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

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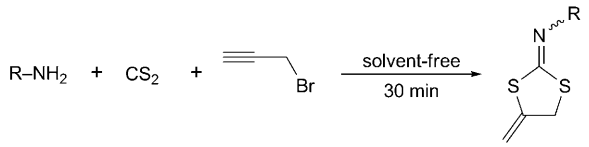
A one-pot synthesis of 2-imino-4-methylidene-1,3-dithiolanes *via* a three-component reaction of propargyl bromide (= 3-bromoprop-1-yne), primary amines, and carbon disulfide (CS_2) is described.

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 CS_2 in good yields (*Scheme 1*).

Scheme 1

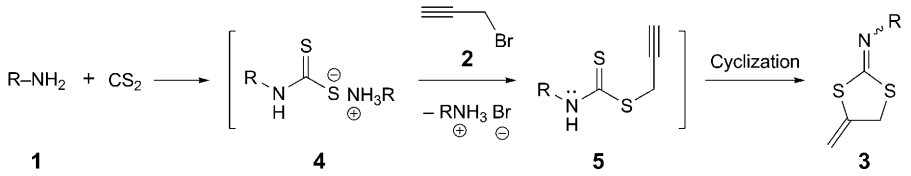


	R			R	Yield [%]
1a	Me	**2**	**3a**	Me	82
1b	Et		**3b**	Et	80
1c	Pr		**3c**	Pr	92
1d	Bu		**3d**	Bu	90
1e	i-Bu		**3e**	i-Bu	94
1f	*t*-Bu		**3f**	*t*-Bu	82
1g	Bn		**3g**	Bn	89
1h	4-MeO–$C_6H_4CH_2$		**3h**	4-MeO–$C_6H_4CH_2$	89
1i	Ph		**3i**	Ph	84
1j	4-MeO–C_6H_4		**3j**	4-MeO–C_6H_4	85
1k	3-Cl–C_6H_4		**3k**	3-Cl–C_6H_4	90

Results and Discussion. – The reaction of primary amines **1** and CS_2 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 ^{1}H- and ^{13}C-NMR spectra. For example, the ^{1}H-NMR spectrum of **3a** exhibited four *singlet*s for MeN (δ(H) 1.38 and 1.43) and CH_2(5) (δ(H) 4.04 and 4.21), along with four *doublet*s (δ(H) 5.24, 5.26, 5.37, and 5.41, ^2J = 1.3 Hz), for C(4)=CH_2. The ^{13}C-NMR spectrum of **3a** showed ten signals in agreement with the presence of two geometrical isomers. The ^{1}H- and ^{13}C-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 CS_2 is attacked by propargyl bromide (**2**) to afford **5**, which is converted to product **3** *via* cyclization reaction and elimination.

