C_5-Alkyl-1,3,4-Oxadiazol-2-ones Undergo Dealkylation upon Nitrogen Insertion to Form 2*H*-1,2,4-Triazol-3-ones: Synthesis of 1,2,4-Triazol-3-one Hybrids with Triazolothiadiazoles and Triazolothiadiazines

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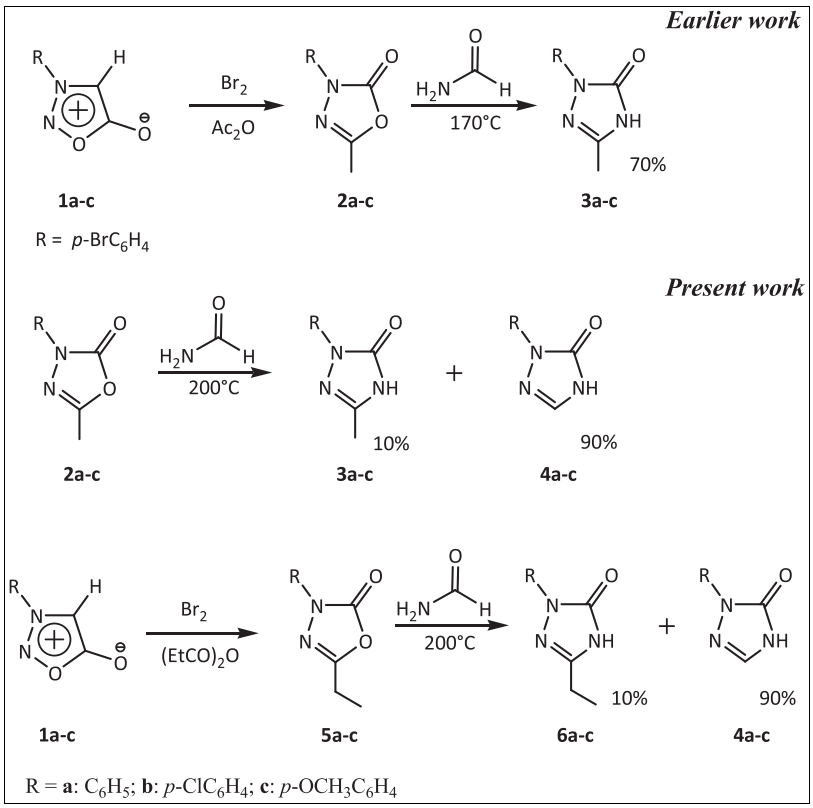


The present study emphasizes on the dealklylation of 3-aryl-5-alkyl-2-oxo-Δ^4-1,3,4-oxadiazoles when reacted with formamide resulting in the formation of 2-aryl-2*H*-1,2,4-triazol-3(4*H*)-ones as major product. Subsequent reactions of 2-aryl-2*H*-1,2,4-triazol-3(4*H*)-one gave triazolo[3,4-*b*][1,3,4]thiadiazoles and triazolo[3,4-*b*][1,3,4]thiadiazines derivatives incorporated with 1,2,4-triazol-3-one.

INTRODUCTION

Ring rearrangements and ring transformations of heterocyclic compounds represent an important tool in the synthesis of new molecules that are otherwise difficult to synthesize. The triazolone nucleus is found in wide variety of pharmaceutically active molecules including antibacterial, antifungal, anti-inflammatory agents, Protoporphyrinogen Oxidase (PPO) inhibitors and antitumor agents [1–6].

Our earlier reported reactions on ring transformation of 3-aryl-5-methyl-2-oxo-Δ^4-1,3,4-oxadiazoles when treated with primary amines namely, ethanolamine [7], hydrazinehydrate [8] and thiosemicarbazide [9] have only afforded 5-methyl-2-aryl-2*H*-1,2,4-triazol-3(4*H*)-one derivatives. On the contrary, in the present investigation, heating 3-aryl-5-alkyl-2-oxo-Δ^4-1,3,4-oxadiazoles with formamide gave 5-alkyl-2-aryl-2*H*-1,2,4-triazol-3(4*H*)-one (minor product) and serendipitously a new dealkylated product 2-aryl-2*H*-1,2,4-triazol-3(4*H*)-one (major product) which was unidentified earlier.

Ring transformations of 3-arylsydnone **1a–c** have gained much attention as they yield pharmaceutically active heterocycles *via* 1,3-dipolar cycloaddition reaction [10–13]. In our present study, 3-arylsydnone **1a–c** was

ring transformed to 3-aryl-5-alkyl-2-oxo-Δ^4-1,3,4-oxadiazole **2a–c** which upon heating with formamide gave predominantly 2-aryl-2*H*-1,2,4-triazol-3(4*H*)-one **4a–c**.

