Available online at www.sciencedirect.com

SciVerse ScienceDirect

Chinese Chemical Letters 23 (2012) 699–702

CHINESE CHEMICAL LETTERS

www.elsevier.com/locate/cclet

Synthesis of alkyl bis(dimethylamino)methylenecarbamodithioates from 1,1,3,3-tetramethylguanidine, CS_2 and oxiranes

Sima Yavari [a], Samira Nasiri-Gheidari [b], Avat (Arman) Taherpour [a], Issa Yavari [b,*]

[a] *Department of Chemistry, Arak Branch, Islamic Azad University, Arak, Iran*
[b] *Department of Chemistry, Tarbiat Modares University, P.O. Box 14115-175, Tehran, Iran*

Received 27 February 2012
Available online 10 May 2012

Abstract

An efficient synthesis of alkyl bis(dimethylamino)methylenecarbamodithioates *via* a one-pot reaction between 1,1,3,3-tetramethylguanidine, carbon disulfide and substituted oxiranes, in good yields, is described.

Keywords: Carbamodithioate; Oxirane; Tetramethylguanidine; Carbon disulfide; One-pot reaction; Solvent free

Carbon–sulfur bond formation is a fundamental approach to introduce sulfur into organic compounds [1–3]. Sulfur is present in many molecules that are of biological, pharmaceutical, and material interest [4]. Organic dithiocarbamates are important in medicinal [5] and agricultural chemistry [6]. These compounds are used in the rubber industry as vulcanization accelerators [7], in controlled radical polymerization techniques [8], and recently, in the synthesis of ionic liquids [9].

Because of the strain induced by the presence of a three-membered ring [10], epoxides are significantly more reactive than other cyclic ethers. Synthetic procedures for opening epoxide ring can be based on nucleophilic or acid-mediated ring opening [11]. Suitable epoxide opening catalysts include Lewis acids, Lewis bases, Brønsted acids, and porphyrin complexes.

1. Experimental

Compounds **1**, **2**, and CS_2 were obtained from Merck and were used without further purification. M.p.: Electrothermal-9100 apparatus. IR spectra (KBr): Shimadzu IR-460 spectrometer; in cm^{-1}. ^1H and ^{13}C NMR spectra: Bruker DRX-500 Avance instrument; in $CDCl_3$ at 500.1 and 125.7 MHz, resp.; δ in ppm, J in Hz. MS: Finnigan-MAT-8430 mass spectrometer, at 70 eV; in m/z (rel. %). Elemental analyses (C, H, N): Heraeus CHN-O-Rapid analyzer.

* Corresponding author.
E-mail address: yavarisa@modares.ac.ir (I. Yavari).

1001-8417/$ – see front matter
http://dx.doi.org/10.1016/j.cclet.2012.04.016

1.1. General procedure

A mixture of **1** (0.23 g, 2 mmol) and CS_2 (0.304 g, 4 mmol) was stirred for 10 min. Then, the epoxide **3** (2 mmol) was added and the reaction mixture was stirred at room temperature. After completion of the reaction (1–2 h, monitored by TLC), the residue was purified by column chromatography (SiO_2; hexane/AcOEt 9:1) to afford pure **4**.

1.1.1. 2-Hydroxypropyl bis(dimethylamino)methylenecarbamodithioate (*4a*)

Pale yellow oil; yield: 0.22 g (87%). Anal. Calcd. for $C_9H_{19}N_3OS_2$ (249.4): C, 43.34; H, 7.68; N, 16.85; S, 25.71%. Found: C, 43.03; H, 7.60; N, 17.05; S, 25.53%. IR (KBr, cm^{-1}): 3371, 2916, 1597, 1397, 1282, 1170, 1022; ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.01 (d, 3H, ^3J = 6.4 Hz), 2.83 (s, 12H, 2× NMe_2), 3.27–3.32 (m, 2H, SCH_2), 3.80–3.81 (m, 1H, C*H*OH), 3.92 (br s, 1H, OH); ^{13}C NMR (125 MHz, $CDCl_3$): δ 22.5 (Me), 40.5 (2× NMe_2), 43.9 (SCH_2), 67.6 (CHOH), 168.3 (C=N), 199.7 (C=S). MS (EI, 70 eV): *m/z* (%) 251 (M^++2, 1), 250 (M^++1, 1), 249 (M^+, 10), 232 (20), 205 (22), 190 (42), 158 (100), 114 (50), 91 (64), 59 (23).

1.1.2. 2,3-Dihydroxypropyl bis(dimethylamino)methylenecarbamodithioate (*4b*)

Pale yellow oil; yield: 0.25 g (95%). Anal. Calcd. for $C_9H_{19}N_3O_2S_2$ (265.4): C, 40.73; H, 7.22; N, 15.83; S, 24.16%. Found: C, 40.56; H, 7.10; N, 15.68; S, 24.33%. IR (KBr, cm^{-1}): 3369, 2911, 1592, 1393, 1283, 1174, 1027; ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.98 (s, 12H, 2× NMe_2), 3.18–3.20 (m, 2H, SCH_2), 3.56 (dd, 2H, $\Delta\nu_{AB}$ = 11.2 Hz, $^3J_{AB}$ = 11.0 Hz, $^3J_{AX}$ = 5.7 Hz, $^3J_{BX}$ = 4.5 Hz, CH_2), 3.80–3.81 (m, 1H, C*H*OH), 4.47 (br s, 1H, OH); ^{13}C NMR (125 MHz, $CDCl_3$): δ 38.7 (2× NMe_2), 39.6 (SCH_2), 64.6 (OCH_2), 71.5 (CHOH), 168.6 (C=N), 199.8 (C=S). MS (EI, 70 eV): *m/z* (%) 267 (M^++2, 1), 266 (M^++1, 1), 265 (M^+, 10), 221 (11), 204 (10), 158 (100), 114 (83), 61 (35).