Scheme 2



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, CS_2, 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, CS_2, 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}. ^{1}H- and ^{13}C-NMR spectra: *Bruker DRX-500 Avance* instrument; in $CDCl_3$ at 500.1 and 125.7 MHz, resp.; δ in ppm rel. to Me_4Si 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), CS_2 (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 (SiO_2; 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. ^{1}H-NMR: 1.38, 1.43 (2*s*, Me); 4.04, 4.21 (2*s*, CH_2S); 5.24, 5.26 (2*d*, ^2J = 1.3, =CH); 5.37, 5.41 (2*d*, ^2J = 1.3, =CH). ^{13}C-NMR: 39.5, 42.5 (Me); 44.1, 42.1 (CH_2S); 109.7, 110.6 (=CH_2); 144.1, 145.1 (*C*=*C*H_2); 159.9, 161.7 (C=N). EI-MS: 145 (23, M^+), 87 (100), 43 (48), 15 (14). Anal. calc. for $C_5H_7NS_2$ (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. ^{1}H-NMR: 1.26, 1.29 (2*t*, ^3J = 6.9, Me); 3.28, 3.34 (2*q*, ^3J = 6.9, CH_2N); 4.01, 4.18 (2*s*, CH_2S); 5.21, 5.24 (2*d*, ^2J = 1.3, =CH); 5.36, 5.39 (2*d*, ^2J = 1.3, =CH). ^{13}C-NMR: 15.3, 15.4 (Me); 39.2, 42.5 (CH_2S); 52.3, 53.5 (CH_2N); 109.6, 110.5 (=CH_2); 141.1, 143.1 (*C*=CH_2); 162.3, 163.3 (C=N). EI-MS: 159 (6, M^+), 101 (100), 57 (56), 29 (11). Anal. calc. for $C_6H_9NS_2$ (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. ^{1}H-NMR: 0.89, 0.94 (2*t*, ^3J = 6.8, Me); 1.67, 1.70 (2*m*, CH_2); 3.25, 3.28 (2*t*, ^3J = 7.0, CH_2N); 4.01, 4.17 (2*s*, CH_2S); 5.22, 5.23 (2*d*, ^2J = 1.4, =CH); 5.35, 5.38 (2*d*, ^2J = 1.4, =CH). ^{13}C-NMR: 11.4, 14.1 (Me); 22.6, 23.9 (CH_2); 39.2, 42.5 (CH_2S); 59.8, 60.9 (CH_2N); 109.6, 110.4 (=CH_2); 141.1, 143.1 (*C*=CH_2); 162.8, 163.4 (C=N). EI-MS: 173 (6, M^+), 115 (100), 71 (56), 43 (23), 39. Anal. calc. for $C_7H_{11}NS_2$ (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. ^{1}H-NMR: 0.87, 0.92 (2*t*, ^3J = 7.0, Me); 1.35, 1.41 (2*m*, CH_2); 1.62, 1.67 (2*m*, CH_2); 3.28, 3.30 (2*t*, ^3J = 6.9, CH_2N); 3.99, (2*s*, CH_2S); 5.20, 5.21 (2*d*, ^2J = 1.3, =CH); 5.34, 5.37 (2*d*, ^2J = 1.3, =CH). ^{13}C-NMR: 13.7, 14.0 (Me); 20.4, 20.5 (CH_2); 32.3, 32.5 (CH_2); 39.1, 42.4 (CH_2S); 57.7, 58.9 (CH_2N); 109.5, 110.3 (=CH_2); 141.0, 143.1 (*C*=CH_2); 162.9, 164.1 (C=N). EI-MS: 187 (5, M^+), 129 (100), 85 (58). Anal. calc. for $C_8H_{13}NS_2$ (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. ^{1}H-NMR: 0.95, 1.32 (2*d*, ^3J = 6.7, 2 Me); 1.98, 2.03 (2*m*, CH); 3.10, 3.12 (2*d*, ^3J = 6.6, CH_2N); 4.01, 4.18 (2*s*, CH_2S); 5.23, 5.24 (2*d*, ^2J = 1.3, =CH); 5.35, 5.38 (2*d*, ^2J = 1.3, =CH). ^{13}C-NMR: 23.7, 23.9 (2 Me); 29.3, 29.6 (CH); 39.1, 42.4 (CH_2S); 65.9, 67.1 (CH_2N); 109.5, 110.3 (=CH_2); 141.1, 143.5 (*C*=CH_2); 158.1, 159.1 (C=N). EI-MS: 187 (9, M^+), 129 (100), 85 (56), 57 (23), 39 (11). Anal. calc. for $C_8H_{13}NS_2$ (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. ^{1}H-NMR: 1.32, 1.34 (2*s*, *t*-Bu); 3.93, 4.24 (2*s*, CH_2S); 5.19, 5.20 (2*d*, ^2J = 0.8, =CH); 5.31, 5.33 (2*d*, ^2J = 0.8, =CH). ^{13}C-NMR: 28.6, 28.7 (*Me*$_3$C); 38.2, 44.9 (CH_2S); 58.2, 58.3 (Me_3C); 108.9, 109.6 (=CH_2); 140.7, 145.4 (*C*=CH_2); 158.2, 160.1 (C=N). EI-MS: 187 (5, M^+), 129 (18), 85 (23), 57 (100). Anal. calc. for $C_8H_{13}NS_2$ (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. ^{1}H-NMR: 4.05, 4.22 (2*s*, CH_2N); 4.54, 4.56 (2*s*, CH_2S); 5.26, 5.27 (2*d*, ^2J = 1.3, =CH); 5.38, 5.41 (2*d*, ^2J = 1.3, =CH); 7.26–7.37 (*m*, Ph). ^{13}C-NMR: 39.4, 42.8 (CH_2S); 61.4, 62.6 (CH_2N); 109.9, 110.9 (=CH_2); 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*=CH_2); 165.1, 166.2 (C=N). EI-MS: 221 (2, M^+), 163 (3), 119 (2), 91 (100), 77 (18), 39 (14). Anal. calc. for $C_{11}H_{11}NS_2$ (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. ^{1}H-NMR: 3.79, 3.81 (2*s*, MeO); 4.03, 4.21 (2*s*, CH_2N); 4.45, 4.48 (2*s*, CH_2S); 5.24, 5.26 (2*d*, ^2J = 1.3, =CH); 5.37, 5.41 (2*d*, ^2J = 1.3, =CH); 6.86, 6.88 (2*d*, ^3J = 8.6, 2 CH); 7.25, 7.27 (2*d*, ^3J = 8.6, 2 CH). ^{13}C-NMR: 39.3, 42.7 (CH_2S); 55.3, 55.4 (MeO); 60.9, 62.1 (CH_2N); 109.9, 110.8 (=CH_2); 113.9, 114.3 (2 CH); 128.4, 129.0 (2 CH); 130.7, 130.9 (C); 141.1, 143.0 (*C*=CH_2); 158.7, 158.8 (C); 164.5, 166.5 (C=N). EI-MS: 251 (1, M^+), 193 (3), 149 (2), 121 (100), 77

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[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. ^{1}H-NMR: 4.14, 4.19 (2*s*, CH_2S); 5.18, 5.31 (2*d*, $^2J = 1.3$, =CH); 5.39, 5.42 (2*d*, $^2J = 1.3$, =CH); 6.70–7.37 (*m*, Ph). ^{13}C-NMR: 39.8, 42.7 (CH_2S); 110.3, 111.0 (=CH_2); 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*=CH_2); 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. ^{1}H-NMR: 3.80, 3.81 (2*s*, MeO); 4.10, 4.17 (2*s*, CH_2S); 5.17, 5.28 (2*d*, $^2J = 1.4$, =CH); 5.37, 5.39 (2*d*, $^2J = 1.4$, =CH); 6.87, 6.89 (2*d*, $^3J = 8.3$, 2 CH); 6.93, 6.95 (2*d*, $^3J = 8.3$, 2 CH). ^{13}C-NMR: 39.5, 42.7 (CH_2S); 55.3, 55.4 (MeO); 110.1, 110.8 (=CH_2); 114.2, 114.5 (2 CH); 121.1, 121.5 (2 CH); 140.9, 143.0 (C); 144.0, 144.9 (*C*=CH_2); 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. ^{1}H-NMR: 4.05, 4.22 (2*s*, CH_2N); 4.58, 4.60 (2*s*, CH_2S); 5.26, 5.27 (2*d*, $^2J = 1.3$, =CH); 5.38, 5.41 (2*d*, $^2J = 1.3$, =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 (=CH_2); 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*=CH_2); 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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