

Preparation and [2 + 3] Cycloaddition of Thienyl Isocyanates with Trimethylsilyl Azide: One-pot Synthesis of Thienyltetrazolin-5-ones

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Efforts to prepare thienyl isocyanates by thermal reactions of thenoyl chlorides with trimethylsilyl azide (TMSA) led preferentially to the formation of 1,4-disubstituted tetrazolin-5-ones, arising by inter-action of the initially formed thienyl isocyanate with TMSA. In fact, 2-thenoyl chloride and benzo[*b*]thiophene-2-carbonyl chloride reacted with 1 equiv. TMSA in refluxing carbon tetrachloride to give 1-(2-thienyl or benzo[*b*]thienyl)-4-(2-thenoyl or benzo[*b*]thiophenecarbonyl)tetrazolin-5-one **4d, e**, whereas 3-thenoyl chloride led to 1-(3-thienyl)-4-trimethylsilyltetrazolin-5-one adduct **II** which was converted, after hydrolytic desilylation, to 1-(3-thienyl)tetrazolin-5(4*H*)-one **4c**. Similar reactions, carried out with more than two equiv. of TMSA, led in all cases to the formation of the corresponding 1-heteroaryltetrazolin-5-one **4a-c** via the corresponding silylated tetrazolin-5-ones **II**, whereas at room temp. such reactions gave essentially thenoyl azides which, after elimination of the excess TMSA, were thermally converted to the corresponding thienyl isocyanates **3** in fairly good yields.

The interest in the synthetic and mechanistic aspects of the chemistry of nitrogen-functionalized five-membered heterocycles arises from the fact that these compounds exhibit chemical or thermal reactivity which is largely dependent on the position of the nitrogen substituent on the ring.¹ In recent papers we reported that under thermal conditions 3-thienyl azides and their benzo derivatives exhibit different chemical behaviour from 2-thienyl azides, which preferentially undergo cleavage of the heterocyclic ring and loss of molecular nitrogen presumably through a concerted process.² Our consequent interest in heteroaryl isocyanates arises from their potential similar behaviour under thermal or photolytic conditions.³ Di- and poly-isocyanates are important also as starting monomers in the manufacture of high-performance polymers, such as polyurethanes.

The synthesis of organic isocyanates may be accomplished by different procedures, the choice of which is mostly dependent on the stability of the target molecule and availability of the starting material. Their syntheses and preparative applications have been reviewed.⁴ Pyrolysis of heterocarbonyl azides to isocyanates, known as the Curtius rearrangement,⁵ appears to be one of the more convenient routes to heteroaromatic isocyanates. The majority of heteroaromatic amines are unstable, which excludes their possible conversion to isocyanates with phosgene. However, in spite of the fact that thenoyl chlorides (or azides) are known of old,⁶ no simple thienyl isocyanates have been prepared from them.†

Organic isocyanates have been prepared more recently by treatment of some carbonyl chlorides with trimethylsilyl azide (TMSA) followed by thermal rearrangement of the intermediate carbonyl azides in a less hazardous one-pot procedure.⁸

We report here our efforts to prepare thienyl isocyanates by this reaction using TMSA and suitable thenoyl chlorides such as 2-thenoyl **1a**, benzo[*b*]thiophene-2-carbonyl **1b** and 3-thenoyl chloride **1c** from which results were found to be effectively dependent on the reaction conditions and type of substrates.

Results and Discussion

Solutions of 2-heteroaryl chloride **1a** or **1b** were treated with 1 equiv. TMSA, in refluxing carbon tetrachloride, and the

resulting mixture was heated for an additional 20 h. Subsequent cooling of the reaction mixture gave a precipitate which was filtered off and characterized as 1-(2-thienyl)-4-(2-thenoyl)-tetrazolin-5-one **4d** and 1-(2-benzo[*b*]thienyl)-4-(benzo[*b*]thiophene-2-carbonyl)tetrazolin-5-one **4e**, respectively in 86 and 83% yields.

