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Reaction of thiocarboxanilide derivatives of 2-phenylimino-3-phenyl-4-thiazolidinone and 1,3-diphenyl-2-thioxo-4-imidazolone with hydrazonoyl halides and active chloromethylene compounds

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ABSTRACT

The potassium salts of thiocarboxanilide of 2-phenylimino-3-phenyl-4-thiazolidinone and 1,3-diphenyl-2-thioxo-4-imidazolone react with hydrazonoyl halides in N,N-dimethylformamide to afford the corresponding 1,3,4-thiadiazoline derivatives. 2-Phenylimino-3-phenyl-4-thiazolidinone reacts with active chloromethylene compounds in N,N-dimethylformamide to give the corresponding thiazolylidenethiazolidin-4-one derivatives. The new compounds were characterized using IR, ^{1}H NMR, ^{13}C NMR and mass spectra.

Keywords: Hydrazonoyl Halides; 1,3,4-Thiadiazoline; Thiazolidinone

1. INTRODUCTION

1,3,4-Thiadiazole and its derivatives possess an interesting biological activity probably conferred to them by the strong aromaticity of this ring system [1]. It is known that many of its derivatives have antibacterial [2], antimicrobial [3], antimycobacterial [4,5], antifungal [6,7], antidepressant [8], anti-inflammatory [9], analgesic[10] activities and cardiotonic [11] action being notable. Besides, the thiazoline ring is associated with a variety of pharmacological actions, including antimicrobial [12], anti-inflammatory [13], anti-tumor [14], and antioxidant [15] actions. Moreover, imidazolinone derivatives constitute an important class of therapeutic activities such as anticonvulsant [16], potent central nervous system (CNS) depressant [17], and acting on α-adrenergic and/or imidazoline receptors [18]. Recently, some new imidazolinone derivatives have been reported as antimicrobial [19,20], histamine H_3-receptor antagonist [21] and L-DOPA prodrugs in the treatment of Parkinson's disease [22]. Some workers have recognized 5-imidazolone as having anticancer activity [20]. Prompted by these findings and due to our interest in the synthesis of new heterocyclic compounds with potential biological activities [23-26] and in continuation of our work on the synthesis of hetaryl-ylidene derivatives [27-29], we report herein the synthesis of some new 1,3,4-thiadiazoline-(thiazoline)-2-hetarylylidene derivatives that might be of pharmacological importance.

2. EXPERIMENTAL

The melting points were determined on an electrothermal melting point apparatus and are uncorrected. IR spectra were recorded in KBr discs on a Pye Unicam SP 3300 and a Shimadzu FT-IR 8101 PC infrared spectrophotometers. The NMR spectra were recorded on a Varian Mercury VX-300 MHz NMR spectrometer in DMSO-d_6 solutions using TMS as an internal reference. ^{1}H NMR spectra were run at 300 MHz and ^{13}C NMR spectra were run at 75.46 MHz in dimethylsulfoxide (DMSO-d_6). Electron impact mass spectra were recorded on a Shimadzu GCMS-QP 1000 EX spectrometer at 70 eV. Elemental analyses were carried out at the Micro Analytical Center at Cairo University, Giza, Egypt. 2-Phenylimino-3-phenyl-4-thiazolidinone 2 [30], 1,3-diphenyl-2-thioxo- 4-imidazolone 13 [31] and hydrazonoyl halides 1a [32], 1b [33], 1c [34], 1d [35], 1e [36], 1f [37], 1g [38], 1h [39], 1i [40], 1j [41] and 1k [42] were prepared according to the reported literature methods.

Synthesis of 3,5-disubstituted 2-[2'-phenylimino-3'-phenyl-4'-oxothiazolidin-5'-ylidene]-2,3-dihydro-1,3,4-thiadiazole derivatives 7a-k, 3,5-disubstituted 2-[1',3'-diphenyl-2'-thioxo-4'-oxoimidazolidin-5'-ylidne]-2,3-dihydro-1,3,4-thiadiazole derivatives 15a-h and 2-

phenylimino-3-phenyl-5-[3'-phenyl-4',5'-disubstituted-thiazol-2'(3'H)ylidene]thiazolidin-4-one derivatives 19a-e: General method [29].

To a stirred suspension of potassium hydroxide (0.23 g, 5 mmol) in dimethylformamide (20 ml) 2-phenylimino-3-phenyl-4-thiazolidinone 2 or 13 (5 mmol) was added. The appropriate arylisothiocyanate (5 mmol) was added to the resulting solution and the reaction mixture was stirred for 30 min at room temperature. A solution of the hydrazonoyl halide 1a-k or active α-chloromethylene compound 16a-e in dimethylformamide was then added to the reaction mixture and stirred for 24 h at room temperature, then treated with methanol (10 ml). The solid formed was collected, washed with water and crystallized from a suitable solvent to give the respective 7a-k, 15a-h and 19a-e.

3,5-Diphenyl-2-[2'-phenylimino-3'-phenyl-4'-oxothiazolidin-5'-ylidene]-2,3-dihydro-1,3,4-thiadiazole 7a, mp 270-1˚C; 67% yield (dimethylformamide); IR (KBr) ν_{max}/cm^{-1} 1625.2 (CO); ^1H NMR (DMSO-d_6) δ 7.12-8.14 (m, Ar-H) ppm. ^{13}C NMR (DMSO-d_6) δ 120.37, 120.75, 123.92, 124.15, 125.12, 125.30, 126.31, 128.11, 128.23, 129.32, 130.46, 131.44 (Ar-CH), 135.21, 137.77, 139.34, 139.64, 142.92, 155.26, 157.22, 159.97, 165.72 (Ar-C, C = C, C = N, C = O) ppm. MS m/z 504, 440, 282, 215, 179, 146, 91; Anal. Calcd. for $C_{29}H_{20}N_4OS_2$ (504.62) C, 69.02; H, 3.99; N, 11.10; S, 12.71. Found: C, 69.10; H, 4.00; N, 11.00; S, 12.69%.

