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ORIGINAL PAPER

A facile and effective procedure for synthesis of polyfunctionalized pyrrolines from simultaneously stirring of carbon disulfide, aniline, arylglyoxals and β-enaminocarbonyls

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Abstract An efficient one-pot synthesis of 2*H*-pyrroline derivatives by a four-component reaction between carbon disulfide, aniline, arylglyoxals and β-enaminocarbonyls in acetonitrile at room temperature under mild reaction conditions is reported. The addition reaction has been done to access broad range of 5-hydroxy-4-phenylcarbamodithioate 2-*H* pyrroline derivatives after about 6 h stirring. All reactions were performed in acetonitrile at room temperature. Reactions are clean, and products were isolated by simple filtration.

Keywords Four-component reaction · Pyrroline derivatives · Arylglyoxals · β-Enaminocarbonyls

Introduction

In recent years, multicomponent reactions (MCRs) play an important role in new primary synthetic chemistry in the view of the fact that, these reactions increase the efficiency by combination of several functional steps without any changes of the conditions and isolation of intermediates [1–10]. Multicomponent reactions (MCRs) are powerful tools for the generation of chemical libraries, and they have attracted significant attention due to their broad applications in medicinal chemistry for the production of different structural scaffolds, and in combinatorial synthesis [11–13]. *N*-substituted pyrrolines are an important class of compounds which exhibit neuritogenic activity [14] and serve as useful synthetic intermediates [15–17]. Organic dithiocarbamates are utilized as substrates for radical chemistry [18–20] and as synthetic intermediates toward thiourea, guanidines and amidines [21–23]. The importance of the reactions of carbon disulfide with *N*-nucleophiles involves addition of carbon disulfide to N–H bonds [24]. The products of these reactions, dithiocarbamate salts, react with 2-chloro-1,3-dicarbonyl compounds [25], epoxides [26, 27], α-haloketones [28], and the other electron deficient compounds that can be converted to dithiocarbamate derivatives. To the best of our knowledge, there has not been any report on the reaction of carbon disulfide, aniline, arylglyoxals and β-enaminocarbonyls. As part of our ongoing project, to develop new synthetic methods for nitrogen-containing heterocycles, we attempted to develop a mild and efficient process for the synthesis of multisubstituted pyrroline. Herein, this paper reports a one-pot four-component synthesis of 5-hydroxy-4-phenylcarbamodithioate 2-*H* pyrroline derivatives from carbon disulfide, aniline, arylglyoxals and β-enaminocarbonyls as starting materials without using any catalysts (Scheme 1).

Experimental procedures

Materials and characterization techniques

All the utilized arylglyoxals were synthesized by the SeO_2-oxidation of the related arylmethyl ketones on the

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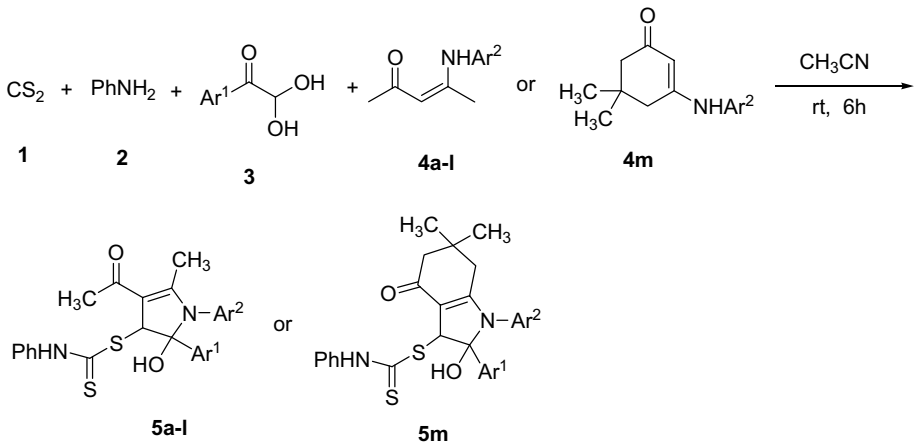
Scheme 1 Reaction between carbon disulfide, aniline, arylglyoxals and β-enaminocarbonyls



basis of the reported procedure and used as their monohydrates [29]. IR spectra were obtained on a Shimadzu IR-470 spectrometer. The proton and carbon-13 NMR spectra were recorded on Bruker DRX-400 Avance spectrometer at 400 and 100 MHz, respectively, with Me_4Si as an internal standard in DMSO. Elemental analyses (C, H, N) were performed with a Heracus CHN-O-Rapid analyzer. The chemicals used in this work purchased from Fluka (Buchs, Switzerland) and were used without further purification. All the products were characterized using NMR and IR spectral and analytical data.