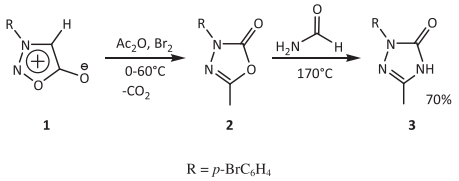
Compounds incorporating fused heterocyclic ring systems are of significant importance because the fusion results in the enhancement of biological properties. In this regard, triazolothiadiazoles and triazolothiadiazines have received considerable attention and are extensively used as scaffolds in various potent molecules [14]. In view of this, we have successfully prepared substituted 1,2,4-triazolo[3,4-*b*]-thiadiazoles **10a–c**, **11a–c** and **12a–c** and 1,2,4-triazolo[3,4-*b*][1,3,4]thiadiazines **13a–c** from newly formed 2-aryl-2*H*-1,2,4-triazol-3(4*H*)-ones **4a–c**.

RESULTS AND DISCUSSION

Initially 3-arylsydnone (**1a–c**) was ring transformed into 3-aryl-5-methyl-2-oxo-Δ^4-1,3,4-oxadiazole (**2a–c**) *via* [3 + 2] cycloaddition with acetic anhydride followed by loss of carbon dioxide. When the compound **2a–c** was heated with formamide at 170°C, we were also under the impression that 5-methyl-2-aryl-2*H*-1,2,4-triazol-3(4*H*)-one **3a–c** would be the sole product as reported by Badami *et al.* earlier [15] (Scheme 1). Interestingly, along with the formation of **3a–c**, thin layer chromatography (TLC) showed the presence of another spot (more polar and intense). We successfully isolated the compound by column chromatography and analyzed for its structure using spectroscopic techniques and single crystal X-ray diffraction study of one of the compound **4b**.

In ^{1}H-NMR spectrum, a singlet around 2.50 ppm for C5 methyl protons was absent; however, a singlet at 8.12 ppm for one proton had appeared. Similarly, in case of ^{13}C-NMR studies, signal around 136 ppm was observed and the signal around 12 ppm corresponding to C5 methyl carbon was absent. The mass spectral study also showed molecular ion peak 14 units lesser than the molecular mass corresponding to compound **3a–c**. The chemical shift values in NMR data affirmed the presence of an imine proton. Consequently, we speculated the structure of the compound would possess an imine proton with the absence of methyl group. Further, we developed the crystals of compound **4b** by slow evaporation of ethanol,

Scheme 1. ***Earlier work.*** Synthesis of 5-methyl-2-aryl-2*H*-1,2,4-triazol-3(4*H*)-one **3**.



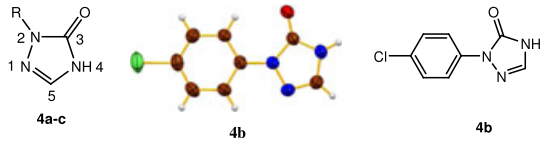


Figure 1. Molecular structure of compound **4b**. Displacement ellipsoids are drawn at the 50% probability level. [Color figure can be viewed at wileyonlinelibrary.com]

and finally, the structure was confirmed by single crystal X-ray crystallographic studies (Fig. 1) [16].

It was interesting to note that, C5-dealkylation of 1,3,4-oxadiazol-2-ones **2a–c** occurred only during ring insertion with formamide. However, ring insertion with other primary amines, *viz*., ethanolamine, hydrazinehydrate, and thiosemicarbazide afforded corresponding triazoles with C5-alkyl group.

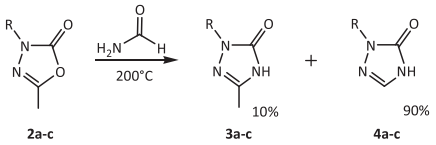
Initially, heating 3-aryl-5-methyl-2-oxo-Δ^4-1,3,4-oxadiazole **2a–c** with formamide at 170°C yielded compounds **3a–c** and **4a–c** in 40:60%, respectively. On the contrary, the reaction carried out at 200°C afforded **4a–c** in about 90% and **3a–c** in about 10% yield (Scheme 2).

