

A Facile Synthesis of 2-Imino-4-methylene-1,3-dithiolanes

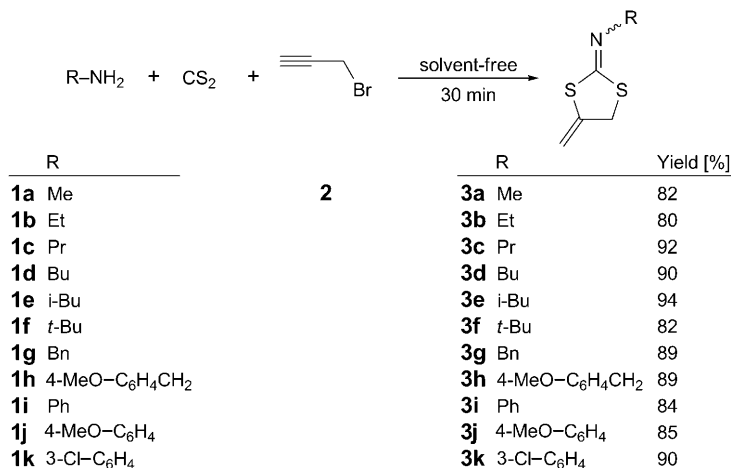
by Issa Yavari* and Saeideh Beheshti

Chemistry Department, Tarbiat Modares University, P.O. Box, 14115-175 Tehran, Iran
(phone: +98-21-82883465; fax: +98-21-82883455; e-mail: yavarisa@modares.ac.ir)

A one-pot synthesis of 2-imino-4-methylidene-1,3-dithiolanes *via* a three-component reaction of propargyl bromide (= 3-bromoprop-1-yne), primary amines, and carbon disulfide (CS₂) is described.

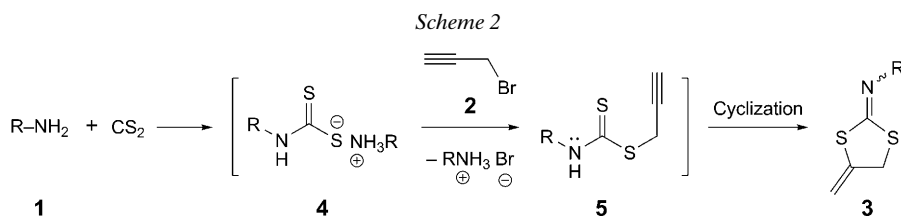
Introduction. – 2-Imino-1,3-dithiolanes are important compounds in crop protection against herbicides. Common synthetic methods for 2-imino-1,3-dithiolanes are the reaction of vicinal dithiocyanates in refluxing HCl [1], reaction of vicinal dithiols and cyanogen chloride (CNCl) [2], acid-catalyzed cyclization of propargyl, allyl, or β -hydroxyalkyl esters of dithiocarbamic acids [3], photolysis of chlorinated *S*-allyl dithiocarbamates [4] and iodocyclization of *S*-allyl dithiocarbamates [5]. All these procedures have certain limitations such as tedious process, long reaction time, harsh reaction conditions, and low yields. As part of our current studies on the development of new routes in heterocyclic synthesis [6–9], we report a facile synthesis of 2-imino-4-methylidene-1,3-dithiolanes from propargyl bromide, primary amines, and CS₂ in good yields (*Scheme 1*).