3-Phenyl-2-[2'-phenylimino-3'-phenyl-4'-oxothiazolidin-5'-ylidene]-5-styryl-2,3-dihydro-1,3,4-thiadiazole 7b, mp 308-9˚C; 63% yield (dimethylformamide); IR (KBr) ν_{max}/cm^{-1} 1625.4 (CO); ^1H NMR (DMSO-d_6) δ 6.62 (d, J = 15 Hz, 1H), 7.54 (d, J = 15 Hz, 1H), 6.92-7.93 (m, 20H, Ar-H) ppm. ^{13}C NMR (DMSO-d_6) δ 120.42, 120.65, 123.91, 124.21, 125.18, 126.42, 126.82, 128.09, 128.11, 128.22, 128.26, 128.80, 129.41, 135.21 (Ar-CH, CH = CH), 137.81, 138.94, 139.66, 142.09, 142.87, 154.72, 155.24, 159.83, 165.70 (Ar-C, C = C, C = N, C = O) ppm. MS m/z 530, 466, 308, 241, 179, 146, 91; Anal. Calcd. for $C_{31}H_{22}N_4OS_2$ (530.66) C, 70.16; H, 4.18; N, 10.56; S, 12.08. Found: C, 70.20; H, 4.20; N, 10.52; S, 12.10%.

3-(4-Nitrophenyl)-2-[2'-phenylimino-3'-phenyl-4'-oxothiazolidin-5'-ylidene]-5-(2-thienyl)-2,3-dihydro-1,3,4-thiadiazole 7c, mp 282-3˚C; 60% yield (ethanol); IR (KBr) ν_{max}/cm^{-1} 1629.1 (CO); ^1H NMR (DMSO-d_6) δ 6.84-8.17 (m, Ar-H) ppm. ^{13}C NMR (DMSO-d_6) δ 119.02, 120.36, 123.71, 123.88, 125.26, 125.92, 128.19, 128.26, 129.31, 134.71, 135.31, 136.72 (Ar-CH), 137.58, 139.58, 142.87, 143.21, 144.52, 155.23, 157.26, 159.74, 165.68 (Ar-C, C = C, C = N, C = O) ppm. MS m/z 555, 491, 332, 265, 224, 191, 136, 83, 51; Anal. Calcd. for $C_{27}H_{17}N_5O_3S_3$ (555.65) C, 58.36; H, 3.08; N, 12.60; S, 17.31. Found: C, 58.40; H, 3.10; N, 12.55; S, 17.23%.

5-(2-Furyl)-3-(4-nitrophenyl)-2-[2'-phenylimino-3'-phenyl-4'-oxothiazolidin-5'-ylidene]-2,3-dihydro-1,3,4-thiadiazole 7d, mp 325-6˚C; 69% yield (dimethylformamide); IR (KBr) ν_{max}/cm^{-1} 1633.4 (CO); ^1H NMR (DMSO-d_6) δ 6.59-8.31 (m, Ar-H) ppm. ^{13}C NMR (DMSO-d_6) δ 112.62, 118.73, 120.41, 122.71, 123.67, 123.84, 125.26, 125.98, 128.32, 129.31, 135.33, 137.63 (Ar-CH), 139.59, 143.28, 144.52, 148.23, 152.82, 155.32, 157.83, 159.78, 165.69 (Ar-C, C=C, C=N, C=O) ppm. MS m/z 539, 475, 316, 249, 224, 191, 136, 67, 51; Anal. Calcd. for $C_{27}H_{17}N_5O_4S_2$ (539.58) C, 60.10; H, 3.18; N, 12.98; S, 11.89. Found: C, 60.00; H, 3.20; N, 13.00; S, 11.82%.

3-(4-Nitrophenyl)-2-[2'-phenylimino-3'-phenyl-4'-oxothiazolidin-5'-ylidene]-5-phenyl-2,3-dihydro-1,3,4-thiadiazole 7e, mp 198-9˚C; 67% yield (ethanol); IR (KBr) ν_{max}/cm^{-1} 1630.3 (CO); ^1H NMR (DMSO-d_6) δ 7.13-8.26 (m, Ar-H) ppm. ^{13}C NMR (DMSO-d_6) δ 118.72, 120.34, 123.63, 123.86, 125.27, 125.30, 125.84, 128.19, 129.33, 130.44, 131.24, 135.40, 137.64, 137.75, 139.61 (Ar-CH), 142.79, 144.54, 155.38, 157.31, 159.76, 165.66 (Ar-C, C = C, C = N, C = O) ppm. MS m/z 549, 485, 327, 260, 223, 191, 135, 77, 51; Anal. Calcd. for $C_{29}H_{19}N_5O_3S_2$ (549.62) C, 63.37; H, 3.48; N, 12.74; S, 11.67. Found: C, 63.31; H, 3.44; N, 12.70; S, 11.61%.

5-Acetyl-3-phenyl-2-[2'-phenylimino-3'-phenyl-4'-oxothiazolidin-5'-ylidene]-2,3-dihydro-1,3,4-thiadiazole 7f, mp 250-2˚C; 68% yield (ethanol); IR (KBr) ν_{max}/cm^{-1} 1661.2 (CO acetyl), 1629.5 (CO thiazolinone); ^1H NMR (DMSO-d_6) δ 2.35 (s, 3H, CH_3), 6.72-7.81 (m, 15H, Ar-H) ppm. ^{13}C NMR (DMSO-d_6) δ 24.76 (CH_3), 120.41, 120.78, 123.91, 124.53, 125.26, 126.40, 128.16, 128.25, 129.23 (Ar-CH), 135.34, 139.52, 139.65, 144.21, 155.31, 156.21, 159.02, 165.74, 188.54 (Ar-C, C = C, C = N, C = O) ppm. MS m/z 470, 406, 248, 181, 178, 147, 91, 77, 51; Anal. Calcd. for $C_{25}H_{18}N_4O_2S_2$ (470.08) C, 63.81; H, 3.86; N, 11.91; S, 13.63. Found: C, 63.74; H, 3.81; N, 11.87; S, 13.60%.

