tracted with ether. The ether solution was dried ($K_2CO_3$) and evaporated to dryness and the gummy residue as redissolved in ether and treated with HCl in isopropyl alcohol. The product was recrystallized from ethanol–ether to give 90 mg (78%) of **3** as its HCl salt. Similarly 100 mg of **6** was converted to 110 mg (95%) of **7**, also characterized as its HCl salt. The physical properties of **3** and **7** are included in Table III.

**General Procedure for the Hydrolysis of the Rearranged Amide.** A mixture of 500 mg of the amide and 20 ml of concentrated HCl was heated in a sealed tube at 130–150° (about 10° above the melting point of the amide) for 24 hr. The reaction mixture was diluted with water and extracted several times with ether. The ether layer was extracted with a saturated solution of $NaHCO_3$. The bicarbonate solution was acidified with HCl, reextracted with ether, dried ($Na_2SO_4$), and evaporated to dryness. The residue was usually recrystallized from hexane to give the carboxylic acid in good yield. (See Table II.)

**Cycloheptyl Phenyl Ketone (11).** Freshly distilled bromobenzene (157 g, 1.0 mol) was converted to phenylmagnesium bromide using 24.0 g of magnesium. A solution of 61.5 g (0.5 mol) of cycloheptanecarbonitrile in 250 ml of dry ether was added drop by drop to the Grignard reagent while the mixture was mechanically stirred. After the addition was complete, the mixture was heated under reflux for 36 hr. It was cooled and 125 ml of 4 *N* HCl was carefully added followed by 250 ml of 4 *N* $H_2SO_4$. The ether was expelled by warming the mixture on a steam bath and the residue was heated under reflux with stirring for 24 hr. The cooled mixture was extracted with ether, washed with water followed by $NaHCO_3$ solution, and dried ($Na_2SO_4$) and the solvent was removed *in vacuo*. The residue was fractionated at 0.1 mm. The fraction boiling at 100–110° (86 g) showed 3% impurities by gc. It was refractionated to give 75.2 g (75%) of **11**: bp 97–100° (0.05 mm); $n^{24}D$ 1.5410; 2,4-dinitrophenylhydrazone, mp 168–170° [lit.[15] bp 115–117° (0.2 mm); $n^{25}D$ 1.5405; 2,4-dinitrophenylhydrazone, mp 170–171°].

**1-Benzoyl-1-bromocycloheptane (12).** A solution of 3.2 g (20 mmol) of bromine in 25 ml of $CCl_4$ was added dropwise to a magnetically stirred solution of 4.04 g (20 mmol) of **11** in 25 ml of $CCl_4$. After the addition of bromine, stirring was continued for 2 hr. The solvent was removed *in vacuo* and the residue was evaporatively distilled (bath temperature 75°, 0.0005 mm) to give 5.06 g (90%) of **12**, $n^{24}D$ 1.5718, $\lambda_{max}$ 251.5 nm ($\epsilon$ 7660).

*Anal.* Calcd for $C_{14}H_{17}BrO$: C, 60.02; H, 6.12; Br, 28.53. Found: C, 60.04; H, 6.06; Br, 28.47.

**Cyclooctyl Phenyl Ketone (13).** Cyclooctyl chloride[16] (103.5 g, 0.7 mol) was converted to cyclooctylmagnesium chloride in ether using 17.0 g of magnesium. A solution of 51.5 g (0.5 mol) of benzonitrile in 200 ml of ether was added dropwise and the mixture was stirred at room temperature for 3 hr and then heated under reflux for 12 hr. The mixture was cooled and 100 ml of 6 *N* $H_2SO_4$ was added carefully. The ether was boiled off and the residue was heated on a steam bath with stirring for 8 hr. The cooled mixture was extracted with ether, the ether layer was washed with water followed by $NaHCO_3$ solution and dried ($Na_2SO_4$), and the solvent was removed. The residue was fractionated at 0.02 mm. The fraction boiling at 112–115° (46.2 g) showed 2% impurities by gc. It was refractionated to give 30.3 g (28%) of **13**, bp 102° (0.01 mm). A sample was evaporatively distilled for analysis, $n^{25}D$ 1.5438.