The structures of these tetrazolinone adducts were assigned on the basis of IR, NMR and exact mass spectral data. The ¹H NMR spectra of compound **4d** revealed the presence of two separate thiophene rings characterized by six typical quartet patterns. Assignment of the three quartets belonging to the thiophene ring bonded directly to the carbonyl group is based on the large downfield shift observed for the 3-H and 5-H protons at δ 8.30 and 7.90, respectively (Table 1). Furthermore, compounds **4d** and **4e** show double carbonyl stretching absorption in the IR spectrum at ν/cm^{-1} 1760 and 1690, and 1770 and 1700, respectively.

High-resolution mass spectral measurement displayed the m/z 278 peak corresponding in mass and isotopic abundances to the molecular ion (M^+) of compound **4d**. Fragmentation of the tetrazolinone ring gives an intense peak at m/z 125, which provides evidence for cycloreversion⁹ with formation of [thienylNCO]⁺ (probably including [thienylN₃]⁺). Both these latter radical ions fragment, by loss of 28 mass units, giving the appropriate thienylnitrenium ion (m/z 97). On the other hand, the mass spectrum of compound **4e** showed, together with the molecular ion peak (m/z 378), analogous fragmentation pattern with base peak at m/z 175 and benzo[*b*]thienylnitrenium ion at m/z 147.

Acyl azides do not normally react with the resulting isocyanate products in the course of a Curtius reaction,‡ however, it is clear that heating aryl isocyanates with organic azides for a prolonged interval leads to the formation of 1,3-dipolar cycloadducts like 1,4-disubstituted tetrazolin-5-ones¹¹ whose orientation is the same as that presumed with our adduct **4d, e**. More likely, thienyl isocyanate **3a** or **3b**, formed by normal

† The actual product of the Curtius rearrangement is the corresponding isocyanate. Thienyl isocyanates have been claimed as intermediates.⁷

‡ The only reported exception appears to be sorboyl azide which is reported to react with the rising sorboyl isocyanate to afford sorboyltetrazolinone.¹⁰

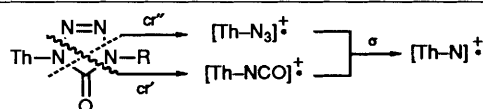
Table 1 ^1H NMR spectroscopic data for thienyl derivatives **1a**, **1c**, **2a**, **2c**, **3a**, **3c**, **4a** and **4d**^a

Compound	δ_3^b	δ_4	δ_5	δ_2	$H_{3,5}^c$	$J_{3,4}$	$J_{4,5}$	$J_{2,4}$	$J_{2,5}$
1a	7.97	7.19	7.83		1.4	3.4	5.0		
1c		7.46	7.20	7.80			5.1	1.9	2.4
2a	7.75	7.05	7.59		1.3	3.8	4.9		
2c		7.54	7.37	8.35			5.1	1.1	3.1
3a	6.65	6.78	6.89		1.4	3.7	5.7		
3c		6.83	6.88	7.21			5.0	1.3	3.4
4a	7.43	7.04	7.23		1.5	3.8	5.5		
4c		6.98	7.25	7.40			5.3	1.4	3.1
4d ^d	7.50	7.06	7.24		1.4	3.9	5.4		
4d ^e	8.30	7.27	7.90		1.2	4.0	5.0		

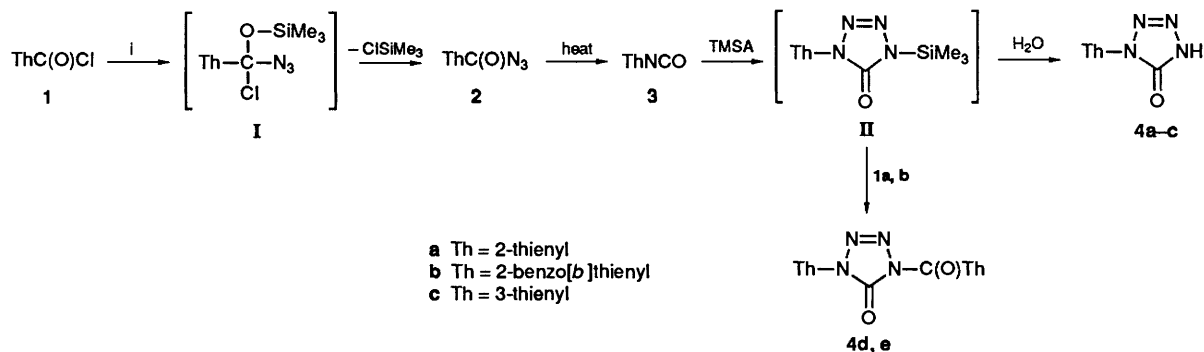
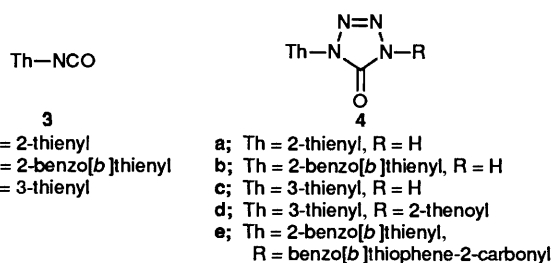
^a Solutions in CDCl_3 . ^b CHCl_3 as internal standard ($\delta = 7.27$). ^c ± 0.1 Hz. ^d 2-Thienyl. ^e Thenoyl.

