A Convenient Synthesis of Mono-, *N,N'*-Di-, and Trisubstituted Selenoureas from Methyl Carbamimidothioates (*S*-Methylpseudothioureas)

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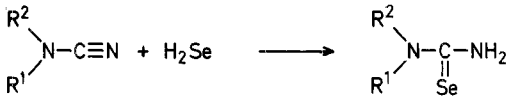
Substituted selenoureas are valuable starting materials for the synthesis of a number of selenium-containing compounds. Their synthesis has hitherto been accomplished by the following methods.

– mono- and *N,N*-disubstituted selenoureas[1-4]:

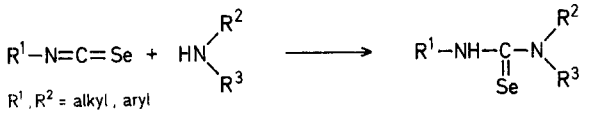


R^1 = alkyl, aryl
R^2 = H, alkyl, aryl

– mono- and *N,N'*-disubstituted selenoureas[4,5]:

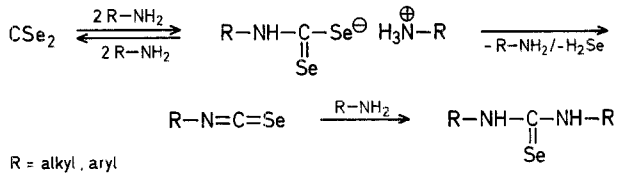
R^1 = alkyl, aryl
R^2 = H, alkyl, aryl

– mono-, *N,N'*- and trisubstituted selenoureas[6-10]:



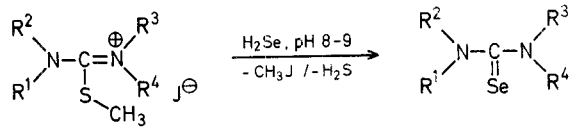
R^1, R^2 = alkyl, aryl
R^3 = H, alkyl, aryl

– *N,N'*-disubstituted selenoureas[11,12]:



R = alkyl, aryl

– mono-, di-, tri-, and tetrasubstituted selenoureas[13]:



R^1 = alkyl, aryl
R^2, R^3, R^4 = H, alkyl, aryl

We have now found that selenoureas (**3**) can be conveniently prepared by reaction of methyl carbamimidothioates (**2**, *S*-methylpseudoureas) with hydrogen selenide in anhydrous ethanol. The starting compounds **2** are obtained by adding concentrated aqueous ammonia to a solution of their hydroiodides (**1**) in water at 0 °C.

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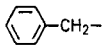
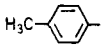
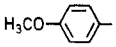
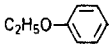
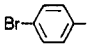
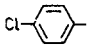
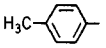
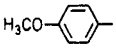
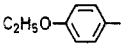
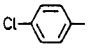
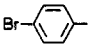
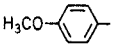
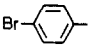
Table 1. Methyl Carbamimidothioate Hydroiodides (**1**, *S*-Methylpseudourea Hydroiodides) prepared