*Anal.* Calcd for $C_{15}H_{20}O$: C, 83.29; H, 9.32. Found: C, 83.51; H, 9.38.

A portion of **13** was converted to its semicarbazone, mp 136–137°.

*Anal.* Calcd for $C_{16}H_{23}N_3O$: C, 70.30; H, 8.48; N, 15.37. Found: C, 70.03; H, 8.76; N, 15.48.

**1-Benzoyl-1-bromocyclooctane (14).** Ketone **13** (4.32 g, 20 mmol) was brominated as described for the preparation of **12**. The product was evaporatively distilled (bath temperature 110°, 0.01 mm) to give 4.7 g (80%) of **14**, $n^{25}D$ 1.5699.

*Anal.* Calcd for $C_{15}H_{19}BrO$: C, 61.05; H, 6.49; Br, 27.07. Found: C, 60.76; H, 6.62; Br, 26.66.

**1-Phenylcyclooctanecarboxylic Acid (19e).** A mixture of 500 mg of **18** and 10 ml of concentrated HCl was heated in a sealed tube at 110° for 12 hr and then at 135–140° for 12 hr. The mixture was diluted with water and extracted with ether. The ether layer was extracted with $NaHCO_3$ solution. From the neutral ether solution was isolated 210 mg (42%) of the starting amide, **18**. The bicarbonate solution was acidified with concentrated HCl, reextracted with ether, and dried ($Na_2SO_4$) and the solvent was removed. The residue was recrystallized from hexane to give 105 mg (50% based on the hydrolyzed amide) of **19e**, mp 103°.

*Anal.* Calcd for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68. Found: C, 77.39; H, 8.63.

**Acknowledgments.** Financial support from the National Science Foundation through Grant GP 8272 is gratefully acknowledged. One of us (P. M. Pillai) also wishes to acknowledge the award of a Frank Knoller Predoctoral Fellowship to him during 1966–1967.

**Registry No.**—**1a,** 6740-66-5; **1b,** 52217-42-2; **1c,** 52123-79-2; **1d,** 6728-52-5; **2,** 52123-80-5; **3** HCl, 52123-81-6; **4a,** 7500-66-5; **4b,** 1135-71-3; **6,** 52123-82-7; **7** HCl, 52217-43-3; **8a,** 52123-83-8; **8b,** 52123-84-9; **9a,** 52123-85-0; **9b,** 52123-86-1; **9c,** 52123-87-2; **10a,** 52123-88-3; **10b,** 52123-89-4; **11,** 6004-52-0; **12,** 52217-44-4; **13,** 6004-59-7; **13** semicarbazone, 52123-90-7; **14,** 52123-91-8; **15,** 51175-78-1; **16,** 52123-92-9; **17,** 52123-93-0; **18,** 52123-94-1; **19e,** 52123-95-2; **20,** 34546-66-2; **21,** 52123-99-6; **22,** 52123-96-3; lithium *o*-toluidide, 52217-45-5; bromobenzene, 108-86-1; cycloheptanecarbonitrile, 32730-85-1; cyclooctyl chloride, 1556-08-7; benzonitrile, 100-47-0; lithium anilide, 20732-26-7.

