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Facile conversion of amides and lactams to selenoamides and selenolactams using tetraethylammonium tetraselenotungstate

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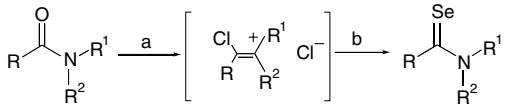
Dedicated to Professor M. V. George on the occasion of his 75th birthday

Abstract—Chloroiminium salts generated in situ from amides and lactams using $(COCl)_2$ or $POCl_3$ react very readily with the new selenium transfer reagent, tetraethylammonium tetraselenotungstate, $(Et_4N)_2WSe_4$, **1**, to afford the corresponding selenoamides and selenolactams in excellent yields under mild reaction conditions.

1. Introduction

Selenoamides[1] have received considerable attention owing to their importance as useful precursors for the synthesis of various selenium containing heterocycles[2] and also due to their varied reactivity.[3,4] Various methods are known in the literature for the synthesis of selenoamides.[5–11] The recent methods employ $(^iBu_2Al)_2Se$,[6a] $(Me_3Si)_2Se$,[6b] $[PhP(Se)(\mu\text{-}Se)_2]$[10] and bis(1,5-cyclooctanediylboryl)selenide[11] for the direct conversion of amides to selenoamides. Elemental selenium has been reduced by carbon monoxide and water system to generate H_2Se in situ and subsequently used for the synthesis of selenoamides from nitriles.[7] A combination of lithium alkyneselenolates, amines and allylic bromides is used in the synthesis of α,α′-disubstituted selenoamides.[8] Selenoamides are also prepared by trapping the chloroiminium salts with selenium nucleophiles such as $LiAlSeH_2$ and NaSeH.[5a,12] Earlier reports from our group have established tetraethylammonium tetraselenotungstate[13] $(Et_4N)_2WSe_4$, **1**, as an effective selenium transfer reagent for the synthesis of diselenides.[14] It was of interest to explore the utility of this reagent in the synthesis of selenoamides. Herein we report our initial results on the use of **1** in the synthesis of selenoamides and selenolactams from the corresponding amides and lactams via the corresponding chloroiminium salts (Scheme 1).



Scheme 1. Reagents and conditions: (a) $(COCl)_2$ or $POCl_3$, CH_2Cl_2, −78 to 25 °C, 0.5–5.5 h; (b) Et_4WSe_4, CH_2Cl_2, −78 to 25 °C, 0.5 h, 60–95%.

Initially we treated the amides directly with **1** (CH_2Cl_2, rt, 72 h, 1.1 equiv), but no product could be obtained even after prolonged reaction time. The nonreactivity can be attributed to the poor electrophilicity of the carbonyl carbon in the amide. This necessitated activation of the carbonyl group. We employed the strategy of trapping the chloroiminium salts with **1**. Accordingly, a number of amides were treated with $(COCl)_2$ (Method A) or $POCl_3$ (Method B) in CH_2Cl_2 (−78 to 25 °C, 0.5–5.5 h, 1.3 equiv) to generate the chloroiminium salt in situ and were subsequently treated with **1** (−78 to 25 °C, 0.5 h, 1.5 equiv) to afford the corresponding selenoamides in moderate to excellent yields.

The results are summarised in Table 1. As can be seen from the table N,N′-disubstituted selenoamides were obtained in excellent yields with $(COCl)_2$ as the promoter (entries 1–7). It is noteworthy that the reaction is

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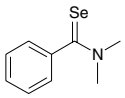
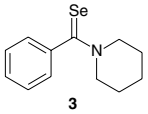
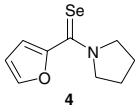
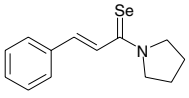
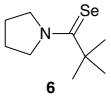
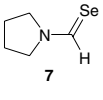
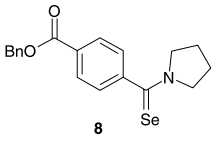
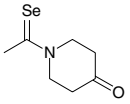
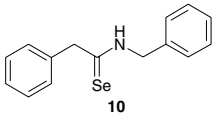
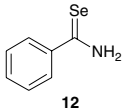
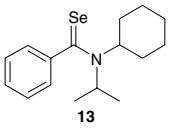
Table 1. Synthesis of selenoamides

Entry	Product	Method	Time (h)	Yield (%)[a,b]
1	 **2**	A	6	65
2	 **3**	A	1	80
3	 **4**	A	1	85
4	 **5**	A	1.5	80
5	 **6**	A	1.5	91
6	 **7**	A	1	90
7	 **8**	A	1.5	79
8	 **9**	B	2	55
9	 **10**	B	1.5	60
10	 **11**	B	1	76
11	 **12**	B	12	0
12	 **13**	A	12	0

[a] Refers to isolated yields.
[b] All the products exhibited expected analytical and spectral data.

effective in the presence of other carbonyl functional groups such as ester and keto groups (entries 7 and 8). This is an advantage over some of the existing methods, which could result in the conversion of both carbonyl groups into selenocarbonyl groups.[6c,11b] The steric bulk of the substitution at the nitrogen atom has a pronounced effect on the reaction.