Scheme 1



Results and Discussion. – The reaction of primary amines **1** and CS₂ with propargyl bromide (= 3-bromoprop-1-yne; **2**) under solvent-free conditions led to 2-imino-4-methylidene-1,3-dithiolanes (**3**) in 80–94% yield (*Scheme 1*). The imino group of compounds **3** can principally appear in (*E*)- and (*Z*)-form due to slow isomerization of the imino moiety at ambient temperatures. In fact, the NMR spectra of these compounds are consistent with the presence of the (*E*)- and (*Z*)-isomers in nearly equal amounts. The structures of compounds **3a–3k** were assigned by IR, and ¹H- and ¹³C-NMR spectra. For example, the ¹H-NMR spectrum of **3a** exhibited four *singlets* for MeN (δ (H) 1.38 and 1.43) and CH₂(5) (δ (H) 4.04 and 4.21), along with four *doublets* (δ (H) 5.24, 5.26, 5.37, and 5.41, ²*J* = 1.3 Hz), for C(4)=CH₂. The ¹³C-NMR spectrum of **3a** showed ten signals in agreement with the presence of two geometrical isomers. The ¹H- and ¹³C-NMR spectra of **3b–3k** were similar to those of **3a**, except for the imino substituents, which showed characteristic signals in the appropriate regions of the spectra. The mass spectra of **3a–3k** displayed molecular-ion peaks at the appropriate *m/z* values.

Although the mechanistic details of the reaction are not known, a plausible rationalization is depicted in *Scheme 2*. Presumably, the intermediate **4** formed from the reaction of **1** and CS₂ is attacked by propargyl bromide (**2**) to afford **5**, which is converted to product **3** via cyclization reaction and elimination.



In conclusion, we have developed a simple procedure for the synthesis of 2-imino-4-methylidene-1,3-dithiolanes by a three-component one-pot reaction of primary amines, CS₂, and propargyl bromide. The present method offers several advantages, including high yields of products, and environmentally benign and an easy workup procedure.

Experimental Part

General. Amines, CS₂, and propargyl bromide (**2**) were obtained from *Merck*, and were used without further purification. IR Spectra: *Shimadzu-IR-460* spectrometer; $\tilde{\nu}$ in cm⁻¹. ¹H- and ¹³C-NMR spectra: *Bruker DRX-500 Avance* instrument; in CDCl₃ at 500.1 and 125.7 MHz, resp.; δ in ppm rel. to Me₄Si as internal standard, *J* in Hz. MS: *Finnigan-MAT-8430EI-MS* mass spectrometer at 70 eV; in *m/z* (rel. %). Elemental analyses: *Vario EL III CHNOS* elemental analyzer.

Compounds 3: General Procedure. Primary amines **1** (1 mmol), CS₂ (0.38 g, 5 mmol), and propargyl bromide (= 3-bromoprop-1-yne; **2**; 0.12 g, 1 mmol) were mixed in an agate mortar. After completion of the reaction (30 min), as indicated by TLC (hexane/AcOEt 4:1), column chromatography (SiO₂; hexane/AcOEt 5:1) afforded pure products.

*N-Methyl-4-methylidene-1,3-dithiolan-2-imine (3a)*¹⁾. Yield: 0.12 g (82%). Brown oil. IR (KBr): 3424, 2925, 2346, 1617, 1462, 1267. ¹H-NMR: 1.38, 1.43 (2s, Me); 4.04, 4.21 (2s, CH₂S); 5.24, 5.26 (2d, ²J = 1.3, =CH); 5.37, 5.41 (2d, ²J = 1.3, =CH). ¹³C-NMR: 39.5, 42.5 (Me); 44.1, 42.1 (CH₂S); 109.7, 110.6 (=CH₂); 144.1, 145.1 (C=CH₂); 159.9, 161.7 (C=N). EI-MS: 145 (23, M⁺), 87 (100), 43 (48), 15 (14). Anal. calc. for C₅H₇NS₂ (145.00): C 41.35, H 4.86, N 9.64, S 44.15; found: C 41.6, H 4.9, N 9.8, S 44.4.

N-Ethyl-4-methylidene-1,3-dithiolan-2-imine (3b). Yield: 0.13 g (80%). Brown oil. IR (KBr): 3418, 3189, 2927, 2671, 1571, 1442, 1184, 1091. ¹H-NMR: 1.26, 1.29 (2t, ³J = 6.9, Me); 3.28, 3.34 (2q, ³J = 6.9, CH₂N); 4.01, 4.18 (2s, CH₂S); 5.21, 5.24 (2d, ²J = 1.3, =CH); 5.36, 5.39 (2d, ²J = 1.3, =CH). ¹³C-NMR: 15.3, 15.4 (Me); 39.2, 42.5 (CH₂S); 52.3, 53.5 (CH₂N); 109.6, 110.5 (=CH₂); 141.1, 143.1 (C=CH₂); 162.3, 163.3 (C=N). EI-MS: 159 (6, M⁺), 101 (100), 57 (56), 29 (11). Anal. calc. for C₆H₉NS₂ (159.02): C 45.25, H 5.70, N 8.79, S 40.26; found: C 45.5, H 5.8, N 8.6, S 40.4.