1	R^1	R^2	R^3	Yield [%]	m.p.	Molecular formula[a]	I.R. (KBr) ν [cm^{-1}] C=N	S–CH$_3$	C–N	C–S
a		H	H	80	104 °C	$C_9H_{13}JN_2S$ (308.2)	1620	1345	1292	715
b		H	H	90	144 °C	$C_8H_{11}JN_2S$ (294.2)	1610	1356	1312	690
c		H	H	95	130 °C	$C_9H_{13}JN_2S$ (308.2)	1615	1315	1300	705
d		H	H	80	164 °C	$C_9H_{13}JN_2OS$ (324.2)	1615	1318	1292	695
e		H	H	82	140 °C	$C_{10}H_{15}JN_2OS$ (338.2)	1618	1320	1292	695
f		H	H	70	216 °C	$C_8H_{10}BrJN_2S$ (373.0)	1622	1300	1282	715
g		H	H	78	172 °C	$C_8H_{10}ClJN_2S$ (328.6)	1618	1308	1282	715
h				82	173 °C	$C_{14}H_{15}JN_2S$ (370.2)	1590	1325	1308	687
i		H		90	193 °C	$C_{16}H_{19}JN_2S$ (398.3)	1585	1305	1288	697
j		H		85	189 °C	$C_{16}H_{19}JN_2O_2S$ (430.3)	1560	1320	1290	697
k		H		80	173 °C	$C_{18}H_{23}JN_2O_2S$ (458.3)	1568	1322	1288	710
l		H		72	204 °C	$C_{14}H_{13}Cl_2JN_2S$ (439.1)	1587	1322	1285	713
m		H		80	205 °C	$C_{14}H_{13}Br_2JN_2S$ (528.0)	1585	1325	1285	712
n	C_2H_5	H		60	164 °C	$C_{12}H_{19}JN_2OS$ (366.2)	1580	1325	1288	700
o		H		75	135 °C	$C_{15}H_{17}HN_2OS$ (400.2)	1560	1325	1290	680
p		H		70	206 °C	$C_{14}H_{13}BrClJN_2S$ (483.5)	1560	1323	1290	680
q	C_2H_5	C_2H_5		85	129 °C	$C_{14}H_{23}JN_2S$ (378.2)	1565	1313	1282	718

[a] The microanalyses of all products were in satisfactory agreement with the calculates values; J, ±0.4.

Table 2. Methyl Carbamimidothioates (**2A**, *S*-Methylpseudoureas) prepared

2	Yield [%]	m.p. found	m.p. reported	Molecular formula[a]	I.R. (KBr) ν [cm^{-1}] C=N	S–CH$_3$	C–N	C–S
a[b]	90	83 °C		$C_9H_{12}N_2S$ (180.3)	1588	1355	1260	700
b	95	87 °C	—[15]	$C_8H_{10}N_2S$ (166.2)	1612	1312	1275	715
c[b]	98	67 °C		$C_9H_{12}N_2S$ (180.3)	1635	1335	1292	718
d	88	115 °C	115 °C[16]	$C_9H_{12}N_2OS$ (196.3)	1635	1335	1303	720
e[b]	92	104 °C		$C_{10}H_{14}N_2OS$ (210.3)	1645	1335	1298	720
f[b]	80	94 °C		$C_8H_9BrN_2S$ (245.1)	1635	1340	1300	720
g[b]	85	83 °C		$C_8H_9ClN_2S$ (200.3)	1635	1335	1292	715
h	90	107 °C	109 °C[17]	$C_{14}H_{14}N_2S$ (242.4)	1578	1322	1288	688
i[b]	98	128 °C		$C_{16}H_{18}N_2S$ (270.4)	1565	1320	1285	700
j	92	96 °C	84–85 °C[18]	$C_{16}H_{18}N_2O_2S$ (302.4)	1595	1320	1295	705
k[b]	95	103 °C		$C_{18}H_{22}N_2O_2S$ (330.4)	1555	1315	1295	705
l	85	131 °C	133 °C[18]	$C_{14}H_{12}Cl_2N_2S$ (311.2)	1595	1317	1292	710
m	72	125 °C	129 °C[19]	$C_{14}H_{12}Br_2N_2S$ (400.1)	1592	1325	1298	718
n[b]	75	68 °C		$C_{12}H_{18}N_2OS$ (238.3)	1555	1310	1258	708
o[b]	87	84 °C		$C_{15}H_{16}N_2OS$ (272.4)	1600	1325	1295	690
p[b]	78	126 °C		$C_{14}H_{12}BrClN_2S$ (355.7)	1590	1320	1292	705
q[b,c]	95	b.p. 181–182 °C/ 4 torr		$C_{14}H_{22}N_2OS$ (266.4)	1555	1340	1265	720

[a] The microanalyses of all products were in satisfactory agreement with the calculated values: C, ±0.38; H, ±0.16; N, ±0.36; S, ±0.32.
[b] New compounds.
[c] In CCl_4.

