

# The conversion of furan-, thiophene- and selenophene-2-carbonyl azides into isocyanates: A DSC Analysis

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**Dedicated to Professor Domenico Spinelli on the occasion of his 70<sup>th</sup> birthday**

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## Abstract:

The Curtius Rearrangement (CR) of five heteroaroyl azides to the corresponding isocyanates was studied by Differential Scanning Calorimetry. The five compounds selected were the furan **1**, the thiophene **2**, 5-methylthiophene **3**, 5-(trimethylsilyl)thiophene **4**, and selenophene-2-carbonyl azide **5**. For each compound, the heat of the transition from the heteroaroyl azide to the isocyanate was measured by DSC under a set of standard conditions both in the absence and presence of an inert medium.

**Keywords:** Heteroaroyl azides, Curtius rearrangement, differential scanning calorimetry

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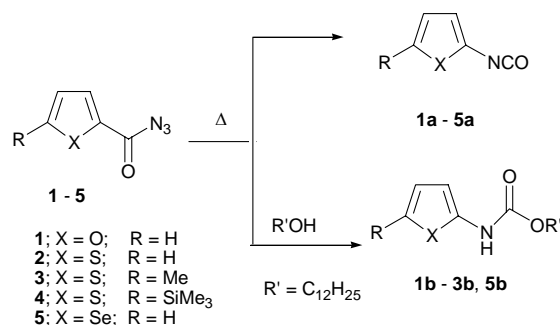
## Introduction

Organic isocyanates have been described as, “an essential tool for today's synthetic chemists”<sup>1</sup> owing to their diverse practical applications and the endless possibilities for the synthesis of isocyanate-based products.<sup>2</sup> Many aliphatic and aromatic mono-isocyanates have been synthesized through a range of procedures, the choice of which is largely dependent on the stability of the target molecule and availability of the starting material. Among the synthetic procedures that involve 1,2-migration from a carbon atom to a formal six-electron nitrogen atom,<sup>3</sup> the Curtius Rearrangement (CR) of carbonyl azides is considered the most convenient and general route,<sup>4</sup> especially for the synthesis of five-membered heteroaroyl isocyanates.<sup>5</sup> Reactions carried out in anhydrous conditions give isocyanates in very good yields, but in the presence of moisture hydrolytic steps may result in the conversion of carboxylic acids into amines, amides, carbamates or other N-linked heteroarenes.<sup>6</sup>

The mechanism of the thermal CR process has been the subject of much debate since the pioneering work of Stieglitz.<sup>7,8</sup> Other experiments gave results consistent with a concerted route for the thermal reaction.<sup>9</sup> Kitagawa *et al.* postulated the ready formation of the three-membered structure  $\text{NCC}=\text{O}$  as an intermediate, basing their conjecture on the observation of rapid thermal dissociation of several heteroaroyl azides.<sup>10</sup> To date, the reported carbonyl nitrenes have been generated only by photolysis, but these do not rearrange to  $-\text{NCO}$  at a rate high enough to make this pathway viable.<sup>11</sup>

In the present study we examine the CR mechanism using Differential Scanning Calorimetry analysis (DSC). This technique is known to provide information which is valuable for the planning of thermochemical reactions that involve organic azides<sup>12</sup> or acryloyl azides.<sup>13</sup> This work was undertaken with a view to uncovering new evidence supporting the direct applicability of the CR to the synthesis of amines from carboxylic acids. Our long-standing interest in nitrogen pseudo-halogens such as azides and isocyanates arises from their utility in the synthesis of nitrogen-linked heteroaryls.<sup>14</sup> The dissociation of five-membered heteroaroyl azides exhibits chemical and thermal reactions dependent on the 2- or 3-azido position on the heteroaroyl ring,<sup>15</sup> and has been studied as a source of nitrogen heteroaryls.<sup>16</sup>

This work was undertaken both to evaluate the thermal conversion of the heteroaroyl azides **1–5** as a less expensive source of nitrogen heteroaryls, and to measure by thermal DSC analysis the energy associated with the CR of the heteroaroyl azides: furan **1**, thiophene **2**, 5-methyl thiophene **3**, 5-(trimethylsilyl) thiophene **4**, and selenophene-2-carbonyl azide **5**, (Scheme 1) to heteroaroyl isocyanates **1a–5a**.<sup>17</sup> The analyses were carried out on both the neat heteroaroyl azides and on solutions in hexadecane ( $\text{C}_{16}\text{H}_{34}$ ). To confirm that the intermediates are exclusively isocyanates we carried out reactions in the presence of 1-dodecanol, which forms the corresponding heteroaroyl carbamates **1b–5b**, usually in good yields.