General procedure for synthesis of compounds 5a–m

A solution of carbon disulfide (1 mmol), aniline (1 mmol), β-enaminocarbonyls (1 mmol) and arylglyoxal monohydrates (1 mmol) in acetonitrile (3 ml) was stirred at room temperature. After 6 h stirring, the resulting precipitate was filtered, washed with acetonitrile (20 mL) to afford the pure product.

Selected spectral data

*1-(4,5-Dihydro-5-hydroxy-2-methyl-1-phenyl-4-(phenylcarbamodithioate)-5-phenyl-1H-pyrrol-3yl) ethanone (**5a**)* Yield: 67%; yellow powder; m.p. 130–132 °C. IR (KBr) ($\bar{\upsilon}_{max}$, cm^{-1}): 3374 (NH), 1594 (C=O). Calcd. for ($C_{26}H_{24}N_2O_2S_2$): C, 67.80; H, 5.25; N, 6.08%. Found: C, 67.69; H, 5.12; N, 6.15%. ^{1}H NMR (d_6-DMSO, 400 MHz): δ = 1.98 (3H, s, CH_3), 2.27 (3 H, s, CH_3), 4.60 (1H, s, CH), 5.76 (1H, s, NH), 6.34 (1H, s, OH), 6.75–7.40 (m, aromatic hydrogens), ^{13}C NMR (d_6-DMSO, 100 MHz): δ = 15.4 (CH_3), 29.9 (CH_3), 52.5 (SCH), 68.0 (C–OH), 97.6, 148.9 (C=C), 110.9, 112.3, 112.4, 113.9, 115.6, 116.3, 128.4, 128.7, 129.1, 137.1 (aromatic carbons), 159.9 (C=S), 194.5 (C=O).

*1-(4,5-Dihydro-5-hydroxy-2-methyl-1-phenyl-4-(phenylcarbamodithioate)-5-(4-nitrophenyl)-1H-pyrrol-3yl)ethanone (**5b**)* Yield: 64%; yellow powder; m.p. 140–142 °C. IR (KBr) ($\bar{\upsilon}_{max}$, cm^{-1}): 3372 (NH), 1598 (C=O). Calcd. for ($C_{26}H_{23}N_3O_4S_2$): C, 61.76; H, 4.59; N, 8.31%. Found: C, 61.69; H, 4.32; N, 8.15%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.12 (3H, s, CH_3), 2.36 (3 H, s, CH_3), 4.06 (1H, s, CH), 4.54 (1H, s, NH), 5.91 (1H, s, OH), 6.56–8.29 (m, aromatic hydrogens), ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 15.4 (CH_3), 29.9 (CH_3), 51.3 (SCH), 70.5 (C–OH), 93.0, 147.0 (C=C), 110.7, 115.1, 120.8, 124.1, 126.3, 128.1, 128.8, 129.1, 129.6, 135.9 (aromatic carbons), 162.6 (C=S), 192.8 (C=O).

*1-(4,5-Dihydro-5-hydroxy-2-methyl-1-phenyl-4-(phenylcarbamodithioate)-5-(4-fluorophenyl)-1H-pyrrol-3yl)ethanone (**5c**)* Yield: 68%; white powder; m.p. 139–140 °C. IR (KBr) ($\bar{\upsilon}_{max}$, cm^{-1}): 3276 (NH), 1603 (C=O). Calcd. for ($C_{26}H_{23}FN_2O_2S_2$): C, 65.25; H, 4.84; N, 5.85%. Found: C, 65.39; H, 4.72; N, 5.75%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.10 (3H, s, CH_3), 2.35 (3 H, s, CH_3), 4.01 (1H, s, CH), 4.51 (1H, s, NH), 5.73 (1H, s, OH), 6.60–7.55 (m, aromatic hydrogens), ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 15.4 (CH_3), 29.1 (CH_3), 49.6 (SCH), 70.6 (C–OH), 93.4, 147.5 (C=C), 107.6, 115.1, 120.4, 127.0, 127.8, 128.9, 129.4, 136.3, 138.5 (aromatic carbons), 163.9 (C=S), 192.8 (C=O).