4-Methylidene-N-propyl-1,3-dithiolan-2-imine (3c). Yield: 0.16 g (92%). Brown oil. IR (KBr): 3197, 2959, 2925, 2871, 2854, 1604. ¹H-NMR: 0.89, 0.94 (2t, ³J = 6.8, Me); 1.67, 1.70 (2m, CH₂); 3.25, 3.28 (2t, ³J = 7.0, CH₂N); 4.01, 4.17 (2s, CH₂S); 5.22, 5.23 (2d, ²J = 1.4, =CH); 5.35, 5.38 (2d, ²J = 1.4, =CH). ¹³C-NMR: 11.4, 14.1 (Me); 22.6, 23.9 (CH₂); 39.2, 42.5 (CH₂S); 59.8, 60.9 (CH₂N); 109.6, 110.4 (=CH₂); 141.1, 143.1 (C=CH₂); 162.8, 163.4 (C=N). EI-MS: 173 (6, M⁺), 115 (100), 71 (56), 43 (23), 39. Anal. calc. for C₇H₁₁NS₂ (173.03): C 48.51, H 6.40, N 8.08, S 37.01; found: C 48.7, H 6.5, N 7.9, S 36.8.

N-Butyl-4-methylidene-1,3-dithiolan-2-imine (3d). Yield: 0.17 g (90%). Brown oil. IR (KBr): 3439, 2938, 2345, 1605, 1447, 1266, 753. ¹H-NMR: 0.87, 0.92 (2t, ³J = 7.0, Me); 1.35, 1.41 (2m, CH₂); 1.62, 1.67 (2m, CH₂); 3.28, 3.30 (2t, ³J = 6.9, CH₂N); 3.99, (2s, CH₂S); 5.20, 5.21 (2d, ²J = 1.3, =CH); 5.34, 5.37 (2d, ²J = 1.3, =CH). ¹³C-NMR: 13.7, 14.0 (Me); 20.4, 20.5 (CH₂); 32.3, 32.5 (CH₂); 39.1, 42.4 (CH₂S); 57.7, 58.9 (CH₂N); 109.5, 110.3 (=CH₂); 141.0, 143.1 (C=CH₂); 162.9, 164.1 (C=N). EI-MS: 187 (5, M⁺), 129 (100), 85 (58). Anal. calc. for C₈H₁₃NS₂ (187.05): C 51.29, H 6.99, N 7.48, S 34.23; found: C 51.7, H 6.8, N 7.6, S 34.6.

4-Methylidene-N-(2-methylpropyl)-1,3-dithiolan-2-imine (3e). Yield: 0.18 g (94%). Brown oil. IR (KBr): 3443, 2955, 2924, 2868, 1605, 1275, 1260. ¹H-NMR: 0.95, 1.32 (2d, ³J = 6.7, 2 Me); 1.98, 2.03 (2m, CH); 3.10, 3.12 (2d, ³J = 6.6, CH₂N); 4.01, 4.18 (2s, CH₂S); 5.23, 5.24 (2d, ²J = 1.3, =CH); 5.35, 5.38 (2d, ²J = 1.3, =CH). ¹³C-NMR: 23.7, 23.9 (2 Me); 29.3, 29.6 (CH); 39.1, 42.4 (CH₂S); 65.9, 67.1 (CH₂N); 109.5, 110.3 (=CH₂); 141.1, 143.5 (C=CH₂); 158.1, 159.1 (C=N). EI-MS: 187 (9, M⁺), 129 (100), 85 (56), 57 (23), 39 (11). Anal. calc. for C₈H₁₃NS₂ (187.05): C 51.29, H 6.99, N 7.48, S 34.23; found: C 51.1, H 7.1, N 7.3, S 34.4.