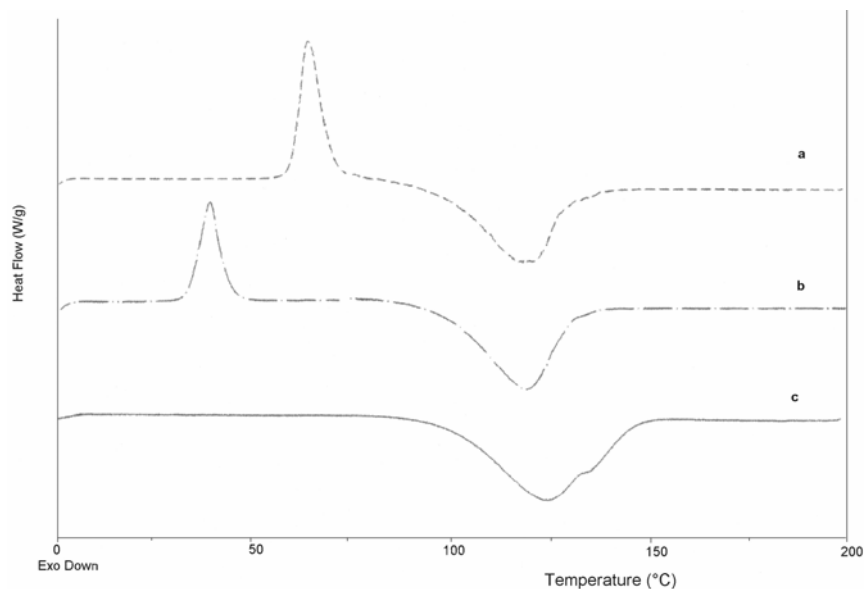


**Scheme 1**

## Results and Discussion

The starting heteroaroyl azides **1–5** were synthesized from the corresponding carboxylic acids via mixed anhydrides, or by using carbonyl chloride and sodium azide, according to the literature

procedures.<sup>18,19</sup> The structures of the products were established using IR, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR and high resolution mass spectroscopy. Pilot thermolysis of the carbonyl azides **1–3** and **5** (1 mmol) at 220 °C for 15 minutes in anhydrous hexadecane (1 dm<sup>-3</sup>) led to the corresponding isocyanates **1a–3a** and **5a**. An exception was observed for the carbonyl azide **4**. In this case the reaction temperature was high that the main product was the desilylation product, 2-thienyl isocyanate **2a**.



**Figure 1.** DSC Thermograms of: (a) carbonyl azide **1**. (b) carbonyl azide **2**. (c) carbonyl azide **4**.

**Table 1.** Thermal data (melting point  $T_f$ , onset and peak temperature  $T_r$  and  $T_p$ , and energy  $E$ ) obtained by Differential Scanning Calorimetry<sup>a</sup> for the decomposition of the heteroaroyl azides **1–5** to isocyanates **1a–3a**, **5a**

