Synthetic Methods

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Procedure-Controlled Selective Synthesis of 5-Acyl-2-iminothiazolines and their Selenium and Tellurium Derivatives by Convergent Tandem Annulation**

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Convergent synthesis is of considerable importance in the construction of complex molecules, with the aim of improving the efficiency of multistep organic synthesis.[1] Tandem annulation enables the quick and efficient construction of important cyclic compounds using common and readily available chemicals.[2] The combination of convergent synthesis and tandem annulation not only improves step economy and operational simplicity for the synthesis of important molecules, but can also change the reaction pathway and lead to unexpected discoveries.

2-Iminothiazoline is a considerably important building block for pharmaceuticals that have powerful biological and pharmacological activities.[3] Although the synthesis of 2-iminothiazolines has received much interest,[4–8] 5-acyl-2-iminothiazoline is rarely seen because of the difficulty in introducing an acyl group at the 5-position of 2-iminothiazoline. Only one method was reported for the synthesis of 5-acyl-2-iminothiazolines and the yields were low.[6] More importantly, the synthesis of 5-acyl-2-iminoselenazolines and 5-acyl-2-iminotellurazolines, which are new types of heterocyclic compounds, are not reported. Thus, a simple, efficient, and general method to synthesize 5-acyl-2-iminothiazolines and their selenium and tellurium derivatives is of great importance to academia and to the pharmaceutical industry. Herein, we report a concise and efficient synthesis of 5-acyl-2-iminothiazolines and their selenium and tellurium derivatives by a convergent tandem annulation using readily available terminal alkynes, chalcogen elements (S, Se, and Te), carbodiimides, and acid chlorides.

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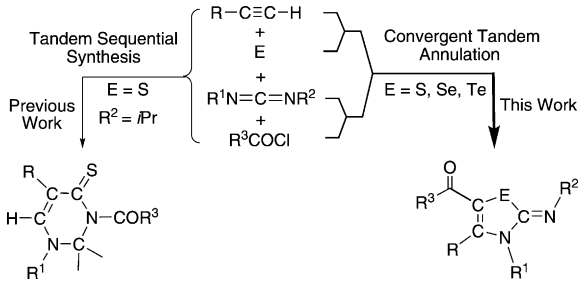
In the course of our study of the tandem sequential synthesis of 2,3-dihydropyrimidinthione from terminal alkynes, elemental sulfur, carbodiimides, and acid chlorides (Scheme 1),[9] we tried adding carbodiimides and acid chlorides simultaneously to lithium alkynethiolate, which had been generated in situ from a lithium acetylide and sulfur.[10] Interestingly, the simultaneous addition of a carbodiimide and an acid chloride, instead of the sequential addition, led to the observation of trace amounts of 5-acyl-2-iminothiazoline. After many screening experiments, a new protocol was established. Thus, after *N*,*N*′-diisopropylcarbodiimide (*i*PrN=C=N*i*Pr) was treated with benzoyl chloride at room temperature for 48 h, then treated with lithium alkynethiolate at 80 °C for 12 hours in THF, 5-acyl-2-iminothiazoline **1a** was obtained in 67% yield upon isolation (Scheme 2). X-ray crystallographic analysis of **1a** revealed unambiguously that the acyl group was at the 5-position of 2-iminothiazoline (Figure 1).



Scheme 1. Procedure-controlled selective synthesis of different N,E-containing compounds from the same starting materials.

The reaction is dependent on the convergent procedure as the result is in striking contrast with our reported tandem sequential reaction, which yielded 2,3-dihydropyrimidinthione,[9] even though the four starting materials: phenylethyne, sulfur, carbodiimide, and acid chloride, remained unchanged (Scheme 1). Representative examples of 5-acyl-2-iminothiazolines, 5-acyl-2-iminoselenazolines, and 5-acyl-2-iminotellurazolines, which were all obtained from the *n*BuLi-mediated convergent coupling of terminal alkynes, chalcogen elements (S, Se, and Te), carbodiimides, and acid chlorides, are shown in Scheme 2.