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## The Selenium Analogs of Biuret

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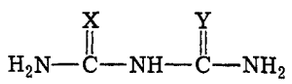
Although the sulfur analogs of biuret (**1**), namely 2-thiobiuret (**2**)[1] and 2,4-dithiobiuret (**3**),[2] were prepared in 1886 and 1945, respectively, the only selenium analog of **1** which is known is 2-seleno-4-thiobiuret (**4**),[3] the synthesis of which was reported comparatively recently from this labo-

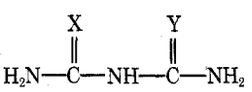
**Table I**
**$^1$H Nmr Chemical Shifts at 60 MHz of Biuret Analogs[a]**



| Compd | δ, –NH | δ, –C(=X)–NH$_2$ | δ, –C(=Y)–NH$_2$ |
|---|---|---|---|
| **1**, X = Y = O | 8.67 (s) | 6.85 (s) | *b* |
| **2**, X = S; Y = O | 8.72 (br s) | 9.52 (br s), 9.77 (s)[c] | 6.58 (s) |
| **3**, X = Y = S | 11.00 (s) | 9.37 (br s) | 9.83 (br s) |
| **4**, X = Se; Y = S | 9.90 (br s) | 10.85 (s) | 8.95 (br s), 9.03 (br s)[c] |
| **5**, X = Se; Y = O | 9.45 (br s) | 10.00 (br s) | 6.67 (br s) |
| **6**, X = Y = Se | 11.60 (br s) | 10.33 (br s) | 10.70 (br s) |

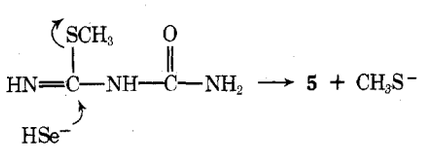
[a] All spectra were measured in DMSO-$d_6$ using TMS as an internal standard except that of **6**, in which TMS was used as an external standard. [b] The four –NH$_2$ protons are equivalent. [c] Each of the two –NH$_2$ protons is nonequivalent.

ratory. We report here the preparation of the remaining two possible selenium analogs of **1**, *i.e.*, 2-selenobiuret (**5**) and 2,4-diselenobiuret (**6**).



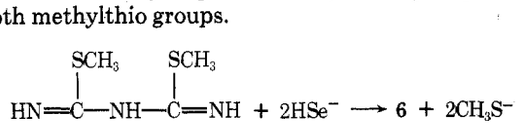
**1**, X = Y = O
**2**, X = S; Y = O
**3**, X = Y = S
**4**, X = Se; Y = S
**5**, X = Se; Y = O
**6**, X = Y = Se

The first, 2-selenobiuret (**5**), was prepared from 2-thiobiuret (**2**) *via* its S-methylated derivative (**7**), which was treated with sodium hydrogen selenide, causing displacement of the methylthio group by the hydrogen selenide anion.[4]



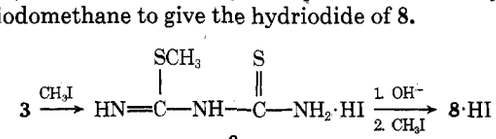
**7**

2,4-Diselenobiuret (**6**) was synthesized from 2,4-dimethyl-2,4-dithiopseudobiuret (**8**) by treatment with 2.5 equiv of sodium hydrogen selenide, causing displacement of both methylthio groups.



**8**

2,4-Dimethyl-2,4-dithiopseudobiuret (**8**) was derived from 2,4-dithiobiuret (**3**) by a stepwise S,S-dimethylation with iodomethane to give the hydriodide of **8**.

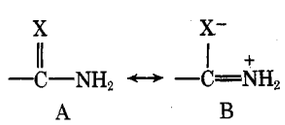


**9**

The sodium hydrogen selenide utilized in the preparation of **6** was generated conveniently in anhydrous ethanol from 2.5 equiv of selenium and 2.5 equiv of sodium borohydride, a procedure recently reported by us.[5] However, this simplified method for the formation of sodium hydrogen selenide was not used in the synthesis of 2-selenobiuret (**5**) because the water-solubility characteristics of **5** and of the by-product of the selenium–borohydride reaction, namely boric acid, were sufficiently similar to cause difficulties in the isolation of **5**. Therefore, in this case the sodium hydrogen selenide was formed by passing gaseous hydrogen selenide[6] into an aqueous ethanolic solution of sodium bicarbonate.