Entry	Carbonyl azides	$T_f/^\circ\text{C}$	Transition	$T_r/^\circ\text{C}$	$T_p/^\circ\text{C}$	$E/\text{cal/g}$	$E/\text{cal/g}$
1	Furan-2-carbonyl azide	63.00	<b>1</b> → <b>1a</b>	75	118	-89.5	-12.3±0.4
2	Thiophene-2-carbonyl azide	39.00	<b>2</b> → <b>2a</b>	91	119	-72.9	-11.2±0.6
3	Thiophene-2-carbonyl azide <sup>b</sup>		<b>2</b> → <b>2a</b>	107	134	-72.9	-11.2±0.5
4	5-Methylthiophene-2-carbonyl azide	59.87	<b>3</b> → <b>3a</b>	84	124	-100.0	-16.7±0.7
5	5-Methylthiophene-2-carbonyl azide <sup>b</sup>		<b>3</b> → <b>3a</b>	106	134	-107.8	-18.0±0.9
6	5-(Trimethylsilyl)-thiophene-2-carbonyl azide <sup>c</sup>	oil	<b>4</b> → <b>2a</b>	75	125	-117.3	-26.4±0.0
7	Selenophene-2-carbonyl azide	33.56	<b>5</b> → <b>5a</b>	71	119	-56.1	-11.2±0.5

<sup>a</sup> (DSC, 10 °C/min). <sup>b</sup> Analysis carried out in anhydrous hexadecane. <sup>c</sup> Undergoes desilylation on running.

The structures of **1a–3a** and **5a** were confirmed by IR- and  $^1\text{H-NMR}$  spectroscopy. In all cases the CRs in hexadecane proved safe, at least on the limited scale studied. On this basis we carried out thermal DSC analyses both for the neat heteroaroyl azides **1–5** and for the carbonyl azides **2** and **3** in hexadecane solutions. Data were obtained from three runs on TA Instruments 2920 CE, using *ca.* 5–15 mg of substance in a sealed aluminum crucible. The DSC thermograms of the neat **1**, **2**, **3** and **5** are characterized by two baseline shifts. The first shift (lower temperature onset) corresponds to the positive enthalpies of fusion ( $s \rightarrow l$ ), and has peak temperatures of 63.0, 39.0, 59.9 and 33.6 °C for **1**, **2**, **3** and **5**, respectively. This peak is not observed for **4**. The second base-line shift (first for **4**) is observed at higher temperature. The onset temperatures of this peak (*i.e.*, the intersection of the baseline with the peak tangent) for compounds **1–5** are *ca.* 100, 97, 100, 100 and 97 °C, respectively. The integral normalized area of this peak is related to the heat capacity of the exothermic CR transition (reactants  $\rightarrow$  products) of the heteroaroyl azides **1–5**. The thermal DSC data are listed in Table 1, entries 1, 2, 4, 6 and 7.

Figure 1 depicts representative DSC thermograms, measured from runs in which neat **1**, **2** and **4** (lines a, b and c, respectively) were heated from 10 to 200 °C at a heating rate of 10 °C/min under nitrogen. The right-hand side of the peak of **4** (line c) is broad; this broadening may be partially due to a contribution from the desilylation reaction. The thermal data roughly correspond to the standard reaction enthalpy (*i.e.*, the change in enthalpy when reactants in their standard states change to products in their standard states) for the equation:



The energies associated with the decomposition of neat samples of **1–5** were measured to be 89.5, 72.9, 100.0, 117.3 and 56.1 cal/g, respectively. Although this technique is known to have relatively low sensitivity, the energy output for each compound appears to be real for intramolecular thermolytic reaction. Calculations of the absolute values of the heats of transition including changes of the physical state are not considered here.<sup>20</sup>

The data obtained for **2** and **3** in hexadecane solution (Table 1, entries 3 and 5) indicate that the changes in energies differ insignificantly from those observed for the neat samples. Thus, no appreciable interaction is expected between ionic (or other) reactive species and the solvent over the course of the thermal reaction. The carbonyl azides in solution show higher onset, and somewhat broader peaks, than the corresponding neat samples. This suggests that the solvent plays a role in controlling the ratio temperature/reactivity of the CR process. As mentioned above, the thermolysis of the compounds **1–4** at 220 °C for 15 min in 1-dodecanol solvent (1:4, w/w) affords the corresponding heteroaroyl carbamates **1b–3b** in high yield. In the same manner, the reaction with azide **5** afforded the carbamate **5b** in 56% yield; the lower yield is probably due to the instability of the product. As expected, the carbonyl azide **4** undergoes a desilylation leading to the exclusive formation of 2-thienyl carbamates **2b**. The thermolysis in 1-dodecanol solvent described here involves a concerted CR mechanism that includes isocyanates as transient species which further react with the alcoholic solvent. The resulting carbamates **1b–3b** and **5b**