N-(tert-Butyl)-4-methylidene-1,3-dithiolan-2-imine (3f). Yield: 0.15 g (82%). Brown oil. IR (KBr): 3438, 2930, 2349, 1613, 1525, 1381, 1265, 1198, 752. ¹H-NMR: 1.32, 1.34 (2s, *t*-Bu); 3.93, 4.24 (2s, CH₂S); 5.19, 5.20 (2d, ²J = 0.8, =CH); 5.31, 5.33 (2d, ²J = 0.8, =CH). ¹³C-NMR: 28.6, 28.7 (Me₃C); 38.2, 44.9 (CH₂S); 58.2, 58.3 (Me₃C); 108.9, 109.6 (=CH₂); 140.7, 145.4 (C=CH₂); 158.2, 160.1 (C=N). EI-MS: 187 (5, M⁺), 129 (18), 85 (23), 57 (100). Anal. calc. for C₈H₁₃NS₂ (187.05): C 51.29, H 6.99, N 7.48, S 34.23; found: C 51.4, H 7.1, N 7.4, S 34.6.

N-Benzyl-4-methylidene-1,3-dithiolan-2-imine (3g). Yield: 0.20 g (89%). Brown oil. IR (KBr): 3036, 2908, 1599, 1433, 1342, 1201, 1007, 896, 742. ¹H-NMR: 4.05, 4.22 (2s, CH₂N); 4.54, 4.56 (2s, CH₂S); 5.26, 5.27 (2d, ²J = 1.3, =CH); 5.38, 5.41 (2d, ²J = 1.3, =CH); 7.26–7.37 (m, Ph). ¹³C-NMR: 39.4, 42.8 (CH₂S); 61.4, 62.6 (CH₂N); 109.9, 110.9 (=CH₂); 126.9, 127.1 (CH); 127.8, 127.9 (2 CH); 128.5, 129.0 (2 CH); 138.6, 138.8 (C); 141.1, 143.0 (C=CH₂); 165.1, 166.2 (C=N). EI-MS: 221 (2, M⁺), 163 (3), 119 (2), 91 (100), 77 (18), 39 (14). Anal. calc. for C₁₁H₁₁NS₂ (221.03): C 59.69, H 5.01, N 6.33, S 28.97; found: C 57.9, H 5.1, N 6.5, S 28.5.

N-(4-Methoxybenzyl)-4-methylidene-1,3-dithiolan-2-imine (3h). Yield: 0.22 g (89%). Brown oil. IR (KBr): 3415, 3184, 2997, 2954, 2928, 2833, 1602, 1511, 1460, 1440. ¹H-NMR: 3.79, 3.81 (2s, MeO); 4.03, 4.21 (2s, CH₂N); 4.45, 4.48 (2s, CH₂S); 5.24, 5.26 (2d, ²J = 1.3, =CH); 5.37, 5.41 (2d, ²J = 1.3, =CH); 6.86, 6.88 (2d, ³J = 8.6, 2 CH); 7.25, 7.27 (2d, ³J = 8.6, 2 CH). ¹³C-NMR: 39.3, 42.7 (CH₂S); 55.3, 55.4 (MeO); 60.9, 62.1 (CH₂N); 109.9, 110.8 (=CH₂); 113.9, 114.3 (2 CH); 128.4, 129.0 (2 CH); 130.7, 130.9 (C); 141.1, 143.0 (C=CH₂); 158.7, 158.8 (C); 164.5, 166.5 (C=N). EI-MS: 251 (1, M⁺), 193 (3), 149 (2), 121 (100), 77

¹⁾ All compounds of type **3** were isolated as 1:1 mixtures of the corresponding (*E*)- and (*Z*)-isomers.