As shown in Scheme 2, carbodiimides, such as *i*PrN=C=N*i*Pr, CyN=C=NCy, PhN=C=NCy, and PhN=C=NPh, could be used as suitable nitrogen sources to give the corresponding compounds **1a**–**z** in moderate to high yields upon isolation. A

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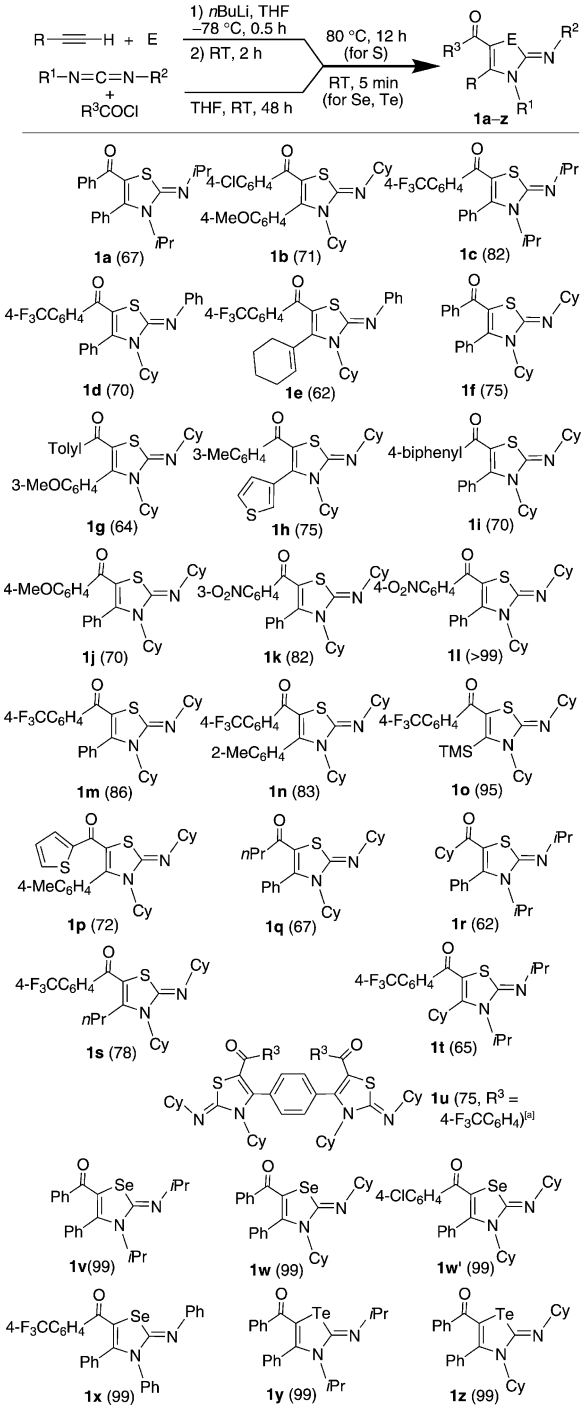

Scheme 2. Isolation and reaction of **2a–c** from symmetric or unsymmetrical carbodiimides and acid chlorides.

wide range of aromatic benzoyl chlorides with either electron-donating and electron-withdrawing groups on either the *meta* or *para* position of the phenyl skeleton gave the corresponding products **1a–o** in good yields. The heteroaromatic acid chloride 2-thienyl chloride (→**1p**) was also an appropriate substrate. Aliphatic acid chlorides also acted as a suitable acyl source to yield the corresponding compounds **1q** and **1r**. As far as the alkynes were concerned, the aromatic terminal alkynes with *ortho*, *meta*, and *para* substituents on the phenyl

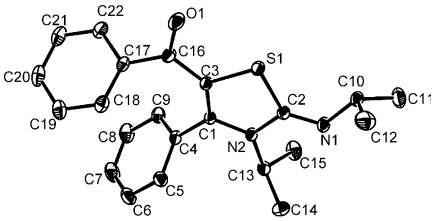

Figure 1. ORTEP drawing of **1a** with 20% thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å]: C1–C3 1.364(2), C2–S1 1.7718(16), C3–S1 1.7625(16), C1–N2 1.3785(19), C2–N2 1.4090(19), C2–N1 1.268(2), C13–N2 1.4879(19), C16–O1 1.232(2).

ring were converted into the corresponding products with high efficiency. The heteroaromatic terminal alkynes, such as 3-ethynylthiophene (→**1h**), showed good reactivity as well. Furthermore, the aliphatic terminal alkynes could also be applied in this reaction to provide the compounds **1e**, **1o**, **1s**, and **1t**. In addition, the *n*BuLi-promoted convergent reaction of the diyne 1,4-diethynylbenzene, elemental sulfur, CyN=C=NCy, and 4-trifluoromethylbenzoyl chloride afforded the corresponding bis(5-acyl-2-iminothiazoline) **1u** in 75% yield upon isolation.