were recovered as solid precipitates after diluting the reaction mixtures with petroleum ether (b.p. 40–60 °C, 1:4, v/v) and maintaining the resulting suspension at 0 °C for 5 h. The new carbamates were recovered by filtration under vacuum and characterized by <sup>1</sup>H-NMR, IR and high resolution mass spectroscopy. It is noteworthy that thermal DSC analyses for the carbonyl azides **2** and **3** in 1-dodecanol solutions showed endothermic global transition (reactants → products) whose onset temperatures are at 130 °C.

The CR process is postulated to occur via a concerted mechanism in which the C-2–N-1  $\sigma$  and N-1–C(O)  $\pi$  bonds form at the same time as the C2–C(O) and N-1–N-2  $\sigma$  bonds rupture. This appears to be confirmed by the absence of any by-product. The energies associated with the whole process were measured to be 0.55 and 0.45 kcal/m, respectively.

## Conclusions

In conclusion, the DSC analysis of the heteroaroyl azides **1–5** provides adequate information about the energetics and thermal stability of the starting compounds. The reactions described can be carried out safely using dose-rate control. The method described here can be utilized as a tool to study the synthetic utility of the CR in a wide range of applications; for example, for access to 2-nitrogen- substituted heteroaryls, and does not require the isolation of the isocyanates.

## Experimental Section

**Materials.** 2-Furoyl chloride, thiophene-2-carbonyl chloride, thionyl chloride, butyl lithium, ethyl chloroformate and sodium azide were purchased from Aldrich Chimica Italiana and used as received. Commercial 1-dodecanol and anhydrous hexadecane were degassed under reduced pressure (0.5 mm) for 1 h and maintained under a nitrogen atmosphere. 5-Methylthiophene-, 5-(trimethylsilyl)thiophene- and selenophene-2-carboxylic acids were prepared from the corresponding 2-lithio-5-methyl thiophene- 2-lithio-5-trimethylsilylthiophene and 2-lithio-selenophene and carbon dioxide according to the literature procedure<sup>21</sup> and confirmed using physical and spectroscopic data of authentic samples obtained by another method.<sup>22</sup> The heteroaroyl azides **1–5** were prepared from the appropriate carboxylic acids via mixed carboxylic–carbonic anhydride, or carbonyl chloride and sodium azide ion following the procedure described by Binder *et al.*<sup>18,19</sup>

**Caution.** Organic azides are potentially explosive! This category of compounds has been subjected to risk evaluation.<sup>17</sup> Explosions may occur when handling organic azides, although we experienced no problems in handling basic solutions of the sodium azide or solid organic azides, which can be stored indefinitely at –18 °C. The heteroaryl isocyanates are potentially toxic chemicals and must be handled with great care. Moreover, isocyanates **1a–5a** are highly reactive and their exposure to atmospheric moisture must be prevented.

**Instrumentation.** Melting points were determined on a Kofler hot-stage apparatus and are uncorrected. IR spectra were recorded in films using a Perkin-Elmer Spectrum 2000, FT-IR spectrometer.  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra were recorded on a Varian Gemini 200 (200 and 50 MHz, respectively) or -300 (300 and 75 MHz, respectively) for solutions in  $\text{CDCl}_3$  using TMS and  $\text{CHCl}_3$  as internal standards.  $J$ -Values are given in Hz. Mass spectra were recorded on VG7070E instruments using electron impact ionization (70 eV). Thermal DSC data were obtained on TA Instruments 2920 CE.

