or less common and have a large area of distribution.

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Organic Selenium Compounds

I. Preparation of Methyl-substituted Selenosemicarbazides

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With the purpose of comparing the infrared spectra of corresponding thiosemicarbazides and selenosemicarbazides, we have prepared several new selenosemicarbazides, expecially methyl-substituted selenosemicarbazides. There will be three monomethyl, five dimethyl, five trimethyl, three tetramethyl and one pentamethyl selenosemicarbazide, in all 17 compounds. The corresponding 17 thiosemicarbazides have all been prepared;[1] however, it does not seem to be possible to prepare all selenosemicarbazides with two methyl groups in the 4-position without the use of the unknown dimethylselenocarbamoyl chloride.

In this paper, we report on the preparation of the eleven methyl-substituted selenosemicarbazides which are not disubstituted in the 4-position. Some 4,4-dialkylselenosemicarbazides have been prepared from (dialkylselenocarbamoylseleno) acetic acids and will be described in a subsequent paper.

The reaction of methyl isoselenocyanate with hydrazine, methylhydrazine, 1,1-dimethylhydrazine, 1,2-dimethylhydrazine, and trimethylhydrazine, respectively, yielded 4-methylselenosemicarbazide, 2,4-dimethylselenosemicarbazide, 1,1,4-trimethylselenosemicarbazide, 1,2,4-trimethylselenosemicarbazide, and 1,1,2,4-tetramethylselenosemicarbazide.

The preparation of in the 4-position unsubstituted selenosemicarbazides in a similar manner as that used for thiosemicarbazides, *i.e.* heating of hydrazinium selenocyanates, could not be used, because extensive decomposition with the formation of selenium took place. According to the sensitive precipitation reaction with nickel salts (*cf.* Jensen and Frederiksen [2]) no selenosemicarbazide was formed in this reaction. However, selenosemicarbazides unsubstituted in the 4-position were obtained in a way which also had been used in our studies of thiosemicarbazides, namely by removal of a *tert.*-butyl group from the 4-position on boiling with concentrated hydrochloric acid. The necessary 4-*tert*-butylselenosemicarbazides could be prepared in excellent yields from hydrazines and *tert*-butyl isoselenocyanate. Unexpectedly, the yields of selenosemicarbazides were much higher than the yields of thiosemicarbazides by the corresponding method. In this way, we succeeded in preparing 2-methylselenosemicarbazide, 1,1-dimethylselenosemicarbazide, 1,2-dimethylselenosemicarbazide, and 1,1,2-trimethylselenosemicarbazide.

The preparation of 1-methylsubstituted thiosemicarbazides had encountered unusual difficulties [1] but a method had been found which was also successful in the case of selenosemicarbazides. An alkyl isoselenocyanate is treated with 1-methyl-1-*tert*-butyloxycarbonylhydrazine [1] and the *tert*-butyloxycarbonyl group is subsequently removed by treatment with cold concentrated hydrochloric acid: See p. 280.

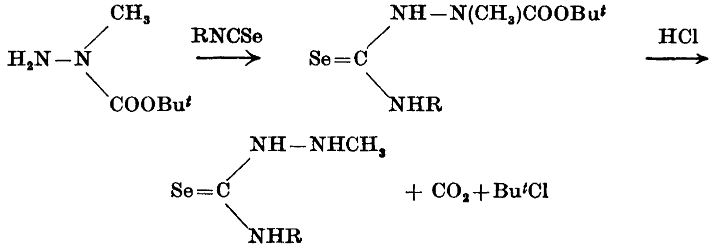
If R is *tert*-butyl this group could be removed subsequently by treatment with hot conc. hydrochloric acid, so that 1-methylselenosemicarbazide can be prepared *via* 1-methyl-4-*tert*-butylselenosemi-

Table 1. Substituted selenosemicarbazides, $R^4NH-CSe-NR^3NR^2R^1$.