1.1.3. 2-Hydroxybutyl bis(dimethylamino)methylenecarbamodithioate (*4c*)

Pale yellow oil; yield: 0.27 g (93%). Anal. Calcd. for $C_{10}H_{21}N_3OS_2$ (263.42): C, 45.59; H, 8.04; N, 15.95; S, 24.34%. Found: C, 45.75; H, 8.12; N, 15.86; S, 24.53%. IR (KBr, cm^{-1}): 3368, 2917, 1596, 1396, 1284, 1170, 1020; ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.84 (t, 3H, ^3J = 7.4 Hz, Me), 1.43–1.46 (m, 2H, CH_2), 2.90 (s, 12H, 2NMe_2), 2.93–2.95 (m, 1H, CH), 2.96–2.99 (m, 1H, CH), 3.04–3.08 (m, 1H, CH), 3.81 (br s, 1H, OH); ^{13}C NMR (125 MHz, $CDCl_3$): δ 9.9 (Me), 29.5 (CH_2), 40.6 (2× NMe_2), 42.3 (SCH_2), 73.2 (CHOH), 168.5 (C=N), 200.9 (C=S). MS (EI, 70 eV): *m/z* (%) 265 (M^++2, 1), 264 (M^++1, 1), 263 (M^+, 10), 219 (13), 204 (11), 234 (15), 191 (34), 158 (100), 59 (13).

1.1.4. 2-Hydroxy-3-phenoxypropyl bis(dimethylamino)methylenecarbamodithioate (*4d*)

Pale yellow oil; yield: 0.30 g (87%). Anal. Calcd. for $C_{15}H_{23}N_3O_2S_2$ (341.49): C, 52.76; H, 6.79; N, 12.30; S, 18.78%. Found: C, 52.47; H, 6.67; N, 12.17; S, 18.62%. IR (KBr, cm^{-1}): 3374, 2918, 1599, 1392, 1281, 1170, 1020; ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.04 (s, 12H, 2× NMe_2), 3.34 (dd, 2H, ^2J = 5.0 Hz, ^3J = 5.8 Hz, CH_2), 4.01 (dd, 2H, ^2J = 5.7 Hz, ^3J = 4.9 Hz, OCH_2), 4.28 (m, 1H, OCH), 4.61 (br s, 1H, OH), 5.23–5.32 (m, 1H, C*H*OH), 6.89–6.91 (m, 3H, 3CH), 7.26 (t, 2H, ^3J = 7.8 Hz, 2× CH); ^{13}C NMR (125 MHz, $CDCl_3$): δ 41.4 (2NMe_2), 42.3 (SCH_2), 71.2 (OCH_2), 71.4 (CHOH), 115.4 (2 CH), 121.7 (CH), 130.2 (CH), 159.4 (C), 169.3 (C=N), 202.4 (C=S). MS (EI, 70 eV): *m/z* (%) 343 (M^++2, 1), 342 (M^++1, 1), 341 (M^+, 10), 297 (11), 227 (10), 184 (44), 158 (100), 115 (55), 71 (80).

1.1.5. 2-Hydroxycyclohexyl bis(dimethylamino)methylenecarbamodithioate (*4e*)

Pale yellow oil; yield: 0.26 g (92%). Anal. Calcd. for $C_{12}H_{23}N_3OS_2$ (289.46): C, 49.79; H, 8.01; N, 14.52; S, 22.16%. Found: C, 49.43; H, 8.13; N, 14.66; S, 22.01%. IR (KBr, cm^{-1}): 3360, 2913, 1599, 1394, 1281, 1178, 1021; ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.53–1.58 (m, 4H, 2× CH_2), 1.89–1.95 (m, 4H, 2CH_2), 2.86 (s, 12H, 2NMe_2), 3.28–3.31 (m, 2H, 2× CH), 4.56 (1H, br s, OH); ^{13}C NMR (125 MHz, $CDCl_3$): δ 23.9 (CH_2), 25.9 (CH_2), 31.0 (CH_2), 35.5 (CH_2), 40.6 (2NMe_2), 55.1 (CH), 75.1 (CHOH), 168.3 (C=N), 201.1 (C=S). MS (EI, 70 eV): *m/z* (%) 291 (M^++2, 1), 290 (M^++1, 1), 289 (M^+, 10), 272 (10), 245 (10), 195 (30), 175 (32), 158 (100), 131 (43).

1.1.6. 3-(Allyloxy)-2-hydroxypropyl bis(dimethylamino)methylenecarbamodithioate (*4f*)

Pale yellow oil; yield: 0.27 g (93%). Anal. Calcd. for $C_{12}H_{23}N_3O_2S_2$ (305.46): C, 47.18; H, 7.59; N, 13.76; S, 20.99%. Found: C, 47.45; H, 7.42; N, 13.53; S, 21.17%. IR (KBr, cm^{-1}): 3368, 2917, 1596, 1396, 1284, 1170, 1020; ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.87 (s, 12H, 2× NMe_2), 2.94 (dd, 1H, ^2J = 12.1 Hz, ^3J = 6.1 Hz, CH_2), 3.18 (dd, 1H, ^2J = 12.1 Hz, ^3J = 7.1 Hz, CH_2), 3.40 (dd, 1H, ^2J = 9.1 Hz, ^3J = 7.1 Hz, CH_2), 3.65 (dd, 1H, ^3J = 9.1 Hz, ^3J = 4.8 Hz,