### General synthetic procedure for the heteroaroyl azides 1–5

To solutions containing 0.05 mol of the 5-methylthiophenecarboxylic acid (7.1 g), 5-trimethylsilylthiophenecarboxylic acid (10.0 g) and selenophene-2-carboxylic acid (8.7 g) in  $75\text{ dm}^3$  of anhydrous acetone at  $0\text{ }^\circ\text{C}$  was added 0.059 mol (5.95 g,  $8.35\text{ dm}^3$ ) of triethylamine in acetone ( $23\text{ dm}^3$ ) and 0.066 mol of ethyl chloroformate (7.2 g) in acetone ( $23\text{ dm}^3$ ). The resulting mixtures were stirred at  $0\text{ }^\circ\text{C}$  for 45 min and then a solution containing 0.085 mol (5.5 g) of sodium azide in  $19\text{ dm}^3$  of water was added dropwise within 1 h, after which the solution was warmed to room temperature and stirred for another 30 min.

The suspension was poured into cold brine and the resulting aqueous mixture was extracted twice with ether. The combined organic layers were washed with water and then dried. The solvent was eliminated under vacuum and the residue was chromatographed on a Florisil (100–200 U. S. mesh, BDH) column using light petroleum (b.p.  $30\text{--}60\text{ }^\circ\text{C}$ ) as the eluant. The resulting heteroaroyl azides **2–5** were characterized by  $^1\text{H}$ -NMR,  $^{13}\text{C}$ -NMR, IR and high-resolution mass spectroscopy. The physical properties and spectroscopic data of the compound **1** were found comparable to those previously reported.<sup>19</sup>

**Thiophene-2-carbonyl azide (2).** Yield 73%; m.p.  $34\text{--}36\text{ }^\circ\text{C}$ ;  $\nu_{\text{max}}/\text{cm}^{-1}$  3089, 2167 and 2128 ( $\text{N}_3$ ), 1678 (CO), 1518, 1410, 1247, 1214, 1048, 978 and 861;  $\delta_{\text{H}}$  (200 MHz;  $\text{CDCl}_3$ ) 7.83 (1H, dd,  $J$  3.8 and 1.2 H-3), 7.65 (1H, dd,  $J$  5.0 and 1.2, H-5) and 7.12 (1 H, dd,  $J$  5.0 and 4.0, H-4);  $\delta_{\text{C}}$  (50.8 MHz;  $\text{CDCl}_3$ ) 166.9, 135.0, 135.0 ( $J$  185.7), 134.7 ( $J$  171.1) and 128.7 (m,  $J$  170.5);  $m/z$ , 153 ( $\text{M}^+$ , 26.9%), 111 (M- $\text{N}_3$ , 100), 96 (21.5), 83 (11.4), 70 (38.4), 57 (27.5), 45 (51.6) and 39 (46.7); Found:  $\text{M}^+$ , 153.9997  $\text{C}_5\text{H}_3\text{N}_3\text{OS}$  requires: M, 153.9997.

**5-Methyl thiophene-2-carbonyl azide (3).** (92%);  $58\text{--}60\text{ }^\circ\text{C}$ ;  $\nu_{\text{max}}/\text{cm}^{-1}$  2920, 2153 ( $\text{N}_3$ ), 1675 (CO), 1463, 1277, 1194, 819 and 715;  $\delta_{\text{H}}$  (200 MHz;  $\text{CDCl}_3$ ) 7.62 (1H, d,  $J$  3.9 H-3), 6.77 (1H, m,  $J$  3.9 and 1.0, H-4) and 2.51 (3 H, d,  $J$  1.0);  $\delta_{\text{C}}$  (75 MHz;  $\text{CDCl}_3$ ) 166.3, 151.0, 135.1 (d,  $J$  170.2), 132.3, 119.6 (m,  $J$  168.0) and 16.0 (q,  $J$  129.5);  $m/z$ , 167 ( $\text{M}^+$ , 4.5%), 139 (M-28, 4.4), 138 (27.6), 125 (100), 111 (19.0), 96 (50.5), 84 (9.5), 78 (10.3), 69 (19.0), 59 (25.8), 53 (18.9) and 45 (33.3); Found:  $\text{M}^+$ , 167.0153  $\text{C}_6\text{H}_5\text{N}_3\text{OS}$  requires: M, 167.0153.