Table 2 Relative abundances of the major fragments in the mass spectra of thienyl tetrazolinones **4a–e**^a

Compound	378	278	218	203	175	168	147	125	97
4a							43	100	57
4b			24		100		19		
4c						100		32	10
4d		21						89	51
4e	13			15	100		24		



cr = cycloreversion
 Th = 2- or 3-thienyl, R = H $m/z = 168$ $m/z = 125$ $m/z = 97$
 Th = 2-benzo[b]thienyl, R = H $m/z = 218$ $m/z = 175$ $m/z = 147$
 Th = 2-thienyl, R = 2-thenoyl $m/z = 278$
 Th = 2-benzo[b]thienyl, R = benzo[b]thiophene-2-carbonyl $m/z = 378$

**Scheme 1** Reagents and conditions: i, TMSA, CCl_4 , 25 °C or 77 °C

Curtius rearrangement of the corresponding carbonyl azide **2a** or **2b**, undergoes a [2 + 3] cycloaddition with the 1,3-dipolar TMSA, affording the intermediate 1-(2-thienyl or 2-benzo[b]thienyl)-4-(trimethylsilyl)tetrazolinone **II** which subsequently undergoes reaction with still unchanged carbonyl chloride **1a** or **1b**, leading to the 4-(2-heteroarylcarbonyl)substituted tetrazolin-5-ones **4d** and **4e**, respectively, as shown in Scheme 1.

These conclusions agree with the fact that similar reaction between 3-thenoyl chloride **1c** and 1 equiv. TMSA led exclusively to the formation of 1-(3-thienyl)tetrazolin-5(4*H*)-one **4c**,

together with unchanged **1c**. The initially formed 1-(3-thienyl)-4-trimethylsilyltetrazolin-5-one adduct **II** was shown to be moisture sensitive and was converted by hydrolytic desilylation to stable solid compound **4c** (36%). The structure of this compound was confirmed by the presence of a single thiophene quartet pattern in the ^1H NMR spectrum (Table 1) and a single carbonyl stretching absorption in the IR spectrum at ν/cm^{-1} 1770, in addition to the NH stretching at ν/cm^{-1} 3300. The mass spectra of 1-(3-thienyl)tetrazolin-5(4*H*)-one **4c** exhibited appropriate molecular fragmentation ions at m/z 168 as base peak together with peaks at m/z 125, 98 and 97. Relative abundance of the major fragments in the mass spectra of all new thienyl derivatives obtained in the present work are collected in Table 2. Furthermore, a stepwise process based on the interception of isocyanates **3** with their precursor, thenoyl azide **2**, is also ruled out by the discovery that good yields of 1-(heteroaryl)tetrazolin-5(4*H*)-one **4a–c** were obtained when we treated the same thenoyl chlorides **1a–c** with more than two equiv. of TMSA in refluxing carbon tetrachloride for ca. 20 h (until GC/MS analysis showed the disappearance of the starting

thenoyl chloride), followed by hydrolysis of the reaction mixtures. Structural assignments of all the new tetrazolinones were made on the basis of IR and ^1H NMR spectroscopy, and exact mass spectral data. It is interesting to note that tetrazolinones **4a–c** exhibit ν/cm^{-1} C=O stretching absorption at high wave number 1740–1770. The mass spectra of 1-(2-thienyl)tetrazolin-5(4H)-one **4a** exhibited appropriate molecular ions at m/z 168 as base peak together with fragmentation peaks at m/z 125 and 97. Analogous fragmentation was observed for compound **4b**: the main decomposition of the molecular ion m/z 218 is the cycloreversion ($\text{M} - \text{HN}_3$ or HNCO) which contributes to the formation of m/z 175 and 147. The rest of the spectrum closely resembles that of the benzo[*b*]thiophene system.