Ethyl 3-phenyl-2-[2'-phenylimino-3'-phenyl-4'-oxothiazolidin-5'-ylidene]-2,3-dihydro-1,3,4-thiadiazole-5-carboxylate 7g, mp 144-5˚C; 68% yield (ethanol); IR (KBr) ν_{max}/cm^{-1} 1745.1 (CO ester), 1629.2 (CO thiazolinone); ^1H NMR (DMSO-d_6) δ 1.41 (t, J = 7.2 Hz, 3H, CH_3), 4.43 (q, J = 7.2 Hz, CH_2), 6.72-7.41 (m, 15H, Ar-H) ppm. ^{13}C NMR (DMSO-d_6) δ 15.32 (CH_3), 64.17 (CH_2), 119.97, 120.39, 123.82, 123.96, 125.31, 125.39, 128.21, 128.31, 129.14 (Ar-CH), 136.10, 139.36, 139.54, 144.62, 154.23, 154.67, 159.13, 165.81, 166.62 (Ar-C, C = C, C = N, C = O) ppm. MS m/z 500, 279, 250, 179, 135, 103, 77, 51; Anal. Calcd. for $C_{26}H_{20}N_4O_3S_2$ (500.59) C, 62.38; H, 4.03; N, 11.19; S, 12.81. Found: C, 62.34; H, 3.97; N, 11.10; S, 12.80%.

3-Phenyl-5-phenylaminocarbonyl-2-[2'-phenylimino-3'-phenyl-4'-oxothiazolidin-5'-ylidene]-2,3-dihydro-1,3,4-thiadiazole 7h, mp 307-8˚C; 70% yield (ethanol); IR (KBr) ν_{max}/cm^{-1} 1661.9 (broad CO); ^{1}H NMR (DMSO-d_6) δ 7.34-8.41 (m, NH, Ar-H) ppm. ^{13}C NMR (DMSO-d_6) δ 120.36, 121.12, 122.38, 122.79, 124.12, 124.54, 124.97, 125.61, 128.18, 128.31, 128.75, 128.91 (Ar-CH), 135.41, 139.42, 139.67, 140.66, 146.68, 153.14, 157.87, 159.18, 165.32, 165.45 (Ar-C, C = C, C = N, C = O) ppm. MS m/z 547, 325, 258, 178, 147, 103, 91, 77; Anal. Calcd. for $C_{30}H_{21}N_5O_2S_2$ (547.65) C, 65.78; H, 3.87; N, 12.79; S, 11.71. Found: C, 65.81; H, 3.94; N, 12.83; S, 11.66%.

5-Benzoyl-3-phenyl-2-[2'-phenylimino-3'-phenyl-4'-oxothiazolidin-5'-ylidene]-2,3-dihydro-1,3,4-thiadiazole 7i, mp 256-7˚C; 65% yield (ethanol); IR (KBr) ν_{max}/cm^{-1} 1674.3 (CO benzoyl), 1629.9 (CO thiazolinone); ^{1}H NMR (DMSO-d_6) δ 7.16-8.34 (m, Ar-H) ppm. ^{13}C NMR (DMSO-d_6) δ 120.32, 120.39, 123.98, 124.54, 125.21, 126.39, 128.24, 128.27, 129.12, 129.19, 129.81, 133.47 (Ar-CH), 135.41, 136.46, 139.43, 139.49, 143.92, 155.61, 156.21, 158.93, 165.80, 182.96 (Ar-C, C=C, C = N, C = O) ppm. MS m/z 532, 310, 243, 178, 163, 147, 103, 91, 77; Anal. Calcd. for $C_{30}H_{20}N_4O_2S_2$ (532.63) C, 67.65; H, 3.78; N, 10.52; S, 12.04. Found: C, 67.70; H, 3.81; N, 10.48; S, 12.00%.

3-Phenyl-2-[2'-phenylimino-3'-phenyl-4'-oxothiazolidin-5'-ylidene]-5-(2-thienoyl)-2,3-dihydro-1,3,4-thiadiazole 7j, mp 122-3˚C; 66% yield (ethanol); IR (KBr) ν_{max}/cm^{-1} 1674.4 (CO thienoyl), 1625.6 (CO thiazolinone); ^{1}H NMR (DMSO-d_6) δ 6.92-8.34 (m, Ar-H) ppm. ^{13}C NMR (DMSO-d_6) δ 119.84, 120.40, 124.31, 124.45, 125.30, 125.87, 128.19, 128.21, 128.32, 129.21, 135.11, 135.42 (Ar-CH), 137.19, 139.39, 139.48, 143.89, 144.12, 154.31, 155.91, 158.94, 165.28, 175.95 (Ar-C, C = C, C = N, C = O) ppm. MS m/z 538, 316, 249, 179, 91, 77; Anal. Calcd. for $C_{28}H_{18}N_4O_2S_3$ (538.66) C, 62.43; H, 3.37; N, 10.40; S, 17.86. Found: C, 62.40; H, 3.35; N, 10.36; S, 17.90%.

5-(2-Naphthoyl)-3-phenyl-2-[2'-phenylimino-3'-phenyl-4'-oxothiazolidin-5'-ylidene]-2,3-dihydro-1,3,4-thiadiazole 7k, mp 118-9˚C; 68% yield (ethanol); IR (KBr) ν_{max}/cm^{-1} 1638.7 (CO naphthoyl), 1629.9 (CO thiazolinone); ^{1}H NMR (DMSO-d_6) δ 7.15-8.39 (m, 21H, Ar-H), 8.85 (s, 1H, naphthoyl α-H) ppm. ^{13}C NMR (DMSO-d_6) δ 119.68, 120.32, 123.68, 124.16, 125.23, 125.49, 126.40, 126.58, 127.76, 127.84, 128.10, 128.18, 129.23, 129.29, 129.87, 132.28 (Ar-CH), 132.51, 132.86, 135.50, 135.61, 139.44, 142.26, 144.18, 155.29, 155.63, 159.13, 165.82, 183.60 (Ar-C, C = C, C = N, C = O) ppm. MS m/z 582, 360, 293, 213, 181, 155, 103, 91, 77; Anal. Calcd. for $C_{34}H_{22}N_4O_2S_2$ (582.69) C, 70.08; H, 3.81; N, 9.62; S, 11.01. Found: C, 70.10; H, 3.80; N, 9.57; S, 11.00%.