*1-(4,5-Dihydro-5-hydroxy-2-methyl-1-p-tolyl-4-(phenylcarbamodithioate)-5-(4-fluorophenyl)-1H-pyrrol-3yl)ethanone (**5d**)* Yield: 70%; gray powder; m.p. 150–152 °C. IR (KBr) ($\bar{\upsilon}_{max}$, cm^{-1}): 3275 (NH), 1621 (C=O). Calcd. for ($C_{27}H_{25}FN_2O_2S_2$): C, 65.83; H, 5.12; N, 5.69%. Found: C, 65.72; H, 5.02; N, 5.75%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.09 (3H, s, CH_3), 2.31 (3 H, s, CH_3), 2.33 (3 H, s, CH_3), 3.99 (1H, s, CH), 4.50 (1H, s, NH), 5.70 (1H, s, OH), 6.59–7.56 (m, aromatic hydrogens), ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 14.8 (CH_3), 20.6 (CH_3), 28.5 (CH_3), 50.0 (SCH), 70.1 (C–OH), 92.8, 146.9 (C=C), 106.8, 114.6,

114.9, 115.2, 120.0, 126.5, 126.6, 128.2, 128.9, 129.1, 133.0, 137.4 (aromatic carbons), 163.4 (C=S), 192.0 (C=O).

1-(4,5-Dihydro-5-hydroxy-2-methyl-1-p-tolyl-4-(phenylcarbamodithioate)-5-(4-nitrophenyl)-1H-pyrrol-3yl)ethanone ***(5e)*** Yield: 65%; yellow powder; m.p. 155–157 °C. IR (KBr) ($\bar{\upsilon}_{max}$, cm^{-1}): 3339 (NH), 1602 (C=O). Calcd. for ($C_{27}H_{25}N_3O_4S_2$): C, 62.41; H, 4.85; N, 8.09%. Found: C, 62.32; H, 5.02; N, 8.15%. ^{1}H NMR (d_6-DMSO, 400 MHz): δ = 1.99 (3H, s, CH_3), 2.17 (3 H, s, CH_3), 2.24 (3 H, s, CH_3), 4.87 (1H, s, CH), 5.92 (1H, d, s, NH), 6.29 (1H, s, OH), 6.77–7.78 (m, aromatic hydrogens), ^{13}C NMR (d_6-DMSO, 100 MHz): δ = 15.3 (CH_3), 20.9 (CH_3), 28.7 (CH_3), 52.6 (SCH), 68.5 (C–OH), 97.2, 147.4 (C=C), 108.6, 112.4, 116.1, 121.6, 128.3, 128.6, 129.7, 135.1, 136.4, 146.3, 146.7 (aromatic carbons), 160.0 (C=S), 193.3 (C=O).

1-(4,5-Dihydro-5-hydroxy-2-methyl-1-p-tolyl-4-(phenylcarbamodithioate)-5-phenyl-1H-pyrrol-3yl)ethanone ***(5f)*** Yield: 62%; white powder; m.p. 120–121 °C. IR (KBr) ($\bar{\upsilon}_{max}$, cm^{-1}): 3279 (NH), 1619 (C=O). Calcd. for ($C_{27}H_{26}N_2O_2S_2$): C, 68.32; H, 5.52; N, 5.90%. Found: C, 68.20; H, 5.43; N, 5.81%. ^{1}H NMR (*d_6-DMSO*, 400 MHz): δ = 2.08 (3H, s, CH_3), 2.30 (3 H, s, CH_3), 2.35 (3 H, s, CH_3), 3.92 (1H, s, CH), 4.51 (1H, s, NH), 5.64 (1H, s, OH), 6.61–7.56 (m, aromatic hydrogens), ^{13}C NMR (d_6-DMSO, 100 MHz): δ = 10.1 (CH_3), 15.8 (CH_3), 23.7 (CH_3), 65.3 (SCH), 71.8 (C–OH), 105.7, 142.1 (C=C), 109.9, 115.2, 119.8, 121.7, 122.6, 122.7, 122.9, 123.0, 123.3, 123.5, 124.2, 124.3, 132.5 (aromatic carbons), 157.8 (C=S), 187.3 (C=O).