Table 3. Selenoureas (**3**) prepared

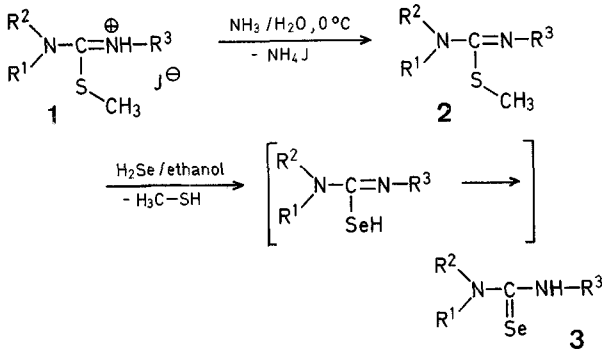
3	Yield [%]	m.p. (solvent) found	reported	Molecular formula[a]	I.R. (KBr) ν [cm^{-1}] (C=S)[b]	C=Se	C=N
a	92	183 °C (ethanol)		$C_8H_{10}N_2Se$ (213.3)	(1300)	1295	1280
b	80	190 °C (ethanol)[d]		$C_7H_8N_2Se$ (199.2)	(1285)	1273	1300
c	90	215 °C (ethanol)	193 °C[7]	$C_8H_{10}N_2Se$ (213.3)	(1280)	1272	1300
d	80	245 °C (butanol)	211 °C[7]	$C_8H_{10}N_2OSe$ (229.3)	(1292)	1292	1305
e	70	186 °C (butanol)		$C_9H_{12}N_2OSe$ (243.3)	(1290)	1285	1300
f[c]	52	236 °C (butanol)		$C_7H_7BrN_2Se$ (278.1)	(1272)	1268	1285
g	55	228 °C (butanol)	202 °C[7]	$C_7H_7ClN_2Se$ (233.7)	(1275)	1270	1285
h	68	209 °C (butanol)[d]	178–182 °C[13] 186 °C[7]	$C_{13}H_{12}N_2Se$ (275.3)	(1335)	1320	1305
i	85	207 °C (butanol)	176 °C[7]	$C_{15}H_{16}N_2Se$ (303.4)	(1305)	1315	1295
j	65	238 °C (butanol)	192 °C[7]	$C_{15}H_{16}N_2O_2Se$ (335.4)	(1325)	1325	1285
k[c]	62	223 °C (butanol)		$C_{17}H_{20}N_2O_2Se$ (363.4)	(1330)	1320	1292
l	60	218 °C (butanol)	177 °C[7]	$C_{13}H_{10}Cl_2N_2Se$ (344.2)	(1303)	1316	1300
m[c]	38	233 °C (butanol)		$C_{13}H_{10}Br_2N_2Se$ (431.5)	(1310)	1315	1295
n[c]	72	144 °C (butanol)		$C_{11}H_{16}N_2OSe$ (271.3)	(1300)	1288	1295
o	81	191 °C (butanol)	174 °C[7]	$C_{14}H_{14}N_2OSe$ (305.3)	(1325)	1320	1292
p[c]	42	221 °C (butanol)		$C_{13}H_{10}BrClN_2Se$ (387.8)	(1305)	1315	1300
q[c]	90	104 °C (ethanol)		$C_{13}H_{20}N_2OSe$ (299.4)	(1350)	1346	1285

[a] The microanalyses of all products were in satisfactory agreement with the calculated values: C, ±0.13; H, ±0.18; N, ±0.22; Se, ±0.19.

[b] C=S absorption of the corresponding thioureas for comparison.

[c] New compounds.

[d] Products prepared according to Ref.[13] had similar m.p.s and mass spectra to our products.



The crude products **3** thus obtained are sufficiently pure; recrystallization does not raise their melting points.