3,5-diphenyl-2-[1',3'-diphenyl-2'-thioxo-4'-oxoimidazolidin-5'-ylidne]-2,3-dihydro-1,3,4-thiadiazole 15a, mp 136-8˚C; 63% yield (ethanol); IR (KBr) ν_{max}/cm^{-1} 1670.1 (CO); ^{1}H NMR (DMSO-d_6) δ 7.12-8.19 (m, Ar-H) ppm. ^{13}C NMR (DMSO-d_6) δ 120.31, 120.40, 120.73, 123.84, 123.98, 124.10, 125.31, 127.93, 128.10, 128.21, 130.36, 131.43 (Ar-CH), 137.71, 138.92, 139.41, 139.52, 142.93, 156.17, 157.22, 165.74, 178.62 (Ar-C, C = C, C = N, C = O, C = S) ppm. MS m/z 504, 341, 274, 238, 206, 135, 103, 91, 77; Anal. Calcd. for $C_{29}H_{20}N_4OS_2$ (504.62) C, 69.02; H, 3.99; N, 11.10; S, 12.71. Found: C, 69.00; H, 4.00; N, 11.00; S, 12.65%.

3-Phenyl-2-[1',3'-diphenyl-2'-thioxo-4'-oxoimidazolidin-5'-ylidne]-5-styryl-2,3-dihydro-1,3,4-thiadiazole 15b, mp 151-2˚C; 65% yield (ethanol); IR (KBr) ν_{max}/cm^{-1} 1675.3 (CO); ^{1}H NMR (DMSO-d_6) δ 6.81 (d, J = 15 Hz, 1H), 7.63 (d, J = 15 Hz, 1H), 7.26-7.83 (m, 20H, Ar-H) ppm. ^{13}C NMR (DMSO-d_6) δ 119.64, 119.85, 120.61, 123.78, 123.94, 124.12, 126.78, 127.92, 128.10, 128.15, 128.19, 128.23, 128.71, 137.76 (Ar-CH, CH = CH), 138.96, 139.12, 140.12, 142.01, 143.26, 154.34, 155.31, 165.74, 178.51 (Ar-C, C = C, C = N, C = O, C = S) ppm. MS m/z 530, 367, 276, 206, 135, 103, 91, 77; Anal. Calcd. for $C_{31}H_{22}N_4OS_2$ (530.66) C, 70.16; H4.18, ; N, 10.56; S, 12.08. Found: C, 70.10; H, 4.15; N, 10.50; S, 12.00%.

3-(4-Nitrophenyl)-2-[1',3'-diphenyl-2'-thioxo-4'-oxoimidazolidin-5'-ylidne]-5-(2-thienyl)-2,3-dihydro-1,3,4-thiadiazole 15c, mp 144-5˚C; 70% yield (ethanol); IR (KBr) ν_{max}/cm^{-1} 1670.9 (CO); ^{1}H NMR (DMSO-d_6) δ 6.85-8.16 (m, Ar-H) ppm. ^{13}C NMR (DMSO-d_6) δ 119.67, 120.03, 120.16, 123.76, 123.92, 124.18, 127.73, 128.13, 128.21, 134.80, 136.64, 137.61 (Ar-CH), 139.54, 139.62, 143.14, 143.34, 144.32, 155.31, 157.32, 165.73, 178.43 (Ar-C, C = C, C = N, C = O, C = S) ppm. MS m/z 555, 420, 392, 251, 136, 90, 77, 51; Anal. Calcd. for $C_{27}H_{17}N_5O_3S_3$ (555.65) C, 58.36; H, 3.08; N, 12.60; S, 17.31. Found: C, 58.43; H, 3.05; N, 12.54; S, 17.27%.

5-Acetyl-3-phenyl-2-[1',3'-diphenyl-2'-thioxo-4'-oxoimidazolidin-5'-ylidne]-2,3-dihydro-1,3,4-thiadiazole 15d, mp 184-5˚C; 70% yield (ethanol); IR (KBr) ν_{max}/cm^{-1} 1734.2 (CO acetyl), 1680.8 (CO imidazoline); ^{1}H NMR (DMSO-d_6) δ 2.42 (s, 3H, CH_3), 6.63-8.12 (m, 15H, Ar-H) ppm. ^{13}C NMR (DMSO-d_6) δ 24.84 (CH_3), 119.23, 120.26, 120.52, 124.18, 124.32, 124.51, 128.19 , 128.26, 128.34 (Ar-CH), 139.36, 139.48, 139.67, 144.32, 155.29, 156.51, 165.69, 179.63, 184.26 (Ar-C, C = C, C = N, C = O, C = S) ppm. MS m/z 470, 406, 307, 240, 135, 103, 91, 77, 43; Anal. Calcd. for $C_{25}H_{18}N_4O_2S_2$ (470.56) C, 63.81; H, 3.86; N, 11.91; S, 13.63. Found: C, 63.80; H, 3.82; N, 11.90; S, 13.60%

Ethyl 3-Phenyl-2-[1',3'-diphenyl-2'-thioxo-4'-oxo-

imidazolidin-5'-ylidne]-2,3-dihydro-1,3,4-thiadiazole-5-carboxylate 15e, mp 221-3˚C; 70% yield (ethanol); IR (KBr) ν_{max}/cm^{-1} 1750.8 (CO ester), 1690.1 (CO imidazoline); ^1H NMR (DMSO-d_6) δ 1.41 (t, J = 7.2 Hz, CH_3), 4.48 (q, J = 7.2 Hz, CH_2), 6.83-7.54 (m, 15H, Ar-H) ppm. ^{13}C NMR (DMSO-d_6) δ 14.93 (CH_3), 64.31 (CH_2), 119.68, 120.13, 120.42, 123.96, 124.16, 124.31, 128.22, 128.29, 128.34 (Ar-CH), 139.48, 139.54, 139.62, 144.61, 154.71, 155.21, 165.74, 166.52, 178.94 (Ar-C, C = C, C = N, C = O, C = S) ppm. MS m/z 500, 337, 135, 103, 77, 51; Anal. Calcd. for $C_{26}H_{20}N_4O_3S_2$ (500.59) C, 62.38; H, 4.03; N, 11.19; S, 12.81. Found: C, 62.34; H, 3.96; N, 11.20; S, 12.77%.

