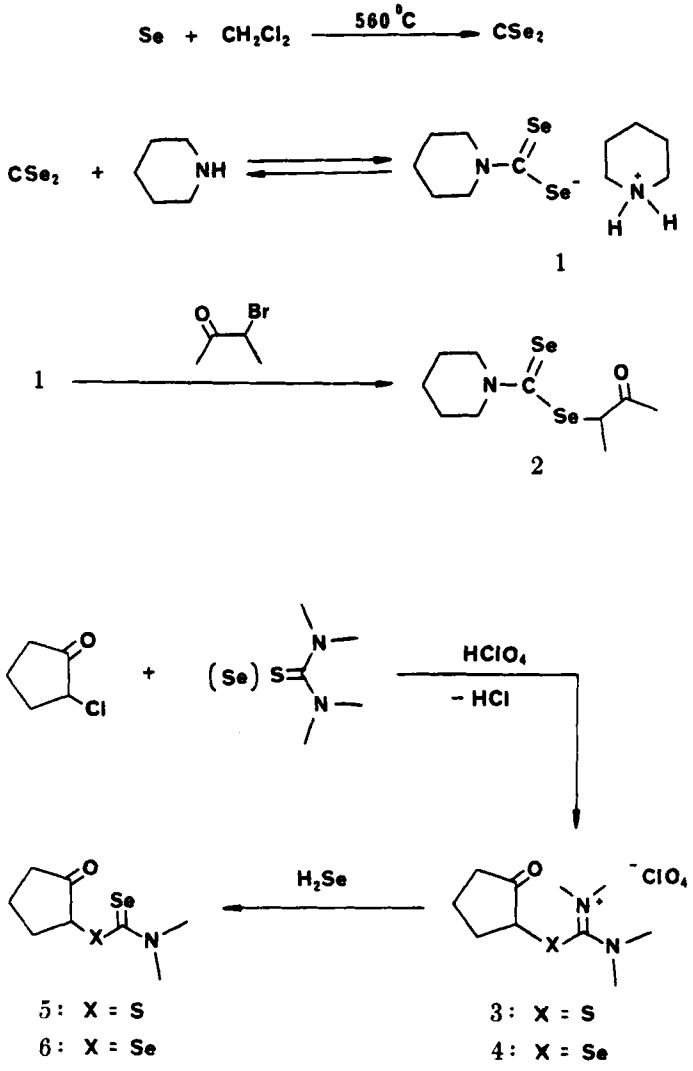
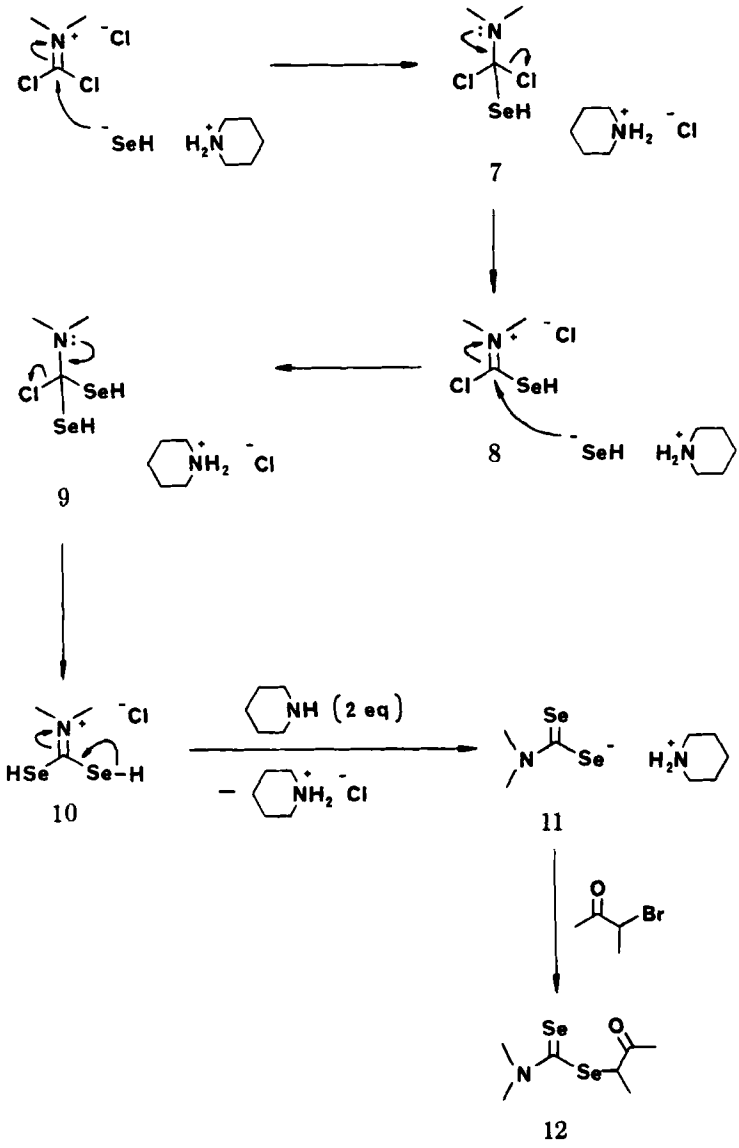