The I.R. spectra of compounds **1** (Table 1) show characteristic C=N bands at 1622–1560 cm^{-1}, S–CH$_3$ bands at 1356–1300 cm^{-1}, C–N bands at 1312–1282 cm^{-1}, and C–S bands between 718 and 680 cm^{-1}. The I.R. spectra of compounds **2** show C=N bands at 1645–1555 cm^{-1}, S–CH$_3$ bands at 1355–1410 cm^{-1}, C–N bands at 1302–1258 cm^{-1}, and C–S bands at 720–688 cm^{-1} (Table 2). The I.R. spectra of the selenoureas **3** show characteristic C=Se bands at 1346–1268 cm^{-1} and C–N bands at 1305–1285 cm^{-1} (Table 3).

All amines used and benzyl isothiocyanate were purchased from commercial sources. Phenyl isothiocyanate and its 4-methyl, 4-methoxy, 4-ethoxy, 4-chloro, and 4-bromo derivatives were prepared by the method described in Ref.[14]. The mono-, di-, and trisubstituted thioureas were prepared from the appropriate alkyl or aryl isothiocyanates by reaction with ammonia or amines following known procedures.

The I.R. spectra were recorded with a Beckman model 20A spectrophotometer. Combustion analyses for C, H, J, N, S, and Se were performed by C.N.R.S. (Service Central de Microanalyse; 2, rue Henry Dunant, 94-Thiais, France), and by Dornis & Kolbe, Mikroanalytisches Laboratorium, Hohenweg 17, D-4330 Mülheim/Ruhr, West Germany. Melting points were measured using a Kofler hot-bench apparatus.

Table 4. Mass Spectral Data for Selenoureas **3**

Product	M.S. (70 eV) *m/e* (relative intensity)
3c	214 (52) + 212 (26, M$^+$); 172 (9); 133 (100, 4-H$_3$C–C$_6$H$_4$–NH–C≡NH$^+$); 106 (57); 91 (56); 77 (16); 65 (21)
3d	230 (46) + 228 (23, M$^+$); 188 (10); 149 (100, 4-H$_3$CO–C$_6$H$_4$–NH–C≡NH$^+$), 108 (11); 99 (18); 92 (14); 75 (20); 43 (19)
3g	236 (25) + 234 (60) + 232 (29, M$^+$); 192 (9); 155 (33) + 153 (100, 4-Cl–C$_6$H$_4$–NH–C≡NH$^+$); 129 (19); 127 (56); 113 (10); 111 (30); 108 (11); 99 (18); 92 (14); 75 (20); 43 (19)
3h	276 (40) + 274 (20, M$^+$); 195 (82, C$_6$H$_5$–NH–C≡NH$^+$); 183 (20); 181 (10); 119 (17); 103 (13); 93 (100); 92 (43); 77 (88); 66 (27); 65 (24); 51 (40)
3i	304 (28) + 302 (14, M$^+$); 223 (66, 4-H$_3$C–C$_6$H$_4$–NH–C≡N–C$_6$H$_4$–CH$_3$-4$^+$); 222 (24); 197 (16); 195 (8); 107 (65); 106 (100); 91 (58); 79 (18); 77 (17); 65 (29)
3j	336 (26) + 334 (13, M$^+$); 255 (66, 4-H$_3$CO–C$_6$H$_4$–NH–C≡N–C$_6$H$_4$–OCH$_3$-4$^+$); 254 (39); 239 (40); 213 (33); 211 (16); 198 (22); 196 (11); 123 (66); 122 (68); 108 (100)
3l	346 (11) + 344 (18) + 342 (8, M$^+$); 265 (23) + 263 [33, (4-Cl–C$_6$H$_4$–NH)$_2$CSe$^+$]; 264 (20); 262 (22); 220 (17); 218 (38); 216 (19); 139 (12); 137 (35); 129 (33); 127 (100); 113 (12); 111 (36); 75 (44)
3o	306 (38) + 304 (19, M$^+$); 225 (100, 4-H$_3$CO–C$_6$H$_4$–NH–C≡N–C$_6$H$_5^+$); 224 (30); 213 (22); 211 (22); 209 (28); 123 (42); 122 (31); 108 (80); 93 (52); 92 (34); 77 (66); 51 (28)