3-Phenyl-2-[1',3'-diphenyl-2'-thioxo-4'-oxoimidazolidin-5'-ylidne]-5-phenylaminocarbonyl-2,3-dihydro-1,3,4-thiadiazole 15f, mp 211-3˚C; 70% yield (ethanol); IR (KBr) ν_{max}/cm^{-1} 3387.3 (NH), 1696.1 (CO imidazoline), 1671.4 (CO amide); ^1H NMR (DMSO-d_6) δ 7.10-8.42 (m, Ar-H, NH) ppm. ^{13}C NMR (DMSO-d_6) δ 119.84, 120.61, 121.31, 122.41, 122.80, 123.84, 124.16, 124.49, 128.26, 128.34, 128.43, 128.68 (Ar-CH), 139.35, 139.62, 139.71, 140.37, 143.96, 155.43, 156.33, 165.46, 165.67, 179.36 (Ar-C, C = C, C = N, C = O, C = S) ppm. MS m/z 547, 384, 178, 146, 120, 104, 91, 77; Anal. Calcd. for $C_{30}H_{21}N_5O_2S_2$ (547.65) C, 65.79; H, 3.87; N, 12.79; S, 11.71. Found: C, 65.74; H, 3.90; N, 12.81; S, 11.68%.

5-Benzoyl-3-phenyl-2-[1',3'-diphenyl-2'-thioxo-4'-oxoimidazolidin-5'-ylidne]-2,3-dihydro-1,3,4-thiadiazole 15g, mp 121-2˚C; 68% yield (ethanol); IR (KBr) ν_{max}/cm^{-1} 1650.9 (broad CO); ^1H NMR (DMSO-d_6) δ 7.19-8.46 (m, Ar-H) ppm. ^{13}C NMR (DMSO-d_6) δ 119.82, 120.41, 120.91, 123.85, 124.38, 124.44, 128.17, 128.28, 128.32, 129.12, 129.75, 133.46 (Ar-CH), 136.51, 138.84, 139.26, 139.63, 143.84, 155.73, 156.31, 165.76, 178.76, 183.55 (Ar-C, C = C, C = N, C = O, C = S) ppm. MS m/z 532, 369, 206, 135, 105, 91, 77; Anal. Calcd. for $C_{30}H_{20}N_4O_2S_2$ (532.63) C, 67.65; H, 3.78; N, 10.52; S, 12.04. Found: C, 67.70; H, 3.81; N, 10.49; S, 12.00%.

3-Phenyl-2-[1',3'-diphenyl-2'-thioxo-4'-oxoimidazolidin-5'-ylidene]-5-(2-thienoyl)-2,3-dihydro-1,3,4-thiadiazole 15h, mp 167-8˚C; 70% yield (ethanol); IR (KBr) ν_{max}/cm^{-1} 1650.8 (broad CO); ^1H NMR (DMSO-d_6) δ 7.14-8.43 (m, Ar-H) ppm. ^{13}C NMR (DMSO-d_6) δ 119.67, 120.23, 120.91, 123.78, 124.13, 124.32, 127.93, 128.14, 128.19, 128.26, 135.12, 136.78 (Ar-CH), 139.34, 139.64, 140.12, 143.21, 144.13, 155.24, 156.32, 165.72, 174.86, 178.74 (Ar-C, C = C, C = N, C = O, C = S) ppm. MS m/z 538, 375, 168, 137, 110, 91, 77; Anal. Calcd. for $C_{28}H_{18}N_4O_2S_3$ (538.66) C, 62.43; H, 3.37; N, 10.40; S, 17.86. Found: C, 62.40; H, 3.34; N, 10.37; S, 17.82%.

Ethyl 3-phenyl-4-methyl-2-[3'-phenyl-2'-phenylimino-4-oxothiazolidin-5'-ylidene]-2(3H) thiazolecarboxylate 19a, mp 294-5˚C; 61% yield (ethanol); IR (KBr) ν_{max}/cm^{-1} 1696.5 (CO ester), 1620.9 (CO thiazolinone); ^1H NMR (DMSO-d_6) δ 1.32 (t, J = 7.1 Hz, CH_3), 2.23 (s, 3H, CH_3), 4.36 (q, J = 7.1 Hz, CH_2), 6.73-7.54 (m, 15H, Ar-H) ppm. ^{13}C NMR (DMSO-d_6) δ 14.38 (CH_3), 14.85 (CH_3), 63.92 (CH_2), 119.82, 120.41, 123.43, 123.83, 125.24, 126.42, 127.93, 128.19, 129.25 (Ar-CH), 153.21, 136.40, 139.35, 140.13, 143.43, 155.42, 157.62, 159.46, 165.71, 166.55 (Ar-C, C = C, C = N, C = O) ppm. MS m/z 513, 291, 203, 194, 90, 77, 73, 51; Anal. Calcd. for $C_{28}H_{23}N_3O_3S_2$ (513.63) C, 65.48; H, 4.51; N, 8.18; S, 12.49. Found: C, 65.51; H, 4.50; N, 8.20; S, 12.52%.

2-Phenylimino-3-phenyl-5-[4'-methyl-3'-phenyl-5'-phenylaminocarbonylthiazol-2'(3'H)ylidene] thiazolidin-4-one 19b, mp 323-5˚C; 70% yield (dimethylformamide); IR (KBr) ν_{max}/cm^{-1} 3340.2 (NH), 1660.6 (broad CO); ^1H NMR (DMSO-d_6) δ 2.24 (s, 3H, CH_3), 6.74-7.53 (m, NH, 20H, Ar-H) ppm. ^{13}C NMR (DMSO-d_6) δ 15.23 (CH_3), 119.82, 120.42, 122.10, 122.63, 124.10, 124.23, 125.34, 125.92, 128.13, 128.25, 128.62, 129.26 (Ar-CH), 133.67, 136.21, 139.41, 140.02, 140.24, 143.13, 155.42, 156.78, 160.34, 165.81, 166.98 (Ar-C, C = C, C = N, C = O) ppm. MS m/z 560, 338, 250, 194, 160, 120, 91, 77; Anal. Calcd. for $C_{32}H_{24}N_4O_2S_2$ (560.68) C, 68.55; H, 4.31; N, 9.99; S, 11.44. Found: C, 68.61; H, 4.30; N, 10.00; S, 11.40%.