(17), 39 (12). Anal. calc. for $C_{12}H_{13}NOS_2$ (251.04): C 57.34, H 5.21, N 5.57, S 25.51; found: C 57.2, H 5.4, N 5.7, S 25.7.

4-Methylidene-N-phenyl-1,3-dithiolan-2-imine (3i). Yield: 0.17 g (84%). Brown oil. IR (KBr): 3431, 2925, 1587, 1475, 1266, 1196, 934, 753. 1H -NMR: 4.14, 4.19 (2s, CH_2S); 5.18, 5.31 (2d, $^2J = 1.3$, =CH); 5.39, 5.42 (2d, $^2J = 1.3$, =CH); 6.70–7.37 (m, Ph). ^{13}C -NMR: 39.8, 42.7 (CH_2S); 110.3, 111.0 (=CH₂); 120.1, 120.2 (2 CH); 124.8, 124.9 (C); 128.8, 129.1 (2 CH); 129.2, 129.4 (C); 141.1, 143.1 (C=CH₂); 150.9, 151.7 (C=N). EI-MS: 207 (8, M^+), 149 (100), 105 (58), 77 (29). Anal. calc. for $C_{10}H_9NS_2$ (207.02): C 57.93, H 4.38, N 6.76, S 30.93; found: C 58.3, H 4.5, N 6.9, S 31.2.

N-(4-Methoxyphenyl)-4-methylidene-1,3-dithiolan-2-imine (3j). Yield: 0.20 g (85%). Brown oil. IR (KBr): 3297, 3046, 3000, 2956, 2834, 1711, 1596, 1502, 1463, 1440. 1H -NMR: 3.80, 3.81 (2s, MeO); 4.10, 4.17 (2s, CH_2S); 5.17, 5.28 (2d, $^2J = 1.4$, =CH); 5.37, 5.39 (2d, $^2J = 1.4$, =CH); 6.87, 6.89 (2d, $^3J = 8.3$, 2 CH); 6.93, 6.95 (2d, $^3J = 8.3$, 2 CH). ^{13}C -NMR: 39.5, 42.7 (CH_2S); 55.3, 55.4 (MeO); 110.1, 110.8 (=CH₂); 114.2, 114.5 (2 CH); 121.1, 121.5 (2 CH); 140.9, 143.0 (C); 144.0, 144.9 (C=CH₂); 156.8, 156.9 (C); 166.8, 167.5 (C=N). EI-MS: 237 (2, M^+), 179 (6), 135 (4), 107 (100), 77 (11). Anal. calc. for $C_{11}H_{11}NOS_2$ (237.03): C 55.67, H 4.67, N 5.90, S 27.02; found: C 55.9, H 4.7, N 5.8, S 27.4.

N-(3-Chlorophenyl)-4-methylidene-1,3-dithiolan-2-imine (3k). Yield: 0.22 g (90%). Brown oil. IR (KBr): 2919, 2357, 2090, 1600, 1440, 1342, 1268, 754. 1H -NMR: 4.05, 4.22 (2s, CH_2N); 4.58, 4.60 (2s, CH_2S); 5.26, 5.27 (2d, $^2J = 1.3$, =CH); 5.38, 5.41 (2d, $^2J = 1.3$, =CH); 7.18–7.49 (m, 4 CH). ^{13}C -NMR: 39.5, 42.9 (CH_2S); 58.4, 59.5 (CH_2N); 110.2, 111.1 (=CH₂); 129.4, 129.6 (CH); 129.7, 129.8 (CH); 128.2, 128.3 (CH); 126.9, 127.1 (CH); 133.0, 133.1 (C); 136.2, 136.4 (C); 141.0, 142.8 (C=CH₂); 166.3, 167.4 (C=N). EI-MS: 241 (4, M^+), 183 (12), 139 (7), 111 (100), 77 (11). Anal. calc. for $C_{10}H_8ClNS_2$ (240.98): C 49.68, H 3.34, N 5.79, S 26.53; found: C 49.5, H 3.4, N 5.9, S 26.6.

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