Methyl Carbamimidothioate Hydrodiodides (1, *S*-Methylpseudourea Hydroiodides); Typical Preparation:

Methyl N-Benzylcarbamimidothioate Hydroiodide (**1a**): Iodomethane (14.3 g, 0.1 mol) is added to a solution of benzylthiourea (16.6 g, 0.1 mol) in the minimum quantity of acetone and the mixture is allowed to stand at room temperature overnight. The mix-

ture is then concentrated, the precipitated product isolated by filtration, washed with ether, and dried; yield: 24.7 g (80%); m.p. 104 °C.

Methyl Carbamimidothioates (2, *S*-Methylpseudoureas); Typical Preparation:

Methyl N-*Phenylcarbamimidothioate* **(2b):** A solution of the hydroiodide **1b** (29.5 g, 0.1 mol) in distilled water (800 ml) is cooled to 0 °C and basified with conc. aqueous ammonia. The precipitated product is collected by filtration, washed thoroughly with water, and dried; yield: 15.7 g (95%); m.p. 87 °C.

Selenoureas (3); Typical Preparation:

Phenylselenourea **(3b):** Dry hydrogen selenide (32.4 g, 0.4 mol; generated from aluminum selenide by addition of water, and dried by passing through a calcium chloride tube) is passed through a solution of methyl *N*-phenylcarbamimidothioate (**2b**; 16.6 g, 0.1 mol) in the minimum quantity of refluxing ethanol over a period of 2 h. The mixture is then allowed to stand at room temperature overnight. It is concentrated on a rotary evaporator, if necessary, and the precipitate isolated by filtration and recrystallized from ethanol; yield: 15.95 g (80%); m.p. 190 °C.

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[19] J. F. Deck, F. B. Dains, *J. Am. Chem. Soc.* **55**, 4986 (1933).

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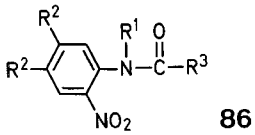
Errata and Addenda 1980

V. N. R. Pillai, *Synthesis* **1980** (1), 1–26;
The structure of compound **86** (p. 12) should be:

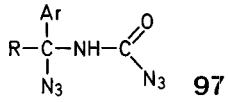


86

V. I. Cohen, *Synthesis* **1980** (1), 60–63;
The alternative name (in brackets) for compounds **1** (p. 62, first experimental procedure) should be ***S*-Methylpseudothiourea Hydroiodides.**

J. R. Mahajan, H. C. de Araújo, *Synthesis* **1980** (1), 64–66;
The authors have erroneously stated that "exaltolide" is a trivial name for pentadecanolide. In fact "exaltolide" is a trademark registered in the name of Firmenich SA, Geneva and should be designated as Exaltolide®.

V. I. Gorbatenko, L. I. Samarai, *Synthesis* **1980** (2), 85–110;
The structure of compound **97** (p. 99) should be:



97

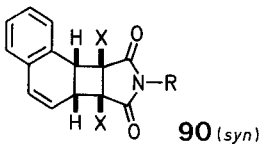
M. Mikołajczyk, P. Bałczewski, S. Grzejszczak, *Synthesis* **1980** (2), 127–129;
The correct name for compound **5a** (first procedure, p. 129) is **Diethyl 1-Phenylthioethanephosphonate.**

G. A. Olah, Y. D. Vankar, M. Arvanaghi, *Synthesis* **1980** (2), 141–142;
The correct name for compound **4** is ***N*-(Chlorosulfonyl)-dimethylsulfilimine.**

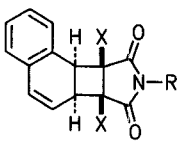
Abstract 5692, *Synthesis* **1980** (2), 159;
The title should be: **Phenols from Aryl Ethyl Ethers.**

Abstract 5698, *Synthesis* **1980** (2) 161;
The title should be: **Enals and Enones from Ketones.**