2-Phenylimino-3-phenyl-5-[3',4'-diphenylthiazol-2'(3'H)ylidene]thiazolidin-4-one 19c, mp 278-9˚C; 65% yield (ethanol); IR (KBr) ν_{max}/cm^{-1} 1615.7 (CO thiazolinone); ^1H NMR (DMSO-d_6) δ 6.16-7.61 (m, 21H, Ar-H) ppm. ^{13}C NMR (DMSO-d_6) δ 119.78, 120.21, 123.96, 124.14, 125.23, 125.84, 126.30, 128.11, 128.31, 129.15, 130.12, 130.93, 132.62 (Ar-CH, CH = C), 135.94, 136.84, 139.40, 140.02, 143.21, 143.63, 155.35, 159.68, 165.76 (Ar-C, C = C, C = N, C = O) ppm. MS m/z 503, 281, 194, 121, 77; Anal. Calcd. for $C_{30}H_{21}N_3OS_2$ (503.63) C, 71.54; H, 4.20; N, 8.34; S, 12.73. Found: C, 71.50; H, 4.16; N, 8.30; S, 12.70%.

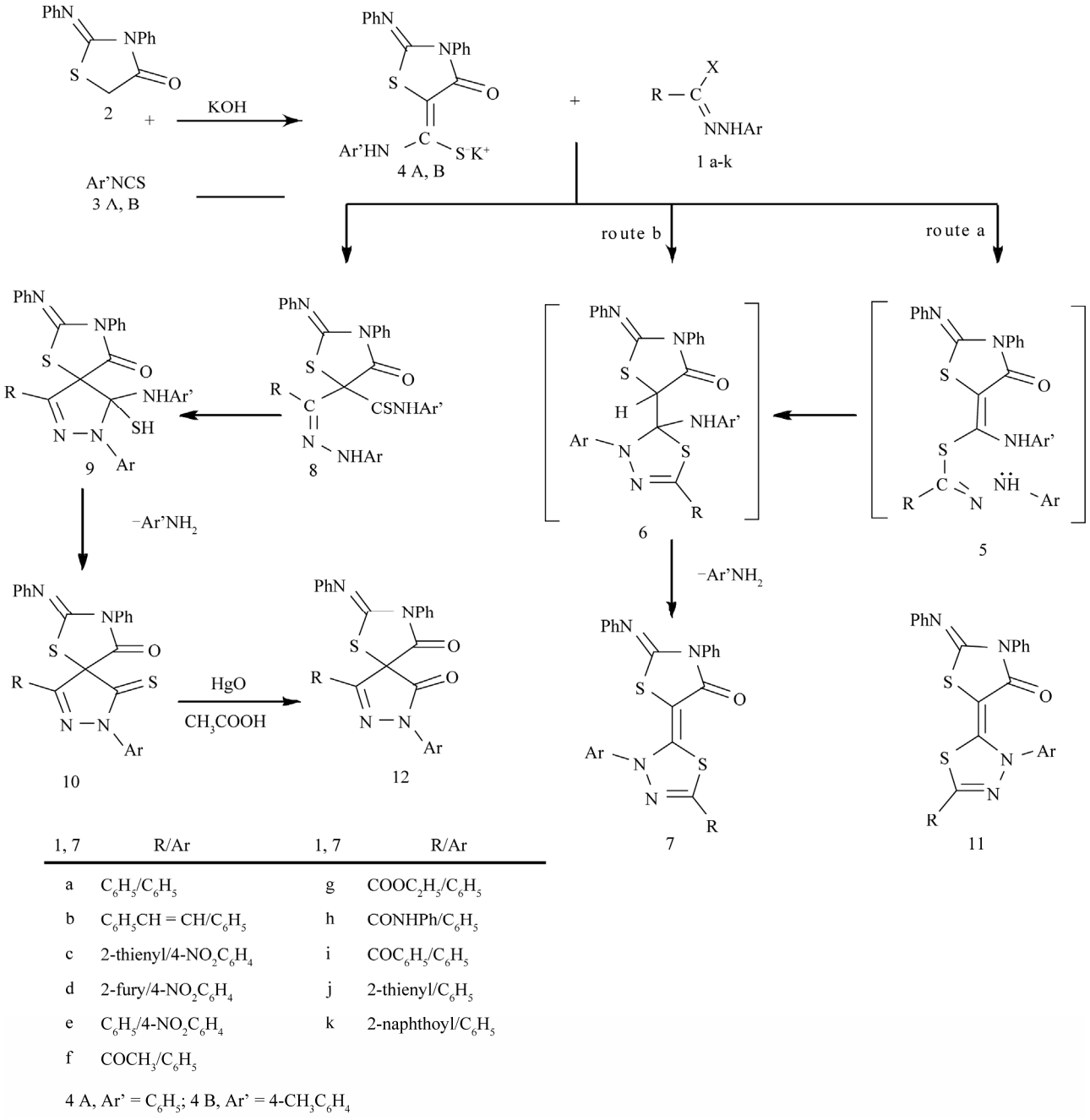
2-Phenylimino-3-phenyl-5-[5'-benzoyl-3',4'-diphenylthiazol-2'(3'H)ylidene]thiazolidin-4-one 19d, mp 345-7˚C; 67% yield (dimethylformamide); IR (KBr) ν_{max}/cm^{-1} 1710.1 (CO benzoyl), 1660.3 (CO thiazolinone); ^1H NMR (DMSO-d_6) δ 6.76-7.62 (m, 25H, Ar-H) ppm. ^{13}C NMR (DMSO-d_6) δ 119.58, 120.16, 123.89, 124.15, 125.36, 125.78, 126.30, 128.15, 128.41, 129.11, 129.23, 129.82, 130.26, 131.36, 133.39 (Ar-CH), 135.34, 135.74, 136.61, 136.84, 139.41, 139.91, 143.19, 155.24, 156.32, 159.69, 166.42, 184.18 (Ar-C, C = C, C = N, C = O) ppm. MS m/z 607, 388, 387, 386, 385, 355, 308, 280, 265, 247, 194, 135, 121, 105, 77, 51; Anal. Calcd. for $C_{37}H_{25}N_3O_2S_2$ (607.74) C, 73.12; H, 4.15; N, 6.91; S, 10.55. Found: C, 73.10; H, 4.10; N, 6.88; S, 10.51%.