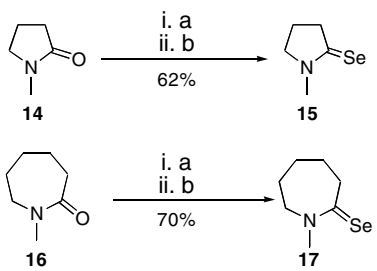
It has been found that the *N*-isopropyl-*N*′-cyclohexyl selenobenzamide could not be obtained by this method (entry 12). However the steric bulk at the carbonyl carbon does not seem to affect the reaction as can be seen in the formation of 1-(selenopivaloyl)pyrrolidine (entry 5). The reaction of the N-monosubstituted amides with $(COCl)_2$ as the promoter resulted in poor yields. The yields improved considerably when $POCl_3$ was used as the promoter for the formation of the chloroiminium intermediate (entries 9 and 10). The reaction of unsubstituted amides gave disappointing results as no product could be obtained as in the case of selenobenzamide (entry 11). The methodology was then extended for the conversion of lactams to selenolactams. *N*-Methylpyrrolidone **14** and *N*-methyl caprolactam **16** were converted to the corresponding selenolactams **15** and **17** in good yields (Scheme 2).

In conclusion, we have demonstrated the utility of tetraethylammonium tetraselenotungstate, **1**, as a selenium transfer reagent as applied to the synthesis of N,N′-disubstituted and N-monosubstituted selenoamides and selenolactams. This method complements and compares favourably with the existing methods in terms of minimising some of the practical difficulties such as harsh conditions, long reaction time, poor yields and selectivity. Further studies on the application of this transformation are currently under progress.

2. Experimental

2.1. General procedure for the synthesis of selenoamides

Method A: To a stirred solution of the amide (1 mmol) in CH_2Cl_2 (3 mL), $(COCl)_2$ (113 μL, 1.3 mmol) was added at −78 °C. The reaction mixture was allowed to warm to room temperature and stirred for 0.5–5.5 h. The solution was then diluted with CH_2Cl_2 (2 mL) and again cooled



Scheme 2. Reagents and conditions: (a) $POCl_3$, CH_2Cl_2, −78 to 25 °C, 45 min; (b) $(Et_4N)_2WSe_4$, −78 to 25 °C, 30 min.

to −78 °C. $(Et_4N)_2WSe_4$, **1**, (1.13 g, 1.5 mmol) was added at once. The reaction mixture was allowed to warm to room temperature and stirred for another half an hour. The solvent was removed under reduced pressure and the black residue was extracted with CH_2Cl_2–Et_2O (3:7, 6×15 mL) and filtered through a Celite pad. The filtrate was concentrated and the crude product was purified by recrystallisation or column chromatography on silica gel.

Method B: $POCl_3$ was used as the promoter instead of $(COCl)_2$.

2.2. Data for selected compounds

1-(Selenopivaloyl)pyrrolidine (**6**) yield 91%, yellow crystals, mp 43–45 °C; IR (KBr) 1510 (C═Se) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.41 (s, 9H, 3 × CH_3), 1.89 (quint, $J = 6.6$ Hz, 2H, CH_2), 2.05 (quint, $J = 6.6$ Hz, 2H, CH_2), 3.66 (t, $J = 6.6$ Hz, 2H, CH_2), 3.94 (t, $J = 6.6$ Hz, 2H, CH_2); ^{13}C NMR ($CDCl_3$, 75 MHz) 23.1, 27.5, 30.9, 46.0, 54.2, 62.4, 213.9; ^{77}Se NMR ($CDCl_3$, 77 MHz) 631.9; MS (EI) m/z 219 [M^+]; HRMS, calcd for $C_9H_{17}NSe$: 220.0604 [M+H]$^+$, found: 220.0585.

4-(Pyrrolidine-1-carboselenoyl)benzoic acid benzyl ester (**8**) yield 79%; yellow crystals; mp 106–108 °C; IR (KBr) 1513 (C═Se), 1715 (C═O) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.04 (quint, $J = 6.6$ Hz, 2H, CH_2), 2.13 (quint, $J = 6.6$ Hz, 2H, CH_2), 3.28 (t, $J = 6.6$ Hz, 2H, CH_2), 3.95 (t, $J = 6.6$ Hz, 2H, CH_2), 5.37 (s, 2H, CH_2), 7. 34–7.45 (m, 7H, Ar) 8.53 (d, $J = 7.8$ Hz, 2H, Ar); ^{13}C NMR ($CDCl_3$, 75 MHz) 24, 26.5, 54.5, 56.9, 66.8, 124.5, 128.1, 128.3, 128.6, 129.7, 129.9, 135.8, 150.6, 165.7, 179.2; ^{77}Se NMR ($CDCl_3$, 77 MHz) 744.5; MS (EI) m/z 373 [M^+]; HRMS, calcd for $C_{18}H_{17}NO_2Se$: 396.0479 [M+Na]$^+$, found: 396.0483.

1-Selenoacetylpiperidine-4-one (**9**) yield 55%; yellow crystals; mp 82–84 °C; IR (KBr) 1481 (C═Se), 1723 (C═O) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.63 (t, $J = 6.6$ Hz, 2H, CH_2), 2.73 (t, $J = 6.6$ Hz, 2H, CH_2), 2.76 (s, 3H, CH_3), 4.02 (t, $J = 6.6$ Hz, 2H, CH_2), 4.62 (t, $J = 6.6$ Hz, 2H, CH_2); ^{13}C NMR ($CDCl_3$, 75 MHz) 37.0, 39.3, 39.5, 47.5, 52.4, 204.2, 204.6; ^{77}Se NMR ($CDCl_3$, 77 MHz) 667.8; MS (EI) m/z 205 [M^+], HRMS, calcd for $C_7H_{11}NOSe$: 206.0084 [M+H]$^+$, found: 206.0096.

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