The monoseleno analogs of biuret, *i.e.*, **4** and **5**, are white or off-white compounds, whereas the diseleno analog **6** is yellow. All of the selenium analogs of biuret are air sensitive, the last being the most sensitive of the three. As with selenoureas,[3] the presence of the selenocarbonyl group was confirmed by the precipitation of red elemental selenium from an ethanolic solution of a selenobiuret to which 1–2 drops of 5% hydrogen peroxide had been added.

**Nmr Spectra of Selenobiurets.** The imidic –NH protons of the selenium analogs of biuret can be assigned on the basis of integration of peak areas. Using biuret (**1**), 2,4-dithiobiuret (**3**), and 2,4-diselenobiuret (**6**) as models, the chemical shifts of the –CONH$_2$, –CSNH$_2$, and –CSeNH$_2$ protons may be seen to appear in the ranges δ 6–7, 9–10, and 10–11, respectively (Table I). Therefore, in 2-seleno-4-thiobiuret (**4**), the peaks at about δ 9.00 are assigned to –CSNH$_2$ and the peak at δ 10.85 to –CSeNH$_2$. In 2-selenobiuret (**5**), the peak at δ 6.67 is attributed to –CONH$_2$ and that at δ 10.00 to –CSeNH$_2$. Also consistent are the chemical shifts in 2-thiobiuret (**2**), where the singlet at δ 6.58 is due to –CONH$_2$ and the two singlets at δ 9.52 and 9.77 to the nonequivalent –CSNH$_2$ protons. There is clear evidence of increased deshielding of the –CXNH$_2$ protons as X varies from oxygen to sulfur to selenium. This phenomenon may be attributed to decreased electron density on nitrogen, indicating a greater contribution from resonance structure B, which has a positive charge on nitrogen. In



A B

agreement with this postulate, Shine[7] has recently summarized evidence indicating that there is a decreased tendency to form a C=X double bond in amides as X goes from oxygen to sulfur to selenium.

The nonequivalence of the –NH$_2$ groups at room temperature in 2,4-diselenobiuret (**6**) suggests hindered rotation about the internal C–N bonds. Magnetic nonequivalence of groups attached to nitrogen has been detected by nmr

studies and has been attributed to hindered rotation about the C–N bond in selenoamides[8,9] and in selenoureas.[10] As the heteroatom X ranges from oxygen to selenium, the barriers to rotation in amides, $RCXNR'_2$, were observed to increase in the same order.[8,9,11] The barriers to rotation in thiourea and in selenourea, which are similar in value, were found to be greater than seen in urea.[10] The results obtained by us (Table I) are consistent with the effects alluded to above, since the four $-NH_2$ protons in biuret (**1**) appear as a singlet, whereas in 2,4-dithiobiuret (**3**) and in 2,4-diselenobiuret (**6**) the two sets of $-NH_2$ peaks appear separated. In 2-thiobiuret (**2**) and, to some extent in 2-seleno-4-thiobiuret (**4**), each of the $-CSNH_2$ protons appear separated as broadened singlets, indicating nonequivalence and hindered rotation about the external C(S)–N bond. This effect would be expected to be operative in the other analogs in the series but is apparently not observable owing to nitrogen quadrupole broadening.

## Experimental Section

Unless otherwise indicated, melting points were determined on a Fisher-Johns melting point apparatus and are uncorrected. Microanalyses were performed by Mr. Joseph F. Alicino, New Hope, Pa., and by Dr. Harry Agahigian of the Baron Consulting Co., Orange, Conn. Infrared spectra were determined in KBr on a Beckman IR-5 spectrophotometer. Nmr spectra were taken in DMSO-$d_6$ on a Varian A-60 using TMS as an internal standard unless otherwise indicated. Mass spectra were obtained on a Hewlett-Packard 5390A quadrupole mass spectrometer at 70 eV with sample introduction *via* a variably heated direct insertion probe.[12] For the selenium-containing ions, only those peaks corresponding to the most abundant selenium isotope, *i.e.*, 80, are reported. In all cases, the relative intensity patterns of the molecular ion clusters compare favorably with those expected from the selenium natural abundances.[13]

*To prevent oxidation, all selenium-containing products were handled in an inert atmosphere.*

**2-Seleno-4-thiobiuret (4).** This compound was prepared by a procedure similar to that previously reported.[3] However, an improvement in the method of generating the sodium hydrogen selenide resulted in doubling the yield of **4**.

