Reaction of diisobutylaluminium hydride with selenium and tellurium: new reagents for the synthesis of seleno- and telluro-amides

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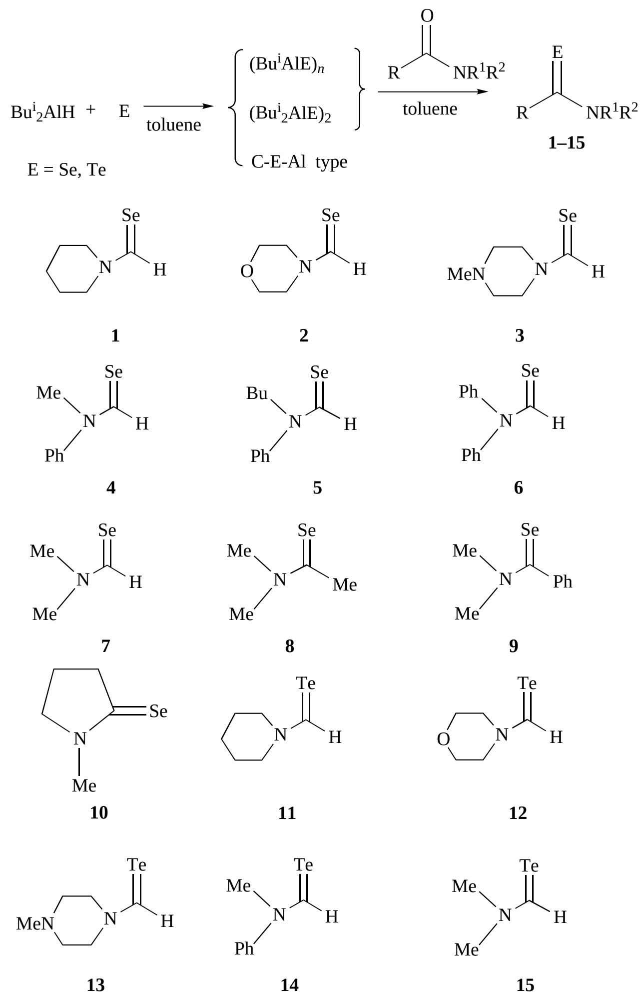
Diisobutylaluminium hydride (Bu^i_2AlH) undergoes reaction with elemental selenium and tellurium to afford new reagents having an Al–Se or an Al–Te bond. These directly convert amides to selenoamides and telluroformamides. This affords a one-pot route to selenoamides and telluroformamides starting from Se and Te, and may be suitable for large scale syntheses.

Introduction

Selenoamides have proved to be useful compounds in organic transformations and several methods for their preparation have been reported.[1] There has been a considerable interest in their tellurium analogs, *viz.*, telluroamides, with respect to their syntheses, structures and reactivities. Telluroamides, like other tellurocarbonyl compounds, are difficult to prepare due to the instability of the C=Te bond. To date, only a very limited number of telluroamides[2] and their first metal complexes[3] have been described. Among currently active studies in the field of organo-selenium and -tellurium chemistry,[4] bis(dimethylaluminium) selenide and telluride, $(Me_2Al)_2E$ where E is Se or Te, have been found to be effective reagents for the conversion of carbonyl groups to seleno- and tellurocarbonyls (C=E).[2b,c,5] Using this procedure, we have successfully synthesized two telluroamides and determined their crystal structures.[2c] In this paper,[6] we report a one-pot synthesis of seleno- and telluro-amides by the reaction of amides with some new Al–Se and Al–Te reagents (Scheme 1). These reagents are prepared by the reaction between diisobutylaluminium hydride and selenium or tellurium powders. They are obtained as a mixture of $(Bu^i_2AlE)_2$ and $(Bu^iAlE)_n$ where E is Se or Te.



Scheme 1

Results and discussion

Under an argon atmosphere, a mixture of Bu^i_2AlH (1.5 M) solution in toluene, 10 ml, 15 mmol) and one equivalent of powdered selenium or tellurium was heated at 120–130 °C for 1–2 h. All of the Se or Te was dissolved. There was first produced a clear colorless solution[7] in the case of Se, which subsequently converted to a white suspension when cooled below 90 °C. A white suspension[7] was obtained when Te was used. During the heating, gaseous evolution was observed.[8] Mass spectrometry confirmed that the gases were hydrogen and isobutane which indicated the formation of dimer $(Bu^i_2AlE)_2$ and oligomer $(Bu^iAlE)_n$.