SCHEME 1



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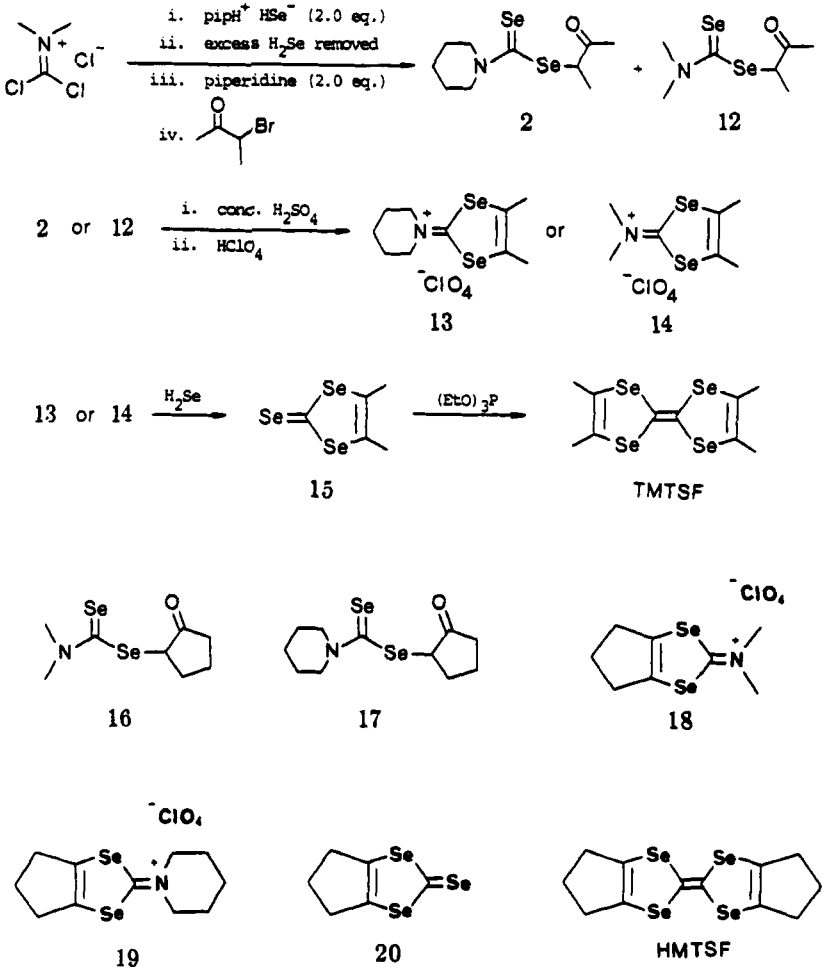

SCHEME 3

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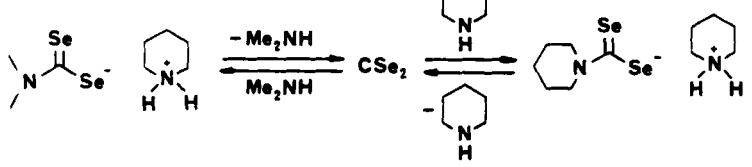
Tedious gas phase generation of carbon diselenide and its toxicity and odor are major drawbacks in the first approach. The second approach, while successful in the preparation of mixed sulfurselenium analogs, gave a low yield in the preparation of 6. When 4 was reacted with hydrogen selenide, elimination of the α-selenidocyclopentanone moiety was the major reaction pathway.