1-(4,5-Dihydro-5-hydroxy-2-methyl-1-benzyl-4-(phenylcarbamodithioate)-5-(4-nitrophenyl)-1H-pyrrol-3yl)ethanone ***(5g)*** Yield: 66%; cream powder; m.p. 135–136 °C. IR (KBr) ($\bar{\upsilon}_{max}$, cm^{-1}): 3280 (NH), 1617 (C=O). Calcd. for ($C_{27}H_{25}N_3O_4S_2$): C, 62.41; H, 4.85; N, 8.09%. Found: C, 62.35; H, 4.65; N, 8.15%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.98 (3H, s, CH_3), 2.44 (3H, s, CH_3), 3.93 (1H, d, $^3J_{HH}$ = 4 Hz, CH), 4.35 (1H, d, $^3J_{HH}$ = 4 Hz, CH_2), 4.38 (1H, s, NH), 5.57 (1H, s, OH), 6.67–7.41 (m, aromatic). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 14.0 (CH_3), 28.8 (CH_3), 46.0 (CH_2), 47.9 (SCH), 69.4 (C–OH), 93.7, 141.7 (C=C), 106.2, 115.0, 120.2, 125.2, 126.7, 127.3, 128.6, 128.7, 129.0, 129.4, 138.1 (aromatic carbons), 164.4 (C=S), 192.3 (C=O).

1-(4,5-Dihydro-5-hydroxy-2-methyl-1-benzyl-4-(phenylcarbamodithioate)-5-p-tolyl-1H-pyrrol-3yl)ethanone ***(5h)*** Yield: 60%; white powder; m.p. 120–122 °C. IR (KBr) ($\bar{\upsilon}_{max}$, cm^{-1}): 3273 (NH), 1600 (C=O). Calcd. for ($C_{28}H_{28}N_2O_2S_2$): C, 68.82; H, 5.78; N, 5.73%. Found: C, 68.75; H, 5.65; N, 5.65%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.97 (3H, s, CH_3), 2.42 (3H, s, CH_3), 2.44 (3H, s, CH_3), 3.96 (1H, d, $^3J_{HH}$ = 4 Hz, CH), 4.34 (1H, s, CH_2), 4.36 (1H, s, NH), 5.53 (1H, s, OH), 6.68–7.45 (m, aromatic). ^{13}C NMR (d_6-DMSO, 100 MHz): δ = 8.8 (CH_3), 16.0 (CH_3), 23.5 (CH_3), 49.0 (CH_2), 64.2 (SCH), 71.6 (C–OH), 101.0, 142.5 (C=C), 109.7, 114.9, 119.9, 121.4, 122.0, 123.4, 124.2, 124.4, 132.9, 133.3, 133.5 (aromatic carbons), 159.2 (C=S), 187.0 (C=O).

1-(4,5-Dihydro-5-hydroxy-2-methyl-1-benzyl-4-(phenylcarbamodithioate)-5-(4-fluorophenyl)-1H-pyrrol-3yl)ethanone ***(5i)*** Yield: 64%; gray powder; m.p. 121–122 °C. IR (KBr) ($\bar{\upsilon}_{max}$, cm^{-1}): 3286 (NH), 1601 (C=O). Calcd. for ($C_{27}H_{25}FN_2O_2S_2$): C, 65.83; H, 5.12; N, 5.69%. Found: C, 65.65; H, 5.34; N, 5.75%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.99 (3H, s, CH_3), 2.43 (3H, s, CH_3), 3.87 (1H, s, CH), 4.33 (1H, s, NH), 4.35 (1H, s, CH_2), 5.58 (1H, s, OH), 6.63–7.55 (m, aromatic). ^{13}C NMR (d_6-DMSO, 100 MHz): δ = 8.8 (CH_3), 23.6 (CH_3), 49.3 (CH_2), 64.4 (SCH), 71.8 (C–OH), 108.7, 142.1 (C=C), 109.7, 109.9, 110.5, 110.7, 115.3, 120.1, 121.4, 121.8, 121.9, 122.1, 123.4, 124.3, 132.6 (aromatic carbons), 158.9 (C=S), 186.9 (C=O).