The products obtained in the reaction between Se and Bu^i_2AlH were characterized by NMR spectrometry. In the ^1H spectra, compared with Bu^i_2AlH, the reaction mixture exhibited resonances at the same region except for the presence of a small doublet at δ 2.65 ppm arising from the CH_2 bonded to Se. This indicates that only a small amount of selenium inserts into the C–Al bond of Bu^i_2AlH to form C–Se–Al type compounds. Most of the selenium inserts between aluminium and the hydride hydrogen. Seven doublets for methyl and methylene protons of Bu^i groups appeared in the ^1H NMR spectra, and eight different carbon resonances were observed in the ^{13}C NMR spectra (Fig. 1). The relatively complicated ^1H and ^{13}C NMR spectra are due to the presence of a mixture of several Al–Se compounds formed in the reaction. In the ^{77}Se NMR spectra (in C_6D_6–toluene), two peaks (δ −184.53, −263.37 ppm) were observed. They arise from two different Al–Se compounds, $(Bu^iAlSe)_n$ and $(Bu^i_2AlSe)_2$. These shifted to δ −211.64 and −430.27 ppm when THF was added.[9]

These results suggest that the reaction between diisobutylaluminium hydride and selenium and tellurium produces a mixture of $(Bu^i_2AlE)_2$ and $(Bu^iAlE)_n$ (E is Se or Te) together with a small amount of C–E–Al type compounds.

Owing to their instability, toxicity, and extremely unpleasant odor, these reagents were neither purified nor fully characterized. We have begun to investigate their reactivities. As listed in Table 1, these reagents prepared *in situ* undergo reaction with amides and efficiently convert them to seleno- and telluro-amides **1**–**15**. In addition, $Bu^i{}_2E_2$, which was identified by ^1H NMR and mass spectrometry, was isolated in all cases in 5–10% yields.[7] Compounds **2**, **4**, **6**, **7**, **12** and **14** are the same as those obtained with the use of $(Me_2Al)_2E$.[2b,c,3] All selenoamides gave the expected NMR (^1H, ^{13}C, ^{77}Se), mass spectral and analytical data. Tellurium compounds (**11**–**15**) gave the expected spectral data, but because of decomposition during delivery they did not give acceptable elemental analyses. Seleno- and telluro-formamides (**1**–**7** and **11**–**14**) were isolated in yields of 49–69%. However, *N*,*N*-dimethyl(selenoacetamide) **8** and a γ-seleno-lactam, 1-methyl-2-selenoxopyrroline **10** were obtained in lower yields. *N*,*N*-dimethyl(selenobenzamide) **9** was isolated in only 30% yield, even under much more vigorous reaction conditions. All attempts to prepare *N*,*N*-dimethyl(telluroacetamide) and *N*,*N*-dimethyl(tellurobenzamide) were unsuccessful. This is probably because the CH_3 of *N*-acetyl or the Ph of *N*-benzoyl hindered the attack from Al–Se or Al–Te reagents into the carbonyl group.

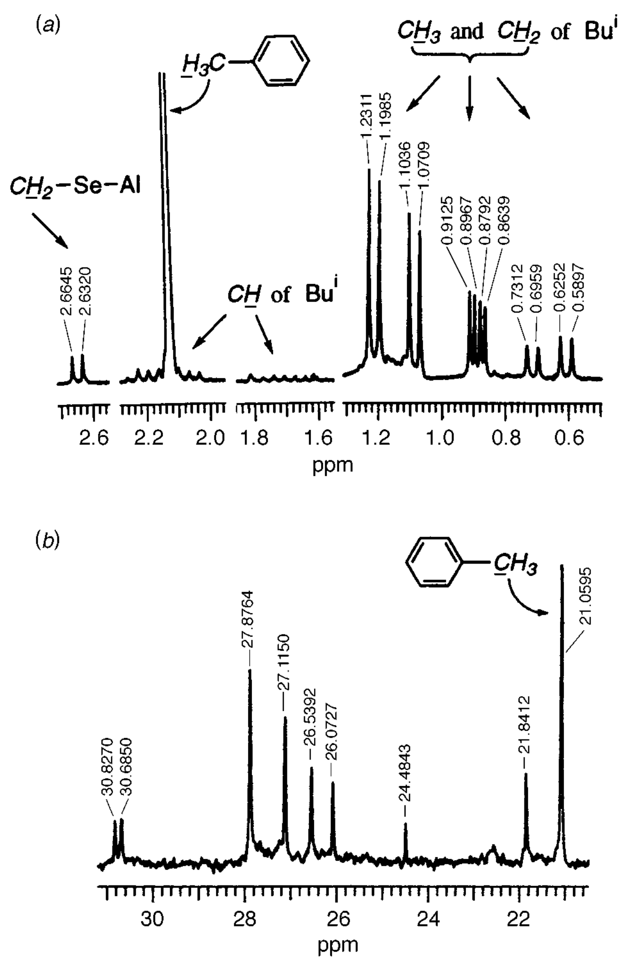


Fig. 1 (*a*) ^1H and (*b*) ^{13}C NMR spectra of Al–Se reagents formed in the reaction of $Bu^i{}_2AlH$ and Se (measured in C_6D_6–toluene, 200.1 Hz for ^1H; 50.3 Hz for ^{13}C)