2-Phenylimino-3-phenyl-5-[4'-methyl-3'-phenylthiazol-2'(3'H)ylidene]thiazolidin-4-one 19e, mp 220-2˚C;

69% yield (ethanol); IR (KBr) ν_{max}/cm^{-1} 1615.3 (CO thiazolinone); ^1H NMR (DMSO-d_6) δ 1.85 (s, 3H, CH_3), 6.15-7.42 (m, 16H, Ar-H) ppm. ^{13}C NMR (DMSO-d_6) δ 15.42 (CH_3), 119.62, 120.31, 123.93, 124.12, 125.41, 125.86, 128.12, 128.26, 129.08, 131.92 (Ar-CH, CH = C), 135.83, 139.34, 139.84, 143.21, 144.18, 155.34, 159.77, 165.77 (Ar-C, C = C, C = N, C = O) ppm. MS m/z 441, 219, 131, 121, 103, 91, 77; Anal. Calcd. for $C_{25}H_{19}N_3OS_2$ (441.56) C, 68.00; H, 4.34; N, 9.52; S, 14.52. Found: C, 67.92; H, 4.28; N, 9.48; S, 14.50%.

3. RESULTS AND DISCUSSION

The intermediates 4A (Ar' = ph) and 4B (Ar' = 4-$CH_3C_6H_4$) were prepared by the reaction of 2-phenylimino-3-phenyl-4-thiazolidinone 2 with arylisothiocyanate 3A,B in dimethylformamide in the presence of potassium hydroxide (**Scheme 1**). Treatment of 4A with hydrazonoyl halides 1a-e in dimethylformamide afforded, in each case, one isolable product as evidenced by TLC analysis of the crude products. Both mass and elemental



1, 7	R/Ar	1, 7	R/Ar
a	C_6H_5/C_6H_5	g	$COOC_2H_5/C_6H_5$
b	$C_6H_5CH = CH/C_6H_5$	h	$CONHPh/C_6H_5$
c	2-thienyl/4-$NO_2C_6H_4$	i	COC_6H_5/C_6H_5
d	2-fury/4-$NO_2C_6H_4$	j	2-thienyl/C_6H_5
e	C_6H_5/4-$NO_2C_6H_4$	k	2-naphthoyl/C_6H_5
f	$COCH_3/C_6H_5$		

4 A, Ar' = C_6H_5; 4 B, Ar' = 4-$CH_3C_6H_4$

Scheme 1.

analyses data of the products isolated are compatible with the two possible structures 7 and 10 (**Scheme 1**). However, the latter structure 10 was discarded as the reaction products were recovered unchanged after treatment with mercuric oxide in boiling acetic acid while the treatment is expected to convert 10 -if present- to 12, the C = S double bond is known to be more reactive dipolarophile than the C = C double bond [43], and reaction of acyclic β-ketothioanilides with 1 has been reported to give 2-alkylidene derivatives [44]. Accordingly, the product isolated from reaction 1a with 4A or 4B is assigned structure 7. This assignment was substantiated by the finding that reactions of 1a with either 4A or 4B yield one product which is the same in both cases indicating the elimination of an arylamine molecule during the reaction to give 7. To account for the formation of 7 it is suggested that the reaction starts with the formation of thiohydrazonate ester 5 followed by intramolecular cyclization to give 6 which in turn eliminated arylamine to give 7.

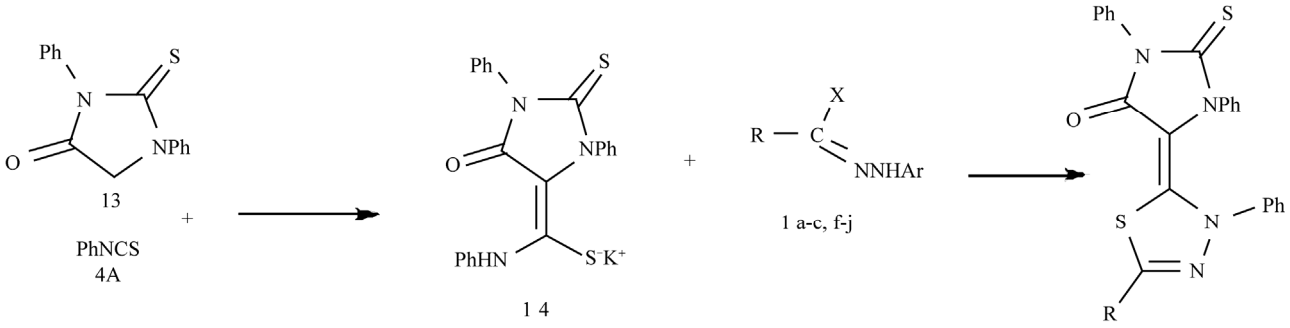
Stereochemically, the isolated products can have either the 7 or 11 configurations. Molecular models indicate that structure 11 suffers severe steric interactions due to the close proximity of N-aryl group and C = O group. On this basis we suggest that the configuration of the products isolated is the less hindered structure 7.

Similarly, treatment of 1,3-diphenyl-2-thioxo-4-imidazolinon-5-thiocarboxanilide 14A (prepared by the reaction of 1,3-diphenyl-2-thioxo-4-imidazolone 13 with phenylisothiocyanate 3A in dimethylformamide in the presence of potassium hydroxide) with hydrazonoyl halides 1a-c,f-j afforded a single product in each case and was assigned structure 15 (**Scheme 2**). The structure of the latter products was established on the basis of its elemental analysis and spectroscopic data (Experimental). The IR spectrum of the isolated product 15a, taken as example, revealed the appearance of ring carbonyl absorption band near 1670 cm^{-1} in addition, its mass spectrum revealed a peak corresponding to the molecular ion m/z 504.