1-(4,5-Dihydro-5-hydroxy-2-methyl-1-phenyl-4-(phenylcarbamodithioate)-5-(2-naphthyl)-1H-pyrrol-3yl)ethanone ***(5j)*** Yield: 64%; brown powder; m.p. 130–132 °C. IR (KBr) ($\bar{\upsilon}_{max}$, cm^{-1}): 3286 (NH), 1624 (C = O). Calcd. for ($C_{30}H_{26}N_2O_2S_2$): C, 70.56; H, 5.13; N, 5.49%. Found: C, 70.62; H, 5.24; N, 5.65%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.11 (3H, s, CH_3), 2.42 (3H, s, CH_3), 4.03 (1H, s, CH), 4.62 (1H, s, NH), 5.83 (1H, s, OH), 6.63–8.08 (m, aromatic). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 14.2 (CH_3), 27.6 (CH_3), 46.3 (CH_2), 53.4 (SCH), 71.2 (C–OH), 96.7, 141.1 (C = C), 108.7, 109.3, 110.4, 110.6, 113.3, 115.8, 118.4, 119.9, 120.9, 121.1, 121.5, 122.3, 122.7, 123.4, 125.8 (aromatic carbons), 160.4 (C = S), 193.9 (C = O).

1-(4,5-Dihydro-5-hydroxy-2-methyl-1-butyl-4-(phenylcarbamodithioate)-5-(4-nitrophenyl)-1H-pyrrol-3yl)ethanone ***(5k)*** Yield: 71%; yellow powder; m.p. 110–112 °C. IR (KBr) ($\bar{\upsilon}_{max}$, cm^{-1}): 3416 (NH), 1606 (C = O). Calcd. for ($C_{24}H_{27}N_3O_4S_2$): C, 59.36; H, 5.60; N, 8.65%. Found: C, 59.48; H, 5.49; N, 8.45%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.78 (3H, t, $^3J_{HH}$ = 8 Hz, CH_3), 1.21 (2H, m, $^3J_{HH}$ = 8 Hz, CH_2), 1.51 (2H, m, $^3J_{HH}$ = 8 Hz, CH_2), 2.08 (3H, s, CH_3), 2.56 (3H, s, CH_3), 2.75 (2H, t, $^3J_{HH}$ = 8 Hz, CH_2), 4.48 (1H, s, CH), 6.55 (1H, s, NH), 6.88 (1H, s, OH), 7.27–8.30 (m, aromatic). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 12.2 (CH_3), 13.6 (CH_2), 16.3 (CH_3), 19.4 (CH_3), 31.1 (CH_2), 44.2 (CH_2), 60.7 (SCH), 73.7 (C–OH), 101.0, 145.3 (C = C), 110.0, 123.1, 123.8, 124.4, 127.5, 129.7, 132.6, 136.9 (aromatic carbons), 164.5 (C = S), 194.5 (C = O).

*1-(4,5-Dihydro-5-hydroxy-2-methyl-1-butyl-4-(phenylcarbamodithioate)-5-(4-phenyl)-1H-pyrrol-3yl)ethanone (**5l**)* Yield: 69%; white powder; m.p. 90–93 °C. IR (KBr) ($\bar{\upsilon}_{max}$, cm^{-1}): 3417 (NH), 1584 (C = O). Calcd. for ($C_{24}H_{28}N_2O_2S_2$): C, 65.42; H, 6.41; N, 6.36%. Found: C, 66.58; H, 6.23; N, 6.25%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.77 (3H, t, $^3J_{HH}$ = 8 Hz, CH_3), 0.90 (2H, m, $^3J_{HH}$ = 8 Hz, CH_2), 1.85 (3H, s, CH_3), 2.08 (3H, s, CH_3), 2.33 (2H, m, $^3J_{HH}$ = 8 Hz, CH_2), 4.66 (2H, t, $^3J_{HH}$ = 8 Hz, CH_2), 4.76 (1H, s, CH), 6.63 (1H, s, NH), 7.14 (1H, s, OH), 7.28–7.48 (m, aromatic). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 13.7 (CH_3), 16.1 (CH_2), 19.5 (CH_3), 20.0 (CH_3), 29.0 (CH_2), 31.5 (CH_2), 44.0 (SCH), 64.1 (C–OH), 102.1, 135.6 (C = C), 125.8, 127.7, 128.3, 128.6, 128.8, 129.1, 129.3, 129.4, 129.5 (aromatic carbons), 164.5 (C = S), 194.5 (C = O).