Notably selenium, which like sulfur is in the chalcogen group, could be utilized in the present procedure to produce 5-acyl-2-iminoselenazolines **1v–x** in quantitative yields.[11] Similarly, 5-acyl-2-iminotellurazolines **1y** and **1z** were obtained with excellent selectivity and quantitative yields (Scheme 2). The reaction conditions required for RC≡CSeLi and RC≡CTeLi were much milder and faster (RT, 5 min) than those required for RC≡CSLi (80 °C, 12 h). To the best of our knowledge, our method demonstrates the first synthesis of the 5-acyl-2-iminoselenazolines and 5-acyl-2-iminotellurazolines, which represent new types of compounds that contain nitrogen and selenium, and nitrogen and tellurium.

These interesting and novel results intrigued us and encouraged us to explore the reaction mechanism, especially with regards to the position of the acyl group. It is reported in the literature that the reaction of a carbodiimide[12–15] with an acid chloride gives either an *N*-acyl chloroformamidine[16] or an *N*-acyliminium salt.[17] So we aimed to isolate and characterize the species produced by the reaction of a carbodiimide with an acid chloride. The reaction between a symmetric carbodiimide and an acid chloride afforded compound **2a** in a quantitative yield at room temperature after 48 hours (Scheme 3). When the unsymmetrical carbodiimide PhN=C=NCy was treated with 4-trifluoromethylbenzoyl chloride, compound **2b** was obtained as the only regioisomer. X-ray crystallographic analysis of **2a** and **2b** revealed unambiguously that they are *N*-acyl chloroformamidines and that the imine C=N bond adopts a *Z* configuration (Figure 2). In addition, the acyl group in **2b** is clearly attached to the nitrogen atom neighboring the phenyl group (Figure 2). These results are the first assured evidence of the structure of the adduct between a carbodiimide and an acid chloride.

Next the isolated *N*-acyl chloroformamidine **2a** was treated with the lithium alkynethiolate and lithium alkyneselenolate. 5-Acyl-2-iminothiazoline **1b** and 5-acyl-2-imino-

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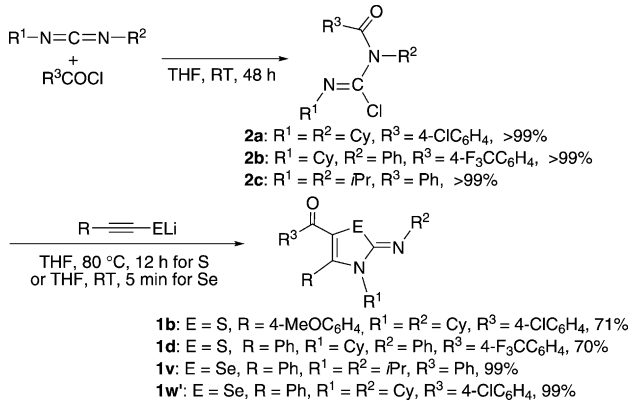


Scheme 3. Formation of 5-acyl-2-iminothiazolenes, 5-acyl-2-iminoselenazolines, and 5-acyl-2-iminotellurazolines. Reaction conditions: terminal alkynes (1 mmol), sulfur, selenium, or tellurium (1 mmol), *n*BuLi (1 mmol), carbodiimides (1 mmol), acid chlorides (1 mmol), THF (10 mL), unless otherwise noted. The yields (%) are of the isolated products. [a] Reaction conditions: terminal dialkyne (1 mmol), sulfur (2 mmol), *n*BuLi (2 mmol), carbodiimide (2 mmol), acid chloride (2 mmol).

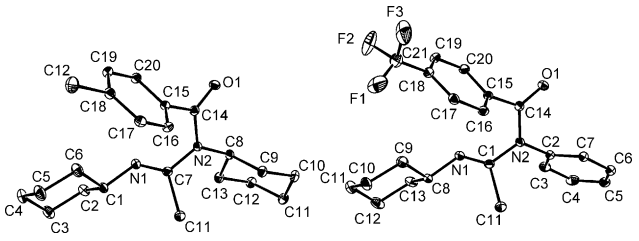
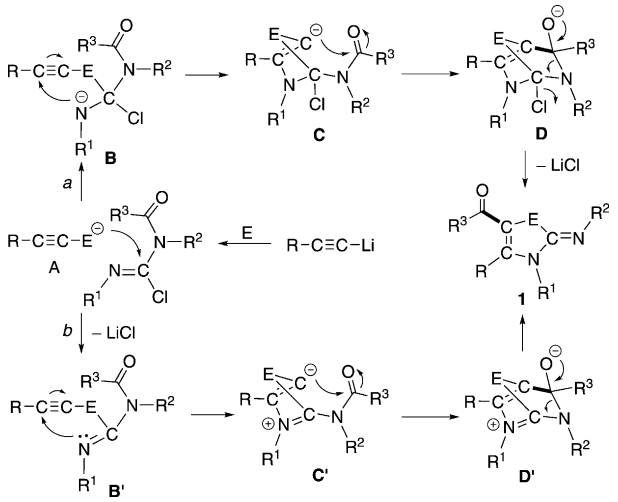