In the course of the previous reaction it was found that the reaction proceeds via elimination of an arylamine to give the product. This finding promoted us to perform the reaction of 4A with active α-chloromethylene compounds 16a-e to investigate if such reaction will lead to thiazoline 19 and/or 1,3-oxathiol 20. Previous literature reports indicated that the reaction of active α-chloromethylene compounds of simple ketones and nitriles with potassium salts of acyclic thioanilide gave the thiazoline derivatives [45], while with cyclic thioanilide gave 1,3-oxathiol derivatives [28].

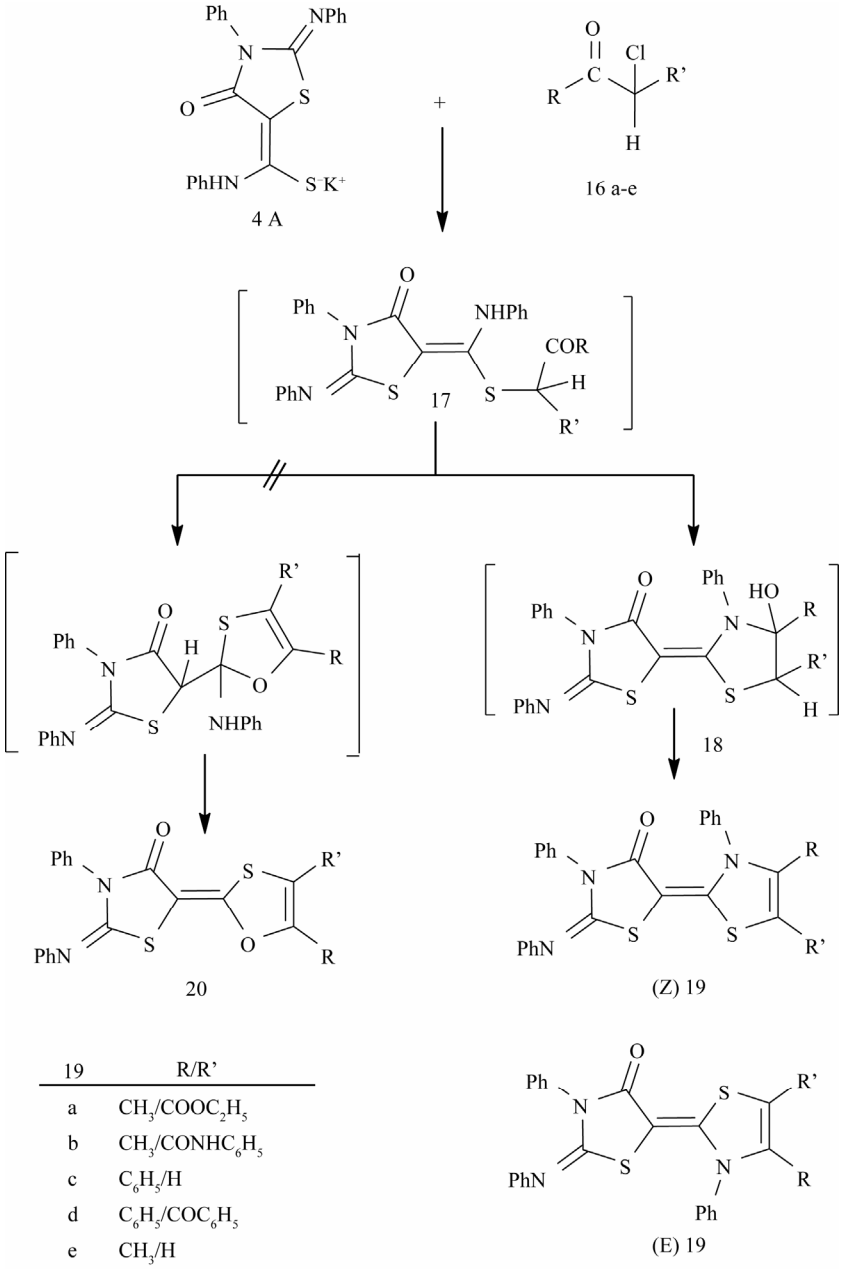
Treatment of 4A with ethyl 2-chloro-3-oxobutanoate 16a in dimethylformamide afforded a single product as evidenced by TLC and ^{1}H-NMR of the crude products (**Scheme 3**).

Both elemental and spectroscopic analyses data were found compatible with 2,3-dihydro-3-phenylthiazole derivatives structure 19 and not the 1,3-oxathiol-2-ylidene derivatives 20 we reported earlier [28]. Compound 4A reacted similarly with varieties of active α-chloromethylene compounds 16b-e and gave the corresponding 19b-e respectively. The reaction pathway that seems to account for the formation of 19 from 5 and 16 is outlined in **Scheme 3**. It is proposed that the reaction involves nucleophilic substitution to give 17. Cyclization of the latter product leads to the formation of 18 which loses the elements of water to give 19. These products can be assigned one of the two stereoisomeric structures (Z)-19



15	R/Ar	15	R/Ar
a	C_6H_5/C_6H_5	e	$COOC_2H_5/C_6H_5$
b	$C_6H_5CH=CH/C_6H_5$	f	$CONHPh/C_6H_5$
c	2-thienyl/4-$NO_2C_6H_4$	g	COC_6H_5/C_6H_5
d	$COCH_3/C_6H_5$	h	2-thienyl/C_6H_5

Scheme 2.



Scheme 3.

or (E)-19 (**Scheme 3**). The present data cannot distinguish between these two isomers, however. The elemental analyses and IR spectroscopic data of compounds 19 were consistent with the assigned structures. The structures of the 19 were also ascertained by the ^{1}H NMR, ^{13}C NMR and MS measurements (Experimental).

4. CONCLUSIONS

The reaction of hydrazonoyl halides 1a-k with thiocarboxanilide derivatives 4 and 14 gave the corresponding 1,3,4-thiadiazole derivatives 7 and 15 similar to the products previously obtained with different thiocarboxanilide derivatives [27]. The reaction of active α-chloromethylene ketones with thiocarboxanilide derivatives gave the thiazoline derivatives 19, contrary to the previous finding we have reported [28] which gave 1,3-oxathiol derivatives.

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