**5-(Trimethylsilyl) thiophene-2-carbonyl azide (4).** (78%); colorless oil;  $\nu_{\text{max}}/\text{cm}^{-1}$  2957, 2145 ( $\text{N}_3$ ), 1684 (CO), 1511, 1420, 1311, 1220 ( $\text{SiMe}_3$ ), 1249 and 840 ( $\text{SiMe}_3$ );  $\delta_{\text{H}}$  (200 MHz;  $\text{CDCl}_3$ ) 7.85 (1H, d,  $J$  3.7, H-3), 7.22 (1H, d,  $J$  3.7, H-4) and 0.33 (9 H);  $\delta_{\text{C}}$  (50.8 MHz;  $\text{CDCl}_3$ ) 166.6, 152.9, 139.4, 135.3 (d,  $J$  170.0), 133.4 (d,  $J$  168.0) and -0.34 (q,  $J$  120.0);  $m/z$ , 225 ( $\text{M}^+$ , 40.5%),

210 (M-Me, 21.5), 197 (3.6), 183 (47.4), 182 (67.9), 166 (7.4), 100 (100), 84 (19.6), 73 (21.2), 70 (9.4), 45 (12.2) and 43 (16.5); Found:  $M^+$ , 225.0391  $C_8H_{11}N_3OSSi$  requires: M, 225.0392.

**Selenophene-2-carbonyl azide, (5).** (74%); 32–34 °C;  $\nu_{max}/cm^{-1}$  3098, 2150 ( $N_3$ ), 1674 (CO), 1527, 1421, 1241, 1208, 1184, 793 and 713;  $\delta_H$  (200 MHz;  $CDCl_3$ ) 8.39 (1H, dd,  $J$  5.5 and 1.3 H-5), 8.08 (1H, dd,  $J$  4.0 and 1.3, H-3) and 7.37 (1 H, dd,  $J$  5.5 and 4.0, H-4);  $\delta_C$  (50.8 MHz;  $CDCl_3$ ) 168.1, 141.6, 141.5 (m,  $J$  187.2), 137.3 (m,  $J$  168.6) and 131.2 (m,  $J$  168.1);  $m/z$ , 201 ( $M^+$ , 60.2%), 173 (M-28, 4.9), 159 (100), 131 (14.4), 118 (26.4), 105 (17.9), 93 (13.9), 80 (11.1), 64 (31.5), 50 (14.9) and 39 (71.0); Found:  $M^+$ , 200.9440  $C_5H_3N_3OSe$  requires: M, 200.9441.

### General synthetic procedure for the heteroaryl isocyanates 3a–5a

Curtius rearrangement was performed using solutions containing 0.01 mol of the carbonyl azides 3–5 (1.7, 2.2 and 2.0 g, respectively) in nitrogen-purged carbon tetrachloride (20  $dm^3$ ). The solutions were heated under nitrogen pressure at 90 °C for 12 h, in a heavy-walled tube sealed with a Teflon septum inlet. The CR was monitored following both the disappearance of the reactant azides (2145–2155  $cm^{-1}$ ) and the formation of the isocyanates (2275–2285  $cm^{-1}$ ) by IR spectroscopy. The heteroaryl isocyanates were characterized by  $^1H$ -NMR,  $^{13}C$ -NMR, IR and high-resolution mass spectroscopy of the residue after removal of the carbon tetrachloride under reduced pressure without further purification. The  $^1H$ -NMR results for compound 4 showed less than 2% of the 2-isocyanatothiophene (a side product of desilylation).

The physical properties and spectroscopic data of **1a**<sup>23a</sup> and **2a**<sup>23b</sup> were found comparable to those previously reported.

**5-methyl-2-thienyl isocyanate, (3a).**  $\nu_{max}/cm^{-1}$  2957, 2280 (NCO), 1582, 1467, 1378, 790 and 721;  $\delta_H$  (200 MHz;  $CDCl_3$ ) 6.36 (1H, d,  $J$  3.7 H-3), 6.34 (1H, m,  $J$  3.7 and 0.9, H-4) and 2.34 (3 H, d,  $J$  0.9);  $\delta_C$  (75 MHz;  $CDCl_3$ ) 135.4, 133.8, 123.8 (d,  $J$  166.2), 120.4 (d,  $J$  168.6) and 15.8 (q,  $J$  129.2);  $m/z$ , 139 ( $M^+$ , 100%), 111 (M-28, 37.8), 96 (65.0), 84 (13.0), 78 (12.3), 69 (16.6), 59 (11.0), 53 (33.5) and 45 (32.0); Found:  $M^+$ , 139.0091  $C_6H_5NOS$  requires: M, 139.0092.