Figure 2. ORTEP drawing of **2a** (left) and **2b** (right) with 20% thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å]: **2a**: C7–Cl1 1.794(2), C7–N1 1.1.242(3), C7–N2 1.406(3), C8–N2 1.485(3), C1–N1 1.461(3), C14–N2 1.387(3), C14–O1 1.214(3); **2b**: C1–Cl1 1.780(5), C1–N1 1.217(5), C1–N2 1.411(5), C2–N2 1.423(5), C8–N1 1.474(5), C14–N2 1.417(5), C14–O1 1.211(4).

selenazoline **1w′** were obtained in 71% and 99% yields, respectively, upon isolation (Scheme 2). Similarly, **1d** and **1v** were obtained in high yields. The phenyl group from the carbodiimide is positioned regioselectively on the nitrogen atom of the imine C=N bond in **1d**.

A cross-over experiment was carried out to determine whether the transfer of the acyl group occurs by an intramolecular or intermolecular process. When a 1:1 molar mixture of **2a** and **2c** was treated with 2 equivalents of the lithium alkyneselenolate, their respective products, **1w′** and **1v**, were quantitatively formed in a 1:1 molar ratio, according to ^{1}H NMR analysis (see the Supporting Information for details), and no cross-over products were detected. This experiment indicated that an intramolecular acyl transfer was operating in the reaction process.

Based on the preliminary results, the proposed mechanisms for the formation of 5-acyl-2-iminothiazolines and their selenium and tellurium derivatives **1** are shown in Scheme 4. The reaction between a lithium acetylide and chalcogen elements (E = S, Se, and Te) should yield the lithium intermediate **A**. After nucleophilic attack by **A** on *N*-acyl



Scheme 4. Possible mechanisms for the formation of **1**.

chloroformamidine, the intermediate **B** would be formed. A five-membered-ring intermediate **C** would then be produced by intramolecular cyclization. The carbanion in **C** could attack the carbon atom of the amide group to give the bicyclic intermediate **D**.[18] Finally, **1** would be generated by an acyl shift through a C–N bond cleavage with LiCl elimination (Scheme 4, pathway a). Alternatively, as shown in pathway b, elimination of LiCl may initially take place, thus affording the final products **1** through intermediates **B′**, **C′**, and **D′**.

These results show a novel acyl 1,5-migration. Acyl migration is one of the fundamental bond-forming transformations in organic chemistry. Although 1,*n*-acyl migrations ($n = 2$, 3, 4) are well established[19,20] the remote 1,5-acyl migration is rare.[21]

In summary, a concise and procedure-controlled selective synthesis of 5-acyl-2-iminothiazolines and their selenium and tellurium derivatives has been achieved for the first time by an organolithium-promoted convergent tandem annulation involving readily available terminal alkynes, chalcogen elements (S, Se, and Te), carbodiimides, and acid chlorides. A novel 1,5-acyl migration is considered to be essential for such a useful and interesting transformation. The application of the 5-acyl-2-iminothiazolines and their selenium and tellurium derivatives as well as a study of the reactions of *N*-acyl chloroformamidines are in progress.

Experimental Section

Preparation of 5-acyl-2-iminothiazoline **1a**: In a 25 mL flask, benzoyl chloride (1 mmol) was added to *N*,*N*′-diisopropylcarbodiimide (1 mmol) in THF (10 mL), and the mixture was stirred at room temperature for 48 h. In another 25 mL flask, *n*BuLi (1 mmol, 1.6 M in *n*-hexane) was added dropwise at −78 °C to a solution of phenylethyne (1 mmol) in THF (5 mL), and the mixture was stirred at −78 °C for 0.5 h. Then sulfur (1 mmol, 32 mg) was added and the reaction mixture was warmed to room temperature for 2 h. The above two reaction solutions were mixed into one flask, which was heated to 80 °C for 12 h in THF. The solvent was evaporated under vacuum and the residue was purified by flash column chromatography on silica gel (eluent 1:1 dichloromethane/petroleum ether) to give product **1a**.