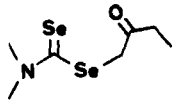
In the present syntheses of TMTSF and HMTSF, dimethylphosgene iminium chloride was allowed to react with two equivalents of piperidinium hydrogen selenide to give intermediate 10. The reaction mechanism is depicted in Scheme 2. Hydrogen selenide ion attacks the dimethylphosgene iminium chloride with loss of chloride ion to give intermediate 8. Subsequent attack by hydrogen selenide ion on 8 followed by loss of a second chloride ion results in 10. Excess hydrogen selenide was removed before the addition of another two equivalents of piperidine to generate an intermediate 11. The reaction of 11 with α-bromoketone gave two major products identified as (2-oxobutyl)-N,N-pentamethylenediselenocarbamate (2) (23%) and (2-oxobutyl)-N,N-dimethyldiselenocarbamate (12) (61%) as shown in Scheme 3. Apparently, an exchange reaction between dimethylamine and piperidine occurs during the formation of the salt of diselenocarbamate. Since it is known that 1 is in equilibrium with piperidine and carbon diselenide, it is reasonable to propose that the piperidinium adduct is derived via the reaction shown in Scheme 4.

NMR spectroscopy indicated that commercially available 3-bromo-2-butanone contains a trace amount of 1-bromo-2-butanone. Several attempts to remove this impurity by chemical and/or physical methods proved unsuccessful. Thus, a distilled sample of 3-bromo-2-butanone containing the isomeric impurity was allowed to react with the diselenocarbamate 11. The product 21 derived from the impurity was separable from 2 and 12 by careful thin layer chromatography.

Cyclization of 2 and/or 12 with concentrated sulfuric acid followed by exchange of the salt with perchloric acid gave 1,3-diselenolium perchlorate salts (13 and/or 14) in 75% yield. The treatment of 13 and/or 14 with hydrogen



SCHEME 4



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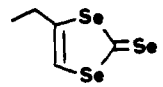

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selenide in absolute methanol gave selone 15 in 95% yield. There was no evidence for any contamination of selone 15 with selone 22. Coupling of selone 15 with trimethylphosphite or triethylphosphite gave TMTSF in 80% yield.

In a similar manner, (2-oxocyclopentyl)-N,N-dimethyldiselenocarbamate (16) and (2-oxocyclopentyl)-N,N-pentamethylenediselenocarbamate (17) could be prepared in 42% yield from dimethylphosgene iminium chloride and 2-bromocyclopentanone (prepared freshly from cupric bromide and cyclopentanone). The mixture was directly cyclized to a mixture of diselenolium salts 18 and 19 in 60% yield. Selone 20 was prepared by the treatment of 18 and 19 with hydrogen selenide in near quantitative yield. Trialkylphosphite-induced coupling of selone 20 gave HMTSF in 65% yield.

EXPERIMENTAL SECTION

(2-Oxobutyl)-diselenocarbamates 2 and 12

To a solution of 20 mmole of piperidine (distilled from CaH_2) in 100 ml of CH_2Cl_2 (distilled from P_2O_5) at 0°C under an inert atmosphere was slowly added an excess of hydrogen selenide to give a clear orange solution of piperidinium hydrogen selenide. Meanwhile, in a glove box 10 mmoles of dimethylphosgene iminium chloride was transferred to a pear-shaped flask. This flask was attached to the reaction flask just prior to the addition of dimethylphosgene iminium chloride to avoid the formation of an insoluble red solid resulting from the reaction between gaseous hydrogen selenide and the solid dimethylphosgene iminium chloride. Addition of dimethylphosgene iminium chloride in small portions over a period of 20 minutes, followed by warming of the reaction mixture to room temperature and stirring at that temperature for one hour, resulted in a white suspension. Excess hydrogen selenide was removed from the reaction by bubbling argon through the solution. The hydrogen selenide was destroyed in a trap containing an aqueous solution of potassium hydroxide and hydrogen peroxide. The reaction mixture was then cooled to 0°C and 20 mmole of piperidine was added