*2,3,4,5,6,7-Hexahydro-2-hydroxy-6,6-dimethyl-4-oxo-1,2-dip-tolyl-1H-indol-3-ylphenylcarbamodithioate (**5m**)* Yield: 62%; pink powder; m.p. 140–142 °C. IR (KBr) ($\bar{\upsilon}_{max}$, cm^{-1}): 3300 (NH), 1606 (C = O). Calcd. for ($C_{31}H_{32}N_2O_2S_2$): C, 70.42; H, 6.10; N, 5.30%. Found: C, 70.53; H, 5.24; N, 5.42%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.66, 0.98, 2.36, 2.40 (12H, s, $4CH_3$), 1.12, 1.13 (4H, s, $2CH_2$), 3.65 (1H, s, CH), 4.97 (1H, s, NH), 5.48 (1H, s, OH), 6.64–7.31 (m, aromatic). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 21.0, 26.9, 28.9, 29.0 ($4CH_3$), 28.2 (C), 32.2, 34.3 ($2CH_2$), 50.1 (SCH), 69.3 (C–OH), 96.5, 144.6 (C = C), 125.1, 125.6, 127.4, 128.6, 129.1, 129.2, 129.5, 129.8, 131.9, 133.8, 135.1 (aromatic carbons), 162.3 (C = S), 193.1 (C = O).

Results and discussion

In a typical reaction, at first carbon disulfide was reacted with aniline in acetonitrile. After 2 min stirring, phenylglyoxal and 4-phenylamino-3-pentene-2-one were added to it. The reaction course was monitored by TLC. After 6 h stirring, the starting materials were disappeared on TLC and one-pot appeared which identified to be the pyrroline derivative **5a**. Compound **5a** was isolated as a yellow solid in 67% yield to offer the highly pure product (Scheme 2).

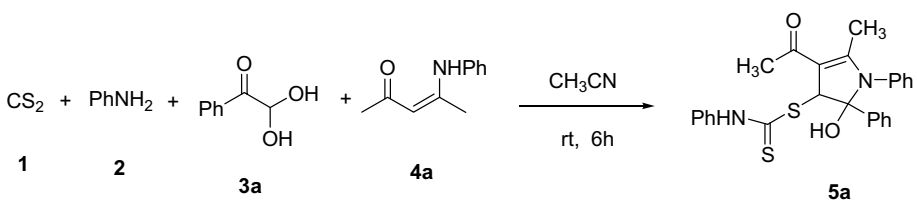
Table 1 Reaction between carbon disulfide, aniline, arylglyoxals and *β*-enaminocarbonyls

5	Ar^1	Ar^2	Yield[a] (%)
a	C_6H_5	C_6H_5	67
b	4-$NO_2C_6H_4$	C_6H_5	64
c	4-FC_6H_4	C_6H_5	68
d	4-FC_6H_4	4-$CH_3C_6H_4$	70
e	4-$NO_2C_6H_4$	4-$CH_3C_6H_4$	65
f	C_6H_5	4-$CH_3C_6H_4$	62
g	4-$NO_2C_6H_4$	C6H4CH_2	66
h	4-$CH_3C_6H_4$	$C_6H_4CH_2$	60
i	4-FC_6H_4	$C_6H_4CH_2$	64
j	2-Naphtyl	C_6H_5	64
k	4-$NO_2C_6H_4$	C_4H_9	71
l	C_6H_5	C_4H_9	69
m	4-$CH_3C_6H_4$	4-$CH_3C_6H_4$	62