R^4	R^3	R^2	R^1	Yield %	M.p. °C	Formula	Analyses (C,H,N)
H	H	H	Me	75[c]	168–169.5	$C_2H_7N_3Se$	Found: 16.02; 4.60; 27.47 Calc.: 15.79; 4.64; 27.63
H	Me	H	H	52[c]	203.5–204.5	$C_2H_7N_3Se$	Found: 15.88; 4.84; 27.72 Calc.: 15.79; 4.64; 27.63
Me	H	H	H	52[a]	155–156	$C_2H_7N_3Se$	Found: 15.58; 4.83; 27.46 Calc.: 15.79; 4.64; 27.63
H	H	Me	Me	50[c]	179.5–180	$C_3H_9N_3Se$	Found: 21.93; 5.28; 25.48 Calc.: 21.69; 5.46; 25.30
H	Me	H	Me	84[c]	149.5–150.5	$C_3H_9N_3Se$	Found: 21.82; 5.61; 25.13 Calc.: 21.69; 5.46; 25.30
Me	H	H	Me	80[c]	158–160	$C_3H_9N_3Se$	Found: 21.82; 5.62; 25.07 Calc.: 21.69; 5.46; 25.30
Me	Me	H	H	50[a]	146–147	$C_3H_9N_3Se$	Found: 21.52; 5.44; 25.53 Calc.: 21.69; 5.46; 25.30
H	Me	Me	Me	87[c]	106.5–108.5	$C_4H_{11}N_2Se$	Found: 26.59; 5.97, 23.06 Calc.: 26.68; 6.16; 23.33
Me	H	Me	Me	28[a]	172–173	$C_4H_{11}N_3Se$	Found: 26.88; 6.27; 22.93 Calc.: 26.68; 6.16; 23.33
Me	Me	H	Me	33[a]	72–73	$C_4H_{11}N_3Se$	Found: 26.51; 6.13; 23.35 Calc.: 26.68; 6.16; 23.33
Me	Me	Me	Me	28[a]	51–52	$C_5H_{13}N_3Se$	Found: 31.07; 6.91; 21.48 Calc.: 30.94; 6.75; 21.65
i-Pr	Me	H	H	33[b]	127–128	$C_5H_{13}N_3Se$	Found: 31.70; 6.66; 21.69 Calc.: 30.94; 6.75; 21.65
i-Pr	H	Me	Me	27[b]	147–148	$C_6H_{15}N_3Se$	Found: 34.72; 7.58; 19.95 Calc.: 34.61; 7.26; 20.18
t-Bu	H	H	H	70[a]	131–133	$C_5H_{13}N_3Se$	Found: 31.12; 7.10; 21.43 Calc.: 30.94; 6.75; 21.65
t-Bu	H	H	Me	90[c]	117.5–119.5	$C_6H_{15}N_3Se$	Found: 34.53; 7.38; 19.99 Calc.: 34.61; 7.26; 20.18
t-Bu	Me	H	H	95[a]	148–150	$C_6H_{15}N_3Se$	Found: 34.75; 7.16; 19.91 Calc.: 34.61; 7.26; 20.18
t-Bu	H	Me	Me	76[a]	154–156	$C_7H_{17}N_3Se$	Found: 38.00; 7.48; 19.03 Calc.: 37.84; 7.71; 18.91
t-Bu	Me	H	Me	69[a]	92–94	$C_7H_{17}N_3Se$	Found: 38.09; 7.66; 18.79 Calc.: 37.84; 7.71; 18.91
t-Bu	Me	Me	Me	62[a]	123–123.5	$C_8H_{19}N_3Se$	Found: 40.41; 8.07; 17.66 Calc.: 40.68; 8.11; 17.79
t-Bu	H	t-BuOCO	Me	95[a]	168.5–169.5	$C_{11}H_{23}N_3O_2Se$	Found: 43.12; 7.74; 14.15 Calc.: 42.85; 7.53; 13.63
Me	H	t-BuOCO	Me	96[a]	161–162.5	$C_8H_{17}N_3O_2Se$	Found: 35.59; 6.55; 15.74 Calc.: 36.10; 6.44; 15.78

[a] Yields based on isoselenocyanates. [b] Yields based on isocyanides. [c] Yields based on selenosemicarbazides.

The melting points were determined on a Kofler microscope hot stage. The substances were recrystallized from methanol, excepting 4-methyl-,2,4-dimethyl- and 1,1,4-trimethylselenosemicarbazide, which were recrystallized from water, and 1,2,4-trimethylselenosemicarbazide, which was recrystallized from water-ethanol.



carbazide in this way. With R = CH_3 the reaction yielded 1,4-dimethylselenosemicarbazide.

In connection with this work, a few 4-isopropylselenosemicarbazides were also prepared from isopropyl isoselenocyanate, but it proved impossible to remove the isopropyl group on heating with hydrochloric acid.

Experimental. Isoselenocyanates were prepared from isocyanides [8,9] and selenium,[2-7] preferably in petroleumether (b.p. 60—90°C). *tert*-Butyl isoselenocyanate has not hitherto been described. It was obtained as colourless crystals with m.p. 49.5—51.5. Yield 64 %, purified by sublimation. (Found: C 37.10; H 5.79. Calc. for C_5H_9NSe: C 37.05; H 5.60).

Selenosemicarbazides were prepared from hydrazines, including 1-methyl-1-*tert*-butyloxycarbonylhydrazine [1] and isoselenocyanates, in ether or ether-petroleumether and were recrystallised from methanol.

The selenosemicarbazides are colourless crystalline substances. Those which contain only one or two methyl groups are easily soluble in methanol or hot water, but almost insoluble in ether; with increasing molecular weight they become less and less soluble in methanol or water and more soluble in ether. The higher melting selenosemicarbazides sublime on heating.