T. Wagner-Jauregg, *Synthesis* **1980** (3), 165–214;
The structures of compounds **90** (p. 175) should be:



90 (*syn*)



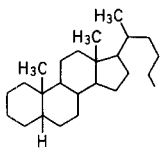
90 (*anti*)

The correct name for compound **251** (p. 188) is **2*H*-Cyclohepta[*gh*]pyrrolizin-Derivat.**

Abstract 5724, *Synthesis* **1980** (3), 254;
The title should be: **Carbamates, Thiocarbamates, and Carbonates from Alcohols or Thiols.**
The first line under the formula scheme should be: Y = O, S.

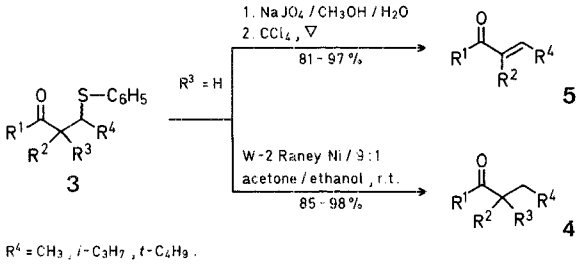
Abstract 5728, *Synthesis* **1980** (3), 256;
The title (and name for compound **3**) should be: ***N*-Sulphenylimines Derived from Amino Acids.**

C. R. Harrison, P. Hodge, *Synthesis* **1980** (4), 299–301;
The 3rd group in the Table, part B (p. 300) should have the structure:



Abstract 5745, *Synthesis* **1980** (4), 334;
The title should be: **Stereocontrolled *cis*-Addition of Organocopper Reagents to 2-Alkynals, 1-Alkynyl Ketones, 2-Alkynoic Acids, and 2-Alkynoic Esters.**

Abstract 5752, *Synthesis* **1980** (4), 336;
The title should be: **α-Alkylation and α-Alkylidenation of Carbonyl Compounds.**
The formula scheme for the conversion **3**→**4** or **5** should be:



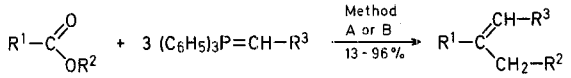
3 **5** **4**

R^4 = CH_3, *i*-C_3H_7, *t*-C_4H_9.

Abstract 5770, *Synthesis* **1980** (4), 342;
The title should be: **Claisen Rearrangement of Ketene Allyl Ethyl Acetals.**

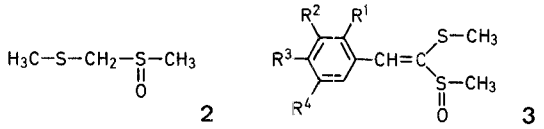
M. A. Alkhader, R. K. Smalley, B. Mohajerani, *Synthesis* **1980** (5), 381–383;
The correct name for compound **6** is **Indazolo[3,2-*b*]naphtho[2,3-*d*]-[1,3] oxazin-6-one.**

Abstract 5782, *Synthesis* **1980** (5), 418;
The formula scheme should be:



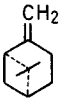
1 **2** **3**

Abstract 5799, *Synthesis* **1980** (5), 424;
The structures of compounds **2** and **3** should be:



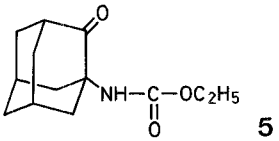
2 **3**

L. M. Harwood, M. Julia, *Synthesis* **1980** (6), 456–457;
The structure of compound (−)-**7** should be:



(−)-**7**

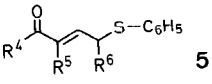
T. Sasaki, S. Eguchi, T. Okano, *Synthesis* **1980** (6), 472–475;
The structure of compound **5** should be:



5

Abstract 5804, *Synthesis* **1980** (6), 498;
The title should be: **Allylic Funtionalisation of Exomethylene Compounds.**

Abstract 5817, *Synthesis* **1980** (6), 503;
The structure of compound **5** should be:



5