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Single crystals of **1a** suitable for X-ray crystallographic analysis were grown in CH_2Cl_2/*n*-hexane at room temperature for 3 days. Yellow solid, yield 67% (243 mg); m.p. 128.3–129.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si): $\delta = 1.21$ (d, $J = 6.2$ Hz, 6H, CH_3), 1.44 (d, $J = 6.8$ Hz, 6H, CH_3), 3.15–3.22 (m, 1H, CH), 3.85–3.92 (m, 1H, CH), 6.96–7.20 ppm (m, 10H, CH); ^{13}C NMR (100 MHz, $CDCl_3$, Me_4Si): $\delta =$ 18.99, 22.97, 51.21, 56.59, 112.57, 127.24, 127.64, 128.11, 129.30, 129.47, 129.89, 130.71, 139.13, 150.19, 151.24, 187.69 ppm; IR (film): $\tilde{\nu} = 1622$ (C=O), 1544 cm^{-1} (C=N); HRMS (ESI): *m*/*z*: calcd for $C_{22}H_{25}N_2OS$: 365.1682 $[M+H]^+$; found: 365.1684.

Isolation of *N*-acyl chloroformamidine **2b**: In a 25 mL flask, 4-trifluoromethylbenzoyl chloride (1 mmol) was added with stirring to *N*-cyclohexyl-*N*′-phenylcarbodiimide (1 mmol) in THF (10 mL) at room temperature. After 48 h, the reaction mixture was concentrated under vacuum to leave *N*-acyl chloroformamidine **2b**. Single crystals of **2b** that were suitable for X-ray crystallographic analysis were grown in THF/*n*-hexane at room temperature under nitrogen for 2 days. Colorless solid, yield >99% (408 mg); m.p. 73.6–74.3 °C; ^{1}H NMR (300 MHz, C_6D_6): $\delta = 1.00$–1.35 (m, 10H, CH_2), 3.41 (brs, 1H, CH), 6.91–7.12 (m, 5H, CH), 7.23 (d, $J = 7.2$ Hz, 2H, CH), 7.53 ppm (d, $J = 7.8$ Hz, 2H, CH); ^{13}C NMR (75 MHz, C_6D_6): $\delta =$ 23.79, 25.567, 31.75, 61.64, 124.30 (q, $J_{C\text{-}F} = 270.7$ Hz), 125.44 (q, $J_{C\text{-}F} =$ 3.7 Hz), 127.25, 128.32, 128.78, 129.59, 130.96, 132.49 (q, $J_{C\text{-}F} =$ 32.1 Hz), 138.45, 139.88, 169.18 ppm; IR (film): $\tilde{\nu} = 1678$ (C=O), 1596 cm^{-1} (C=N); HRMS (ESI): *m*/*z*: calcd for $C_{21}H_{21}ClF_3N_2O$: 409.1289 $[M+H]^+$; found: 409.1300.

Crystallographic data for **1a**: $C_{22}H_{24}N_2OS$, $M_r = 364.49$ g mol^{-1}, $T = 293(2)$ K, monoclinic, space group $P21/c$, $a = 10.780(2)$, $b =$ 11.792(2), $c = 16.146(3)$ Å, $\beta = 99.50(3)°$, $V = 2024.2(7)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.196$ Mg m^{-3}, $\mu = 0.172$ mm^{-1}, GOF = 1.012, reflections collected: 18372, independent reflections: 4628 ($R_{int} = 0.0718$), final *R* indices $[I > 2\sigma I]$: $R_1 = 0.0471$, $wR_2 = 0.1037$, *R* indices (all data): $R_1 =$ 0.0754, $wR_2 = 0.1099$.

Crystallographic data for **2b**: $C_{21}H_{20}ClF_3N_2O$, $M_r =$ 408.84 g mol^{-1}, $T = 293(2)$ K, triclinic, space group $P\bar{1}$, $a =$ 5.9765(12), $b = 12.421(3)$, $c = 13.768(3)$ Å, $\alpha = 81.27(3)$, $\beta = 86.25(3)$, $\gamma = 84.71(3)°$, $V = 1004.5(4)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.352$ Mg m^{-3}, $\mu =$ 0.231 mm^{-1}, GOF = 1.002, reflections collected: 5259, independent reflections: 3899 ($R_{int} = 0.0534$), final *R* indices $[I > 2\sigma I]$: $R_1 = 0.0746$, $wR_2 = 0.1776$, *R* indices (all data): $R_1 = 0.1708$, $wR_2 = 0.1993$.

CCDC 804431 (**1a**), 804429 (**2a**), and 804430 (**2b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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