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dropwise via a syringe. After stirring at 0°C for an additional 10 minutes, 15 mmole of 3-bromo-2-butanone was added. The resultant mixture was slowly warmed to room temperature and stirred for four hours. At the end of the reaction, 50 ml of 10% HCl was added and the mixture was extracted with methylene chloride. The organic extract was then washed with water and dried over $MgSO_4$. Evaporation of the solvent gave a crude oil, which was column chromatographed on silica gel using AcOEt-hexane/1:5 as eluant, to obtain 2 and 12 (R_f = 0.2). Compounds 2 and 12 could be separated by thin layer chromatography (silica gel; AcOEt-hexane/1:3) and were isolated in 23% and 61% yield, respectively. Spectral data for compound 2 has been reported,[2] characterization of 12 is as follows: NMR ($CDCl_3$); δ 1.65 (d, 3H, J = 8 Hz), 2.36 (s, 3H), 3.40 (s, 3H), 3.72 (s, 3H), and 5.14 (q, 1H, J = 8 Hz); m/e 287 (m^+), 217 (m^+-C_4H_6O), and 137 (m^+-C_4H_6O-Se). IR ($CHCl_3$): 2930, 1710 (s), 1665 (s), 1495, 1460, 1405, 1375 (s), 1305 (w), 1250, 1130, 892 (s).

1,3-Diselenolium perchlorate salts 13 and 14

A mixture of purified 2 and 12 (810 mg, 2.7 mmole) was added dropwise with stirring (a drop was added after the previous drop homogeneously dispersed into the viscous solution) to 2 ml of concentrated sulfuric acid cooled in a cold water bath. After the resulting mixture was stirred for one hour, an orange suspension was obtained. Ethyl acetate (3 ml) was added with cooling. The suspension was filtered into a mixture of absolute ethanol (10 ml) and 70% perchloric acid (0.8 ml). The resulting solution was then further filtered into 500 ml of anhydrous ether to give a precipitate after the mixture was cooled in a freezer. The precipitate was isolated and dissolved in acetonitrile. The acetonitrile solution was decolorized and filtered into anhydrous ether to produce a white precipitate of 13[2] and 14 (75% yield).

1,3-Diselenole-2-selone 15

Diselenolium perchlorate salts 13 and 14 (630 mg, 1.7 mmole) were suspended in 40 ml of absolute methanol at -30°C under an inert atmosphere. An excess of hydrogen selenide was bubbled into the suspension. The mixture was stirred at -30°C for one hour and at 0°C for three hours. The excess hydrogen selenide was removed and destroyed in a trap containing an aqueous mixture of potassium hydroxide and hydrogen peroxide. Methylene chloride was then added to the

reaction mixture. The resulting solution was washed with water, dried, filtered, and the solvent evaporated to give 510 mg (98%) of selone 15[2] as red crystals. The physical properties are the same as those reported earlier.[2]

Tetramethyltetraselenafulvalene (TMTSF)

A mixture of 550 mg of selone 14, 10 ml of benzene, and 3 ml of trimethylphosphite was refluxed under argon for five hours. The resulting suspension was cooled to cause further precipitation. The precipitate was filtered and washed with hexane to give 320 mg of product. The mother liquor was concentrated to 3 ml, which upon cooling gave another 25 mg of product. The combined products were chromatographed on silica gel using benzene as an eluant and then recrystallized from hexane-methylene chloride to give 315 mg (80%) of TMTSF as purple crystals. Physical properties of TMTSF are identical to those reported earlier.[2]

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