As examples we give the details for the preparations of 1-methyl- and 2-methylselenosemicarbazide (for analyses and melting points, see Table 1):

1-Methylselenosemicarbazide. tert-Butyl isoselenocyanate (1.21 g) was dissolved in ether (10 ml) and 1-methyl-1-*tert*-butyloxycarbonylhydrazine (1.10 g) was added with stirring. After *ca.* 20 h, the colourless crystals of 1-methyl-1-*tert*-butyloxycarbonyl-4-*tert*-butylselenosemicarbazide were isolated by filtration (yield 2.2 g, 95 %) and recrystallised from methanol.

The last mentioned compound (0.40 g) was treated at room temperature with conc. hydrochloric acid (3 ml) until the CO_2 evolution had stopped; then an additional 1 ml of conc. hydrochloric acid was added and the solution heated to boiling. The solution was evaporated rapidly *in vacuo* to dryness, the residue dissolved in water, and the solution neutralised with aqueous ammonia. A colourless crystalline precipitate (mixed with some red selenium) separated. The precipitate was filtered and recrystallied from methanol. Yield 0.15 g (75 %).

The intermediate product, 1-methyl-4-*tert*-butylselenosemicarbazide, can be isolated in a similar way when the treatment with hot hydrochloric acid is omitted.

2-Methylselenosemicarbazide. 2-Methyl-4-*tert*-butylselenosemicarbazide (0.40 g) was suspended in conc. hydrochloric acid (3 ml) and the mixture heated to boiling. The selenosemicarbazide dissolved and there was some precipitation of red selenium. After boiling for 1/4 min, the solution was evaporated to dryness *in vacuo*. The residue was dissolved in water, neutralised with dilute aqueous ammonia, and cooled at *ca.* 6°C for ½ h at which time 2-methylselenosemicarbazide separated as colourless crystals which were recrystallised from methanol (yield 0.15 g, 52 %).

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Organic Selenium Compounds

II. Preparation of Tetraalkylselenoureas

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In a study of the infrared spectra of thioamides and selenoamides we were interested in comparing the infrared spectra of tetraalkylthioureas and tetraalkylselenoureas. The latter had not hitherto been prepared. Since dialkylselenocarbamoyl chlorides are unknown the selenoureas could not be prepared in a similar manner as the corresponding thioureas. However, an obvious method to try was the reaction of a tetraalkylurea with phosphorus pentaselenide. Curiously enough, the preparation of thioureas from ureas and phosphorus pentasulfide do not seem to have been reported, so we first tried to prepare thioureas in this way to see whether there were some unexpected difficulties connected with this method. However, tetraethylthiourea was prepared in good yield from tetraethylurea and phosphorus pentasulfide. This may well be a convenient method of preparing tetraethylthiourea because the reaction of diethylthiocarbamoyl chloride with diethylamine has, in our hands, repeatedly yielded a tetraethylthiourea which was difficult to purify. That the method is not restricted to tetraalkylthioureas was shown by the preparation of benzylthiourea from benzylurea; however, for the preparation of mono-, di-, and trialkylthioureas other methods will usually be more convenient.

For the preparation of the thioureas the urea was treated with phosphorus pentasulfide in pyridine solution. This method could, however, not be used to prepare the selenoureas, because these are very sensitive to treatment with water and acid. Instead, the urea was refluxed with phosphorus pentaselenide in benzene solution. This reaction is very slow, and even after reflux for one week only a few percent of the urea had been transformed into the selenourea. However, in this way we succeeded in preparing tetramethylselenourea as a beautifully crystalline compound. It is possible that a higher yield may be obtained by another method; since, however, we were only interested in having a small sample of the pure compound, we found the method used wholly satisfactory.

Tetraethylurea yielded, in a similar manner, an oil which according to its infrared spectrum was fairly pure tetraethylselenourea. Attempts at high vacuum distillation caused complete decomposition with the formation of red selenium.

Experimental. Tetraethylthiourea. To a solution of tetraethylurea (25 g) in pyridine (50 ml), phosphorus pentasulfide (25 g) was added with stirring and the mixture was refluxed for 3 h. After cooling, the pyridine solution was decanted from the solid mass and extracted with ether. The ethereal solution was washed several times with water, then with dilute (*ca.* 0.1 N) hydrochloric acid and finally, again, with water. The solution was dried over $MgSO_4$, the ether removed by evaporation and the oily residue distilled *in vacuo*. Yield 11.5 g (45.5 %) of a colourless oil with b.p. 93—95°C at 0.8 mm Hg. (Found: C 57.20; H 10.84; N 15.17. Calc. for $C_9H_{20}N_2S$: C 57.45; H 10.64; N 14.90). Tetraethylselenourea could *not* be prepared in this manner.