**5-(Trimethylsilyl)-2-thienyl isocyanate, (4a).**  $\nu_{max}/cm^{-1}$  2972, 2279 (NCO), 1475, 1421, 1220 ( $SiMe_3$ ) and 840 ( $SiMe_3$ );  $\delta_H$  (200 MHz;  $CDCl_3$ ) 6.69 (1H, d,  $J$  3.5, H-3), 6.91 (1H, d,  $J$  3.5, H-4) and 0.28 (9 H);  $\delta_C$  (50.8 MHz;  $CDCl_3$ ) 138.3, 136.8, 132.9 (d,  $J$  167.0), 125.9, 133.4 (d,  $J$  169.0) and -0.06 (q,  $J$  120.0);  $m/z$ , 197 ( $M^+$ , 28.7%), 182 (M-Me, 100), 118 (22.8), 117 (23.4), 100 (28.3), 91 (5.4), 73 (11.6), 45 (7.4) and 43 (9.0); Found:  $M^+$ , 225.0391  $C_8H_{11}N_3OSSi$  requires: M, 225.0392.

**2-Isocyanatoselenophene, (5a).**  $\nu_{max}/cm^{-1}$  3098, 2278 (NCO), 1466, 1527, 1378, 1223, 1208, 1014, 791, 721 and 673;  $\delta_H$  (200 MHz;  $CDCl_3$ ) 7.56 (1H, dd,  $J$  6.1 and 1.4 H-5), 6.95 (1H, dd,  $J$  6.1 and 3.9, H-4) and 6.74 (1H, dd,  $J$  3.9 and 1.4, H-3);  $\delta_C$  (50.8 MHz;  $CDCl_3$ ) 137.5, 128.2 (d,  $J$  166.5), 127.2 (d,  $J$  189.5), 126.1 and 123.0 (d,  $J$  168.6);  $m/z$ , 173 ( $M^+$ , 100%), 145 (M-28, 51.1),

118 (43.7), 105 (7.6), 93 (17.4), 80 (11.9), 64 (49.2), 50 (4.0) and 39 (34.9); Found:  $M^+$ , 172.9379  $C_5H_3NOSe$  requires:  $M$ , 172.9380.

**Pilot thermolysis of carbonyl azides 1–5 in hexadecane.** Reactions were carried out at 220 °C for 15 min in a screw-cap sealed tube containing solutions in anhydrous hexadecane of the heteroaryl azides (*ca.* 1:3, w/w). Reaction mixtures were analyzed by  $^1H$ -NMR and IR spectroscopy without further manipulation. In all cases the reactions were insensitive to the nitrogen-purged hexadecane solvent, and the CRs to the isocyanates **1a–3a**, **5a** were found to be complete. In the case of the carbonyl azide **4**, the CR resulted in the formation of the 2-thienyl isocyanate **2a** as the main product.

**Thermolysis of carbonyl azides 1–5 in 1-dodecanol.** A solution of the heteroarylcarbonyl azide in neat 1-dodecanol (1:4 w:w), previously degassed under vacuum, was allowed to react in a screw-cap tube at 220 °C for 15 min. Excess co-solvent was removed by the addition of *n*-pentane and the mixture was maintained at 0 °C for 5 h. The resulting suspension was rapidly filtered under vacuum and the solid residue washed with cold pentane and then characterized by  $^1H$ -NMR, IR, and high-resolution mass spectroscopy.

The following carbamates (**1b–3b**, and **5b**) were obtained.