To a solution of sodium hydrogen selenide (0.015 mol), obtained from 1.16 g (0.015 mol) of selenium and 0.62 g (0.016 mol) of sodium borohydride in 75 ml of ethanol under argon,[5] was added 2.0 g (0.013 mol) of 2-methyl-2,4-dithiopseudobiuret (**9**) (free base) in 150 ml of ethanol. Stirring and heating at 45° was continued for *ca.* 14 hr until evolution of methyl mercaptan ceased. After cooling the solution to room temperature, 40 ml of deoxygenated water was added followed by a dropwise addition of 3 *N* hydrochloric acid until the pH was about 5. The mixture was purged with argon to remove excess hydrogen selenide which was trapped in a 5% aqueous lead acetate solution. The elemental selenium present in the mixture was removed by filtration and the filtrate was concentrated to about 40 ml. 2-Seleno-4-thiobiuret (1.0 g, 41%), separated at room temperature as tiny, white needles with a pink tinge: mp 171–174° dec (capillary, Thomas-Hoover melting point apparatus); ir (KBr) 3135 (broad, NH), 1615 and 1550 $cm^{-1}$ (amide II); nmr (DMSO-$d_6$) $\delta$ 10.85 (2), 9.90 (1), 9.03 (1), 8.85 (1), all broadened singlets; mass spectrum (70 eV) *m/e* (rel intensity) 183 ($M\cdot^+$, 66), 156 (20), 135 (35), 124 (18), 103 (36), 80 (14), 76 (18), 60 (62), 43 (100). The infrared spectrum of **4** was identical with that of an authentic sample.

**2-Selenobiuret (5).** Sodium hydrogen selenide solution, prepared by passing hydrogen selenide[6] into 8.2 g (0.1 mol) of sodium bicarbonate dissolved in 100 ml of ethanol and 300 ml of water at 0°, was added to a solution of 13.05 g (0.05 mol) of 2-methyl-2-thiopseudobiuret (**7**) hydriodide in 35 ml of ethanol. This was immediately followed by the addition of 4.2 g (0.05 mol) of sodium bicarbonate in 20 ml of water. When the evolution of carbon dioxide ceased, the flask was stoppered and allowed to stand at room temperature for *ca.* 15 hr. The solution was then purged with nitrogen to remove methyl mercaptan, acidified with glacial acetic acid, and concentrated, causing separation of 6.9 g (83%) of 2-selenobiuret (**5**) as a cream-colored solid. The analytical sample was recrystallized in an argon atmosphere from chloroform–acetonitrile to give white crystals which sublimed and then melted at 185–187° dec: ir (KBr) 3400, 3165 (NH), 1695, 1675 (amide I), and 1597, 1525 $cm^{-1}$ (amide II); nmr (DMSO-$d_6$) $\delta$ 10.00 (2), 9.45 (1), 6.67 (2), all broadened singlets; mass spectrum (70 eV) *m/e* (rel intensity) 167 ($M\cdot^+$, 70), 124 (30), 80 (14), 43 (100).

*Anal.* Calcd for $C_2H_5N_3OSe$: C, 14.47; H, 3.04; N, 25.31; Se, 47.56. Found: C, 14.53; H, 3.05; N, 25.22; Se, 47.73.