From the above results, the Curtius rearrangement of the acyl azides **2**, arising *via* reaction of the corresponding acyl chlorides **1** with TMSA and loss of TMSCl from the intermediate **I**, gives the isocyanates **3** which are subsequently trapped by facile interaction with the excess TMSA (Scheme 1). The highly polarized C=N bonds of the thienyl isocyanates **3a–c** undergo thermal [2 + 3] cycloadditions presumably, with the α -nitrogen and the terminal nitrogen of the azido-function of the TMSA, respectively, to give intermediates **II**. This process is in agreement with a concerted mechanism in which the reactants approach from the least hindered direction as well as orbital symmetry considerations.^{11c}

Repetition at room temp. of the reactions of carbonyl chlorides **1a–c**, in carbon tetrachloride with more than two equiv. of TMSA, show their difference in reactivity and the contemporary presence in the reaction of thienyl azides **2** and thienyl isocyanates **3**. In fact, daily GC/MS examinations of the reaction mixtures indicated that the disappearance of the gas-chromatographic peaks of the starting carbonyl chlorides were virtually complete in *ca.* 240, 200 and 110 h, respectively, giving mainly corresponding carbonyl azides **2a** and **2b**, together with small amounts of thienyl isocyanate **3a** and **3b**, as indicated by IR absorption spectra (ν/cm^{-1} 2140 and 2280) of the reaction mixtures. In addition to the GLC peak of the carbonyl azide **2a** and thienyl isocyanate **3a**, a fairly consistent chromatographic peak with different retention time but with the same m/z 125 base peak, presumably corresponding to the cycloreversed mass spectrum of the intermediate adducts **II**, together with a small peak (5–10%, m/z 201), possibly indicative for the intermediate **I**, were in both cases detected by GC/MS.

The approximately halved reaction time in the formation of carbonyl azide **2c**, with respect to the azide **2a** would be significant for a tetrahedral mechanism of displacement, *via* intermediate **I**, strongly dependent on the nature of the starting carbonyl.¹²

Finally, isocyanates **3a–c** have been isolated and characterized from these room temp. reactions. After the required reaction time the solvent and the excess of TMSA were removed under reduced pressure and the residues solubilized in fresh carbon tetrachloride. The resulting solutions were heated for *ca.* 1 h at 90 °C in a sealed tube, after which the reaction mixtures were distilled under reduced pressure to give pure isocyanates **3a** (52%), **3b** (79%) and **3c** (70%). These compounds were found to be very unstable and moisture sensitive but can be stored in carbon tetrachloride solution, under nitrogen, for longer. ^1H NMR, IR and mass spectra were obtained for all these heteroaryl isocyanates (see Experimental section).

Experimental

Materials.—Azidotrimethylsilane (TMSA), thionyl chloride and 2-thenoyl chloride **1a** were purchased from Aldrich-Chimica Italiana. 3-Thenoyl **1c** and benzo[*b*]thiophene-2-carbonyl chloride **1b** were prepared from the corresponding

carboxylic acid and thionyl chloride according to the general procedures developed by Steinkopf and co-workers.¹³ IR spectra were recorded with a Perkin-Elmer Model 257 instrument. ^1H and ^{13}C NMR spectroscopic data were obtained with a Varian Gemini 200 MHz instrument for solutions in CDCl_3 using CHCl_3 as internal standard unless otherwise stated. *J* Values are given in Hz.

Reactions of Heteroaryl Azides 1a–c with 1 Equiv. TMSA in Refluxing Carbon Tetrachloride. General procedure.—Carbon tetrachloride solutions (20 cm^3) of heteroaryl chlorides **1a–c** (20 mmol) and TMSA (22 mmol) were refluxed for the appropriate time, until GC/MS analysis and IR spectra of an aliquot showed the absence of the starting azide (*ca.* 20 h). The reactions which left solid products **1a**, **1b** were filtered off and the solid repeatedly washed with pure hexane–diethyl ether (1:1) and then characterized.