**Dodecyl *N*-(2-furyl) carbamate (1b).** (93%); m.p. 70–72 °C;  $\nu_{max}/cm^{-1}$  3262 (NH), 2920, 2850 and 1700 (CO);  $\delta_H$  (200 MHz;  $CDCl_3$ ) 7.08 (1H, dd, *J* 2.1 and 1.0 H-5), 6.72 (1H, bm, NH), 6.35 (1H, dd, *J* 3.5 and 2.1, H-4), 6.09 (1 H, bm, 3-H), 4.16 (2H, t), 1.65 (2H, bm), 1.28 (18H, bs) and 0.90 (3H, bt); *m/z*, 295 ( $M^+$ , 8.8%), 208 (M- $C_6H_{15}$ , 8.6), 110 (7.6), 83 (84.6), 69 (15.0), 57 (32.0), 55 (12.9), 53 (10.7) and 43 (100); Found:  $M^+$ , 295.2147  $C_{17}H_{29}NO_3$  requires:  $M$ , 295.2147.

**Dodecyl *N*-(2-thienyl) carbamate (2b).** (94%); m.p. 65–67 °C;  $\nu_{max}/cm^{-1}$  3266 (NH), 2920, 2848 and 1689 (CO);  $\delta_H$  (200 MHz;  $CDCl_3$ ) 7.03 (1H, bm, NH), 6.86 (1H, dd, *J* 5.5 and 1.6 H-5), 6.81 (1H, dd, *J* 5.5 and 3.5, H-4), 6.59 (1 H, dd, *J* 3.5 and 1.6, 3-H), 4.18 (2H, t), 1.65 (2H, bm), 1.26 (18H, bs) and 0.88 (3H, bt); *m/z*, 311 ( $M^+$ , 21.8%), 143 (M- $C_{12}H_{24}$ , 12.5), 125 (4.0), 99 (61.4), 85 (7.5), 71 (16.6), 57 (54.1), 55 (43.0) and 43 (100); Found:  $M^+$ , 311.1919  $C_{17}H_{29}NO_2S$  requires:  $M$ , 311.1919.

**Dodecyl *N*-(5-methyl-2-thienyl) carbamate (3b).** (92%); m.p. 72–74 °C;  $\nu_{max}/cm^{-1}$  3262 (NH), 2920, 2848 and 1689 (CO);  $\delta_H$  (200 MHz;  $CDCl_3$ ) 6.81 (1H, bm, NH), 6.45 (1H, m, *J* 3.6 and 1.1, H-4), 6.39 (1H, d, *J* 3.6, H-3), 4.16 (2H, t), 2.39 (3H, d, *J* 1.1, Me), 1.65 (2H, bm), 1.26 (18H, bs) and 0.88 (3H, bt); *m/z*, 325 ( $M^+$ , 72.9%), 157 (M- $C_{12}H_{24}$ , 34.8), 139 (10.9), 113 (100), 85 (5.2), 71 (26.2), 57 (63.5), 55 (41.0) and 43 (85.1); Found:  $M^+$ , 325.2074  $C_{18}H_{31}NO_2S$  requires:  $M$ , 325.2075.

**Dodecyl *N*-(2-selenophenyl) carbamate (5b).** (56%); m.p. 66–68 °C;  $\nu_{max}/cm^{-1}$  3259 (NH), 2921, 2851, 1688 (CO), 1584, 1515, 1277, 1253, 1072, 814 and 793;  $\delta_H$  (300 MHz;  $CDCl_3$ ) 7.49 (1H, dd, *J* 6.1 and 1.3 H-5), 7.40 (1H, bm, NH), 7.05 (1H, dd, *J* 6.1 and 4.0, H-4), 6.57 (1 H, dd, *J* 4.0 and 1.3, H-4), 4.20 (2H, t), 1.65 (2H, bm), 1.26 (18H, bs) and 0.88 (3H, bt); *m/z*, 359 ( $M^+$ ,



14.3%), 191 (M- C<sub>12</sub>H<sub>24</sub>, 9.1), 147 (17.8), 83 (10.1), 71 (23.5), 57 (59.4) and 43 (100); Found: M<sup>+</sup>, 359.1363 C<sub>17</sub>H<sub>29</sub>NO<sub>2</sub>Se requires: M, 359.1363.

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