Both the reagents described in this paper, $(Bu^i{}_2AlE)_2$ and $(Bu^iAlE)_n$ where E is Se or Te, and the closely related analog $(Me_2Al)_2E$ are good for the conversion of amides to selenoamides and telluroformamides. The former are much easier to prepare. The yields of selenoamides and telluroformamides obtained in the present work are generally lower than that prepared by the procedure using $(Me_2Al)_2E$.[2b,c] However, 4-(telluroformyl)morpholine (**12**) was obtained almost in the same yield: 66% in this work and 69.5% when $(Me_2Al)_2Te$ was used. In addition, $(Me_2Al)_2E$ compounds are useful for the preparation of selenoaldehydes, selenoketones, telluroaldehydes and telluroketones.[5] Further investigations on the utilization of the reagents $(Bu^i{}_2AlE)_2$ and $(Bu^iAlE)_n$ are in progress.

In conclusion, the present procedure provides a convenient synthetic route for the preparation of a variety of selenoamides and telluroformamides, and can easily be adapted to large scale syntheses with proper safety precautions in handling large amounts of diisobutylaluminium hydride toluene solutions.

Experimental

General

THF was refluxed over potassium metal and distilled under argon prior to use. All other chemicals were used as received. ^1H and ^{13}C NMR spectra were recorded on a Varian XL-200 spectrometer (200.1 MHz for ^1H, 50.3 MHz for ^{13}C). ^{77}Se and ^{125}Te NMR spectra were measured on a Varian XL-200 broad-band spectrometer (38.2 MHz for ^{77}Se, 63.1 MHz for ^{125}Te) with Ph_2Se_2 (δ 460 ppm referenced to Me_2Se)[10a] or Ph_2Te_2 (δ 420.8 referenced to Me_2Te)[10b] as the external standards. Mass spectra were run using a VG-70S spectrometer in the +FAB/DP or EI/DP mode. Melting points were determined on a Fisher-Johns melting point apparatus and are uncorrected. Elemental analyses were performed by Galbraith Laboratories,

Table 1 Preparation of seleno- and telluro-amides (**1**–**15**) from amides[a]

Reaction conditions					
°C	h	Product	Form	Mp (°C)	Yield (%)[b]
60–70	4	**1**	yellow solid	45.0–47.0	65.5
60–70	4	**2**	yellow solid	77.0–78.0	69
60–70	3	**3**	yellow oil		64
60–70	3	**4**	yellow oil		64
60–70	3	**5**	yellow oil		63
60–70	4	**6**[c]	yellow solid	128.0–130.0	60
60–70	3	**7**	yellow oil		58.8
60–70	5	**8**	yellow solid	78.0–80.0	34.6
100–110	12	**9**	orange solid	49.0–50.0	30
60–70	4	**10**	red oil		41
20–30	3	**11**	orange-red solid	50.0–55.0 (decomp.)	50
20–30	3	**12**	orange-red solid	83.0–85.0 (decomp.)	66
20–30	3	**13**	red oil		49
20–30	3	**14**	deep purple oil		51
20–30	3	**15**	deep red oil		25

[a] All reactions were performed on a 15 mmol scale (10 ml of 1.5 M $Bu^i{}_2AlH$ toluene solution, 15 mmol of Se or Te, and 15.5 mmol of an amide). [b] Isolated yield based on Se or Te. [c] The starting material, *N*,*N*-diphenylformamide, was dissolved in 5 ml of THF (dry) prior to adding to the suspension (Al–Se reagents in toluene).

Inc (USA) and Canadian Microanalytical Service, Ltd (Canada).

General procedure for one-pot synthesis of selenoamides

A mixture of selenium (1.185 g, 15 mmol) and Bu^i_2AlH (1.5 M in toluene, 10 ml, 15 mmol) was heated at 120–130 °C for 1 h under argon, and then cooled to room temperature. To this, 15.5 mmol of the appropriate amide was added. The mixture was stirred under the conditions shown in Table 1. Following evaporation, the residue was chromatographed on Silica gel column with hexane followed by CH_2Cl_2 as the solvents.[11] Evaporation of the eluate gave the corresponding selenoamides.