The reaction mixture of compound **1c** was treated with water (5 cm^3) and hexane (10 cm^3) and stirred for 5 h at room temp. The solid precipitate which had formed was filtered, washed with pure hexane–diethyl ether (1:1) and then characterized as **4a**.

The following new 1,4-disubstituted-tetrazolin-5(4H)-ones **4d–e** and 1-substituted-tetrazolin-5(4H)-one **4c** were obtained:

1-(2-Thienyl)-4-(2-thenoyl)tetrazolin-5-one **4d** (2.4 g, 86%), m.p. 110–16 °C (decomp.); $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 3100, 1760 (exocyclic C=O stretching) and 1690 (C=O); $\delta_{\text{H}}(200 \text{ MHz}; \text{CDCl}_3)$ 8.30 (1 H, dd, *J* 1.2 and 4.0), 7.90 (1 H, dd, *J* 1.2 and 5.0), 7.50 (1 H, dd, *J* 1.4 and 3.9), 7.27 (1 H, dd, *J* 4.0 and 5.0), 7.24 (1 H, dd, *J* 1.4 and 5.4) and 7.06 (1 H, dd, *J* 3.9 and 5.4); m/z 278 (M^+ , 21%), 125 (89), 111 (100), 97 (51), 83 (12) and 70 (30) (Found: M^+ , 277.9933. $\text{C}_{10}\text{H}_6\text{N}_4\text{O}_2\text{S}_2$ requires *M*, 277.9932).

1-(2-Benzo[*b*]thienyl)-4-benzo[*b*]thiophene-2-carbonyltetrazolin-5-one **4e** (3.2 g, 83%), m.p. 206–208 °C (decomp.); $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 1770 (exocyclic C=O stretching) and 1700 (C=O); $\delta_{\text{H}}[60 \text{ MHz}; (\text{CD}_3)_2\text{SO}]$ 7.9–8.3 (4 H, m), 7.9 (1 H), 7.7 (1 H) and 7.4–7.6 (4 H, m); m/z 378 (M^+ , 13%), 203 (15%, $\text{M} - 175$), 175 (100), 161 (77), 147 (24), 146 (25), 133 (11), 120 (23), 103 (11) and 89 (16) (Found: M^+ , 378.0240. $\text{C}_{18}\text{H}_{10}\text{N}_4\text{O}_2\text{S}_2$ requires *M*, 378.0245).

1-(3-Thienyl)tetrazolin-5(4H)-one **4c** (1.2 g, 36%), m.p. 116–118 °C; $\nu_{\text{max}}/\text{cm}^{-1}$ 3320 (NH) and 1760 (C=O); $\delta_{\text{H}}(200 \text{ MHz}; \text{CDCl}_3)$ 7.40 (1 H, dd, *J* 1.4 and 3.1), 7.25 (1 H, dd, *J* 3.1 and 5.3), 7.10 (1 H, br, NH) and 6.98 (1 H, dd, *J* 1.4 and 5.3); m/z 168 (M^+ , 100%), 125 [32%, ($\text{M} - \text{HN}_3$)] 97 (10), 83 (14), 70 (20) and 45 (76) (Found: M^+ , 168.0103. $\text{C}_5\text{H}_4\text{N}_4\text{OS}$ requires *M*, 168.0106).

Reactions of Heteroaryl Azides 1a–c with Excess TMSA in Refluxing Carbon Tetrachloride.—General procedure. These reactions were carried out with the same procedure described above for **1a–c** apart from the use of excess TMSA (45 mmol). After cooling, the reaction mixture was treated with water (5 cm^3) and hexane (10 cm^3), and the resulting mixture stirred for 3 h at room temp. The solid precipitate which had formed was filtered, washed with pure hexane–diethyl ether (1:1). The following new 1-substituted-tetrazolin-5(4H)-ones **4a**, **b** were obtained:

1-(2-Thienyl)tetrazolin-5(4H)-one **4a** (2.4 g, 72%), m.p. 153–157 °C (decomp.); $\nu_{\text{max}}/\text{cm}^{-1}$ 3350 (NH), 3100 and 1740 (C=O); $\delta_{\text{H}}(200 \text{ MHz}; \text{CDCl}_3)$ 7.43 (1 H, dd, *J* 1.5 and 3.8), 7.23 (1 H, dd, *J* 1.5 and 5.5) and 7.04 (1 H, dd, *J* 3.8 and 5.5); m/z 168 (M^+ , 43%), 125 (100, $\text{M} - \text{HN}_3$ or $-\text{HNCO}$), 97 (57), 83 (3) and 70 (38) (Found: M^+ , 168.0104. $\text{C}_5\text{H}_4\text{N}_4\text{OS}$ requires *M*, 168.0106).

1-(2-Benzo[*b*]thienyl)tetrazolin-5(4H)-one **4b** (3.6 g, 82%), m.p. 216–18 °C (decomp.); $\nu_{\text{max}}/\text{cm}^{-1}$ 3420 (NH) and 1750 (C=O); $\delta_{\text{H}}[60 \text{ MHz}; (\text{CD}_3)_2\text{SO}]$ 7.7 (2 H, m), 7.63 (1 H, s) and 7.4 (2 H, m); m/z 218 (M^+ , 24%), 175 (100, $\text{M} - \text{HN}_3$ or $\text{M} -$

HNCO), 147 (19), 146 (21), 120 (19), 103 (10) and 89 (5) (Found: M^+ , 218.0262. $C_9H_6N_4OS$ requires 218.0262).

Syntheses of Isocyanates 3a-c.—Carbon tetrachloride solutions (20 cm³) of **1a-c** (20 mmol) and TMSA (45 mmol) were allowed to react in sealed tubes at room temp. After the required reaction times (240, 190 and 110 h, respectively) the solvent and the excess of TMSA were removed under reduced pressure and the residues solubilized in fresh carbon tetrachloride. The resulting solutions were heated for ca. 1 h at 90 °C in sealed tubes, after which the reaction mixtures were distilled under reduced pressure. The following isocyanates **3a-c** were obtained:

2-Thienyl isocyanate 3a (1.3 g, 52%), b.p. 55 °C/0.1 mmHg; $\nu_{\max}/\text{cm}^{-1}$ 2280 (N=C=O); δ_{H} (200 MHz; CDCl_3) 6.89 (1 H, dd, J 1.4 and 5.7), 6.78 (1 H, dd, J 3.7 and 5.7) and 6.65 (1 H, dd, J 1.4 and 3.7); m/z 125 (M^+ , 100%), 97 (75, $M - \text{CO}$), 70 (58), 52 (11) and 45 (49) (Found: M^+ , 124.9936. $C_5H_3\text{NOS}$ requires 124.9935).

2-Benzo[b]thienyl isocyanate 3b (2.8 g, 79%), b.p. 110–112 °C/0.1 mmHg; $\nu_{\max}/\text{cm}^{-1}$ 2280 (N=C=O); δ_{H} (200 MHz; CDCl_3) 7.64 (2 H, m), 7.31 (2 H, m) and 6.87 (1 H, s); m/z 175 (M^+ , 100%), 147 (38%, $M - 28$), 146 (42), 120 (36), 103 (16) and 87 (14) (Found: M^+ , 175.0094. $C_9H_5\text{NOS}$ requires 175.0092).

3-Thienyl isocyanate 3c (1.7 g, 70%), b.p. 82–83 °C/15 mmHg; $\nu_{\max}/\text{cm}^{-1}$ 2280 (N=C=O); δ_{H} (200 MHz; CDCl_3) 7.21 (1 H, dd, J 3.4 and 5.0), 6.88 (1 H, dd, J 3.4 and 1.3) and 6.83 (1 H, dd, J 1.3 and 5.0); m/z 125 (M^+ , 100%), 97 (23, $M - \text{CO}$), 82 (25), 70 (20), 52 (10) and 45 (46) (Found: M^+ , 124.9936).

Acknowledgements

This research was supported by MURST. One of the authors (P. Z.) is grateful to Mr. L. Zuppiroli for the recording of NMR and mass spectra.

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Paper 2/00302C

Received 20th January 1992

Accepted 5th February 1992