**2,4-Diselenobiuret (6).** To a solution of sodium hydrogen selenide (0.026 mol), prepared as previously described[5] from 2.04 g (0.026 mol) of selenium and 1.08 g (0.028 mol) of sodium borohydride in 80 ml of ethanol under argon, was added 2,4-dimethyl-2,4-dithiopseudobiuret (**8**) (free base) in 30 ml of ethanol. The reaction mixture was stirred and heated at 50° for 20 hr until evolution of methyl mercaptan virtually ceased. The solution was acidified with 30 ml of deoxygenated hydrochloric acid and purged with argon to remove excess hydrogen selenide which was trapped. The reaction mixture was filtered to remove the trace of Se which separated, concentrated to about 30 ml, and cooled, causing separation of 1.5 g (63%) of 2,4-diselenobiuret (**6**) as a yellow, crystalline material which was analytically pure: mp 165° dec; ir (KBr) 3120 (NH) and 1610, 1540 $cm^{-1}$ (amide II); nmr (DMSO-$d_6$, external TMS) $\delta$ 11.60 (1), 10.70 (2), 10.33 (2), all broadened singlets; mass spectrum (70 eV) *m/e* (rel intensity) 231 ($M\cdot^+$, 9), 124 (62), and 80. The *m/e* 124 peak was observed to intensify with increasing sample time in the probe, suggesting possible thermal decomposition of **6**.

*Anal.* Calcd for $C_2H_5N_3Se_2$: C, 10.49; H, 2.20; N, 18.35; Se, 68.96. Found: C, 10.49; H, 2.13; N, 18.20; Se, 68.77.

**2,4-Dimethyl-2,4-dithiopseudobiuret (8) Hydriodide.** To 10.4 g (0.037 mol) of 2-methyl-2,4-dithiopseudobiuret (**9**) hydriodide[3] dissolved in 90 ml of water was added slowly 3.1 g (0.037 mol) of sodium bicarbonate in 24 ml of water. The thick white precipitate which formed was collected, suspended in acetonitrile, and treated with 8.5 g (0.06 mol) of iodomethane. The mixture was heated under reflux for 1 hr and concentrated, causing separation of 7.7 g (72% of 2,4-dimethyl-2,4-dithiopseudobiuret (**8**) hydriodide as cream-colored crystals which were analytically pure: mp 170–171° dec; ir (KBr) 3225 (NH), 3096 (CH), 1613 (C=N), and 1567 $cm^{-1}$ (NH).

*Anal.* Calcd for $C_4H_{10}N_3S_2I$: C, 16.50; H, 3.46; N, 14.43; S, 22.02; I, 43.58. Found: C, 16.36; H, 3.38; N, 14.44; S, 21.94; I, 43.26.

**2,4-Dimethyl-2,4-dithiopseudobiuret (8)** was prepared by suspending 1.5 g (0.005 mol) of **8** hydriodide in 20 ml of chloroform followed by the addition of 1.0 g (0.007 mol) of potassium carbonate in 20 ml of water. After the two phases were stirred for 15 min, the chloroform layer was separated, dried, and evaporated, yielding a colorless oil which crystallized upon standing. The 2,4-dimethyl-2,4-dithiopseudobiuret (**8**), after washing with hexane, was analytically pure, mp 92–93°. The compound has a strong odor of methyl mercaptan indicative of slow decomposition and was generally used immediately after preparation.

*Anal.* Calcd for $C_4H_9N_3S_2$: C, 29.43; H, 5.56; N, 25.74; S, 39.28. Found: C, 29.38; H, 5.68; N, 25.72; S, 38.72.

**Registry No.**—**1**, 108-19-0; **2**, 23228-74-2; **3**, 541-53-7; **4**, 21347-30-8; **5**, 52216-82-7; **6**, 52175-64-1; **7** HI, 34277-75-3; **8**, 15013-75-9; **8** HI, 52175-65-2; **9**, 40056-40-4; **9** HI, 21347-31-9; sodium hydrogen selenide, 12195-50-5.

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