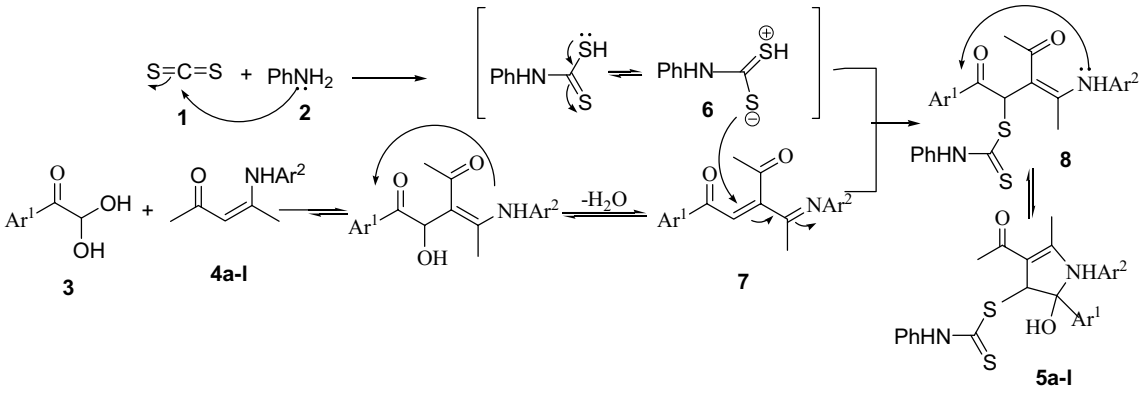
Conditions: MeCN, rt, 6 h

[a]Isolated yield

We also examined the reaction in the presence of 2 ml ethanol instead of acetonitrile, but the expected 5-hydroxy-4-phenylcarbamodithioate 2-*H* pyrroline derivatives were not obtained in good yields. When aliphatic amines such as benzyl amine were used instead of aniline as amine component, it was observed that the reaction was done in this style after 3 h; however, due to the formation of by-products, the corresponding 5-hydroxy-4-phenylcarbamodithioate 2-*H* pyrrolines were obtained in low yields, and the removal of impurities was very difficult. We tried to investigate the reaction in the presence of substituted anilines such as 2,4-xylidine instead of aniline in the reaction conditions, but product is not obtained in good yield. So, the reaction was investigated with aniline instead of aliphatic amines or substituted anilines. Then, we examined the influence of different temperatures on a typical reaction for synthesis of **5a**. To our satisfaction, when the reaction was carried out at room temperature in 6 h, the product was 67% yield but at reflux conditions in the same time the product was 30% yield. To investigate the generality of the reaction, different arylglyoxals with electron donor and electron withdrawing groups were treated with aromatic and aliphatic enaminocarbonyls and the related 5-hydroxy-4-phenylcarbamodithioate 2-*H* pyrroline derivatives were



Scheme 2 A typical reaction between carbon disulfide, aniline, **3a** and **4a**



Scheme 3 Suggested mechanism for formation of 5-hydroxy-4-phenylcarbamodithioate 2-*H* pyrroline derivatives **5a–l**

obtained in acetonitrile at room temperature after 6 h stirring and the products were simply isolated by filtration and washing with acetonitrile. All the reactions were observed to produce good yields (60–71%) compared to other existing procedures. The outcome was listed in Table 1. This process has many advantages such as high efficiency, selectivity, easy separation, purification, and mild reaction conditions. They are not only environmentally benign, but also economically beneficial because toxic wastes can be minimized or eliminated. All these facts have prompted us to achieve the multicomponent synthesis of 5-hydroxy-4-phenylcarbamodithioate 2-*H* pyrrolines **5a**–**m** at room temperature by the mentioned method. All the products shown in Table 1 are stable solids, and the structure of compounds **5a**–**m** was deduced from their spectral and analytical data. For example, the ^{1}H NMR spectrum of 5a exhibited two singlets at 1.98 and 2.27 ppm for two methyl groups. The CH of pyrroline ring was observed as a singlet at 4.60 ppm. Two singlets at 5.76, and 6.34 ppm are for NH and OH protons, respectively. The aromatic protons resonated between 6.75 and 7.40 ppm. ^{13}C NMR spectrum of **5a** showed ten distinct signals for aromatic carbons in consistent with the proposed structure, thiocarbonyl and carbonyl resonating at 159.9 and 194.5 ppm, respectively. The structure of compound 5a was also confirmed by its IR spectrum, which exhibited two absorption bands at 1594 and 3374 cm^{-1} are for C = O and NH groups, respectively.

A suggested mechanism for formation of 5-hydroxy-4-phenyl carbamodithioate derivatives **5a–l** by reaction between carbon disulfide **1**, aniline **2**, arylglyoxals **3** and *β*-enaminocarbonyls **4** is shown in Scheme 3. The reaction sequence consists of an initial nucleophilic addition of aniline to carbon disulfide, followed by the nucleophilic attack of carbamodithioic acid **6**, so obtained to the condensation product **7** of arylglyoxals with enaminoketones, also promoted the formation of intermediate **8** and finally ring closure by intramolecular attack of nitrogen to carbonyl group of arylglyoxal to afford the related pyrroline ring **5**.

Conclusions

In summary, we report herein the reaction between carbon disulfide, aniline, arylglyoxals and *β*-enaminocarbonyls in the absence of any catalysts to afford 5-hydroxy-4-phenylcarbamodithioate 2-*H* pyrroline derivatives in good yields. The advantages of this method are readily available starting materials, neutral reaction conditions, catalyst-free, simple isolation and purification of products.

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