1-(Selenoformyl)piperidine 1. *m*/*e* (+FAB mode) 178 ([M + H]$^+$, ^{80}Se) (Anal. Calcd for $C_6H_{11}NSe$: C, 40.92; H, 6.30; N, 7.95. Found: C, 40.96; H, 6.28; N, 7.96%); $\delta_H(CDCl_3)$ 10.26 (s, 1H), 3.78 (br s, 2H), 3.36 (br s, 2H), 1.45 (br s, 6H); $\delta_C(CDCl_3)$ 186.35, 58.24, 48.29, 25.60, 23.83, 22.80; $\delta_{Se}(CDCl_3)$ 496.1.

4-(Selenoformyl)morphline 2. All analytical and spectral data have been reported previously.[3]

4-Methyl-1-(selenoformyl)piperazine 3. *m*/*e* (+FAB mode) 193 ([M + H]$^+$, ^{80}Se) (Anal. Calcd for $C_6H_{12}N_2Se$: C, 37.70; H, 6.33; N, 14.66. Found: C, 37.61; H, 6.20; N, 13.99%); $\delta_H(CDCl_3)$ 10.61 (s, 1H), 4.13 (t, 2H), 3.62 (t, 2H), 2.45–2.55 (m, 4H), 2.32 (br s, 3H); $\delta_C(CDCl_3)$ 189.02, 57.46, 54.71, 53.40, 48.12, 45.50; $\delta_{Se}(CDCl_3)$ 535.2.

***N*-Methyl(selenoformanilide) 4.** *m*/*e* (+FAB mode) 200 ([M + H]$^+$, ^{80}Se) (Anal. Calcd for C_8H_9NSe: C, 48.50; H, 4.58; N, 7.07. Found: C, 49.13; H, 4.66; N, 7.12%); $\delta_H(CDCl_3)$ 11.17 (s, 1H), 7.30–7.50 (m, 3H), 7.20–7.30 (m, 2H), 3.76 (s, 3H). $\delta_C(CDCl_3)$ 192.38, 147.06, 129.72, 127.77, 121.48, 41.71; $\delta_{Se}(CDCl_3)$ 696.6.

***N*-Butyl(selenoformanilide) 5.** *m*/*e* (+FAB mode) 242 ([M + H]$^+$, ^{80}Se) (Anal. Calcd for $C_{11}H_{15}NSe$: C, 55.00; H, 6.29; N, 5.83. Found: C, 54.98; H, 6.31; N, 5.71%); $\delta_H(CDCl_3)$ 11.04 (s, 1H), 7.30–7.50 (m, 3H), 7.15–7.30 (m, 2H), 4.37 (t, 2H), 1.50–1.80 (m, 2H), 1.20–1.50 (m, 2H), 0.90 (t, 3H); $\delta_C(CDCl_3)$ 192.28, 146.06, 129.77, 128.06, 122.77, 52.93, 28.21, 19.91, 13.67; $\delta_{Se}(CDCl_3)$ 651.4.

***N*,*N*-Diphenyl(selenoformamide) 6.** Analytical and spectral data have been reported in ref. 2*c*.

***N*,*N*-Dimethyl(selenoformamide) 7.** *m*/*e* (EI mode) 137 (M$^+$, ^{80}Se) (Anal. Calcd for C_3H_7NSe: C, 26.48; H, 5.19; N, 10.29. Found: C, 26.92; H, 5.51; N, 10.18%); $\delta_H(CDCl_3)$ 10.56 (br s, 1H), 3.30 (br s, 3H), 3.26 (br s, 3H); $\delta_C(CDCl_3)$ 190.44, 47.79, 40.50; $\delta_{Se}(CDCl_3)$ 553.5.

***N*,*N*-Dimethyl(selenoacetamide) 8.** *m*/*e* (EI mode) 151 (M$^+$, ^{80}Se) (Anal. Calcd for C_4H_9NSe: C, 32.01; H, 6.04; N, 9.33. Found: C, 31.81; H, 5.79; N, 8.99%); $\delta_H(CDCl_3)$ 3.48 (s, 3H), 3.15 (s, 3H), 2.55 (s, 3H); $\delta_C(CDCl_3)$ 202.33, 48.29, 42.45, 36.82; $\delta_{Se}(CDCl_3)$ 620.2.

***N*,*N*-Dimethyl(selenobenzamide) 9.** *m*/*e* (+FAB mode) 214 ([M + H]$^+$, ^{80}Se) (Anal. Calcd for $C_9H_{11}NSe$: C, 50.95; H, 5.23; N, 6.60. Found: C, 50.95; H, 5.66; N, 6.41%); $\delta_H(CDCl_3)$ 7.25 (m, 5H), 3.63 and 3.61 (2 × s, 3H); 3.04 and 3.02 (2 × s, 3H); $\delta_C(CDCl_3)$ 204.67; 145.77, 128.10, 127.76, 124.34, 47.01, 44.54; $\delta_{Se}(CDCl_3)$ 726.1.

1-Methyl-2-selenoxopyrroline 10. *m*/*e* (+FAB mode) 164 ([M + H]$^+$, ^{80}Se) (Anal. Calcd for C_5H_9NSe: C, 37.05; H, 5.60; N, 8.64. Found: C, 37.13; H, 5.55; N, 8.30%); $\delta_H(CDCl_3)$ 3.67 (br t, 2H), 3.32 (br s, 3H), 3.02 (br t, 2H), 2.04 (br, quintet, 2H); $\delta_C(CDCl_3)$ 202.96, 58.68, 49.04, 38.30, 20.01; $\delta_{Se}(CDCl_3)$ 372.0.

General procedure for one-pot synthesis of telluroamides

In an aluminium-foil-wrapped, very dry, and air-free three-necked flask, tellurium (1.915 g, 15 mmol) and Bu^i_2AlH (1.5 M in toluene, 10 ml, 15 mmol) was stirred at 120–130 °C for 2 h. To this, 15.5 mmol of an amide was added at room temperature. The mixture was stirred at 20–30 °C for 3 h, and then evaporated. The telluroamide was isolated by flash column chromatography on Florisil with hexane followed by CH_2Cl_2 as the solvents.[11]

1-(Telluroformyl)piperidine 11. *m*/*e* (+FAB mode) 227 (M$^+$, ^{130}Te); $\delta_H(C_6D_6)$ 12.52 (s, 1H), 3.69 (t, 2H), 2.48 (t, 2H), 1.05–1.25 (m, 2H), 0.70–1.00 (m, 4H); $\delta_C(C_6D_6)$ 177.03, 61.28, 55.00, 25.11, 24.62, 23.33; $\delta_{Te}(C_6D_6)$ 511.2.

4-(Telluroformyl)morphline 12. Full analytical and spectral data have been reported in ref. 3.

4-Methyl-1-(telluroformyl)piperazine 13. *m*/*e* (+FAB mode) 242 (M$^+$, ^{130}Te); $\delta_H(C_6D_6)$ 12.61 (s, 1H), 3.84 (t, 2H), 2.60 (t, 2H), 1.90 (t, 2H), 1.77 (s, 3H), 1.64 (t, 2H); $\delta_C(C_6D_6)$ 178.66, 59.99, 54.09, 54.04, 53.01, 44.91; $\delta_{Te}(C_6D_6)$ 542.5.

***N*-Methyl(telluroformanilide) 14.** $\delta_{Te}(C_6D_6)$ 875.3. For other spectral data, see ref. 2*b*.

***N*,*N*-Dimethyl(telluroformamide) 15.** *m*/*e* (EI mode) 187 (M$^+$, ^{130}Te); $\delta_H(C_6D_6)$ 12.47 (br s, 1H), 2.76 (s, 3H), 2.12 (s, 3H); $\delta_C(C_6D_6)$ 179.92, 49.57, 46.13; $\delta_{Te}(C_6D_6)$ 598.9.

Acknowledgements

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6 A part of this work has been presented at the 7th International Conference on the Chemistry of Selenium and Tellurium (ICCST-7), July 1997, Vaalsbroek Castle, The Netherlands.

7 By reaction with less fresh Bu^i_2AlH toluene solution, selenium gave a yellow solution and tellurium gave a brown-red suspension. It needed to reflux longer (3–4 h) to dissolve all selenium or tellurium powder, and the yields of by-product $Bu^i_2E_2$ (E: Se, Te) increased up to 20%.

8 As a controlled experiment, DIBAL-H (1.5 M solution in toluene) was heated at 120–130 °C for 2 h, but no gas was evolved and the NMR (^{1}H, ^{13}C) measurement has proved that DIBAL-H is stable under these conditions.

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11 Using hexane to remove $Bu^i_2Se_2$ or $Bu^i_2Te_2$, and then CH_2Cl_2 to elute selenoamides or telluroamides. For compounds **3** and **13**, acetone was used as the final solvent.

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