Similar investigation was carried out for 3-aryl-5-ethyl-2-oxo-Δ^4-1,3,4-oxadiazole **5a–c** obtained by [3+2] cycloaddition of 3-arylsydnone **1a–c** with propionic anhydride followed by loss of carbon dioxide (Scheme 3). When **5a–c** was heated with formamide at 170°C, we observed formation of two products in the ratio 40:60. However, heating **5a–c** with formamide at 200°C also gave **4a–c** in about 90% and **6a–c** in about 10%. From these reactions (Schemes 2 and 3) we could confirm the C5-dealkylation of 3-aryl-5-alkyl-2-1,3,4-oxadiazoles **3a–c** and **5a–c** when heated with formamide at elevated temperature mainly afford 2-aryl-2*H*-1,2,4-triazol-3(4*H*)-one **4a–c**.

The plausible mechanism for the formation of compound **3a–c**, **6a–c,** and **4a–c** has been depicted in Scheme 4. The lone pair of electrons on nitrogen atom of formamide attacks the carbonyl carbon of lactone. Ring opening and intramolecular attack by nitrogen atom gave lactum intermediate in both the cases (**iii** and **vii**). However, an unstable *N*-formyl intermediate was observed in the formation of **3a–c** and **6a–c**, while a more favorable loss of carboxylic acid was observed during the formation of **4a–c**. Hence, **4a–c** was formed predominantly over **3a–c** and **6a–c**.

Further, we have successfully explored **4a–c** for the synthesis of various fused heterocyclic compounds which have been depicted in Schemes 5 and 6. 2-Aryl-2*H*-1,2,4-triazol-3(4*H*)-one **4a–c** undergone *N*-alkylation upon reaction with ethylbromoacetate in presence of sodium ethoxide under reflux condition. The ester **7a–c** obtained was heated with hydrazinehydrate (99%) to get corresponding acid hydrazide **8a–c** which was reacted with carbon disulfide in presence of potassium hydroxide

Scheme 2. ***Present work.*** Synthesis of 2-aryl-2*H* -1,2,4-triazol-3(4*H*)-one **4a-c**.



R = **a**: C_6H_5; **b**: *p*-ClC_6H_4; **c**: *p*-$OCH_3C_6H_4$

followed by heating with hydrazine hydrate to obtain 4-(4-amino-5-mercapto-4*H*-1,2,4-triazol-3-yl)methyl)-2-aryl-2*H*-1,2,4-triazol-3(4*H*)-one **9a–c**. Upon heating **9a–c** with acetic acid in phosphorusoxychloride, corresponding 3,6-disubstituted [1,2,4]triazolo[3,4-*b*][1,3,4]thiadiazoles **10a–c** were obtained. Compound **9a–c** when refluxed with formic acid gave 3-substituted [1,2,4]triazolo[3,4-*b*][1,3,4] thiadiazoles **11a–c**. 3-Substituted 6-mercapto-[1,2,4] triazolo[3,4-*b*][1,3,4]thiadiazoles **12a–c** were obtained by the reaction of **9a–c** with carbon disulfide in presence of potassium hydroxide. Corresponding 3,6-disubstituted [1,2,4]triazolo[3,4-*b*][1,3,4]thiadiazines **13a–c** were prepared by refluxing compound **9a–c** with phenacyl bromide. All the newly synthesized compounds were characterized by ^{1}H and ^{13}C-NMR, mass spectral and elemental analyses. And also, we have carried out the single crystal X-ray diffraction studies for compound **10b** (Figs. 2 and 3).

EXPERIMENTAL

All the reagents were of analytical grade and were used directly when required. TLC was performed on 0.20 mm Aluchrosep silica gel 60 F_{254} plates (S.D. Fine, Mumbai). Melting points were determined in open capillaries and are uncorrected. The ^{1}H-NMR spectra were recorded at 400 MHz on Bruker Avance FT NMR spectrometer in DMSO-d_6 with tetramethylslane as internal standard. ^{13}C-NMR spectra were recorded at 100 MHz on Bruker Avance FT NMR spectrometer (Bruker Corporation, Billerica, MA) in DMSO-d_6 with tetramethylslane as internal standard. The mass spectra were recorded on Shimadzu GC–MS operating at 70 eV.

Compound **2a–c** was prepared from 3-arylsydnone **1a–c** according to reported method [10].

General procedure for synthesis of 3-aryl-5-ethyl-2-oxo-Δ^4-1,3,4-oxadiazoles (5a–c). A mixture of 3-arylsydnone (**1a–c**, 1 g) and propionic anhydride (10 mL) was stirred at 0–5°C and to this bromine (0.5 mL) in propionic anhydride (10 mL) was added drop-wise. After completion of addition, the reaction mixture was stirred at room temperature for half an hour. Then, the reaction mixture was warmed on water bath at 60°C till the evolution of CO_2 ceases. The reaction mixture was warmed with 2 N NaOH (20 mL) on water bath for 1 h. The reaction mixture was cooled and neutralized with dil HCl to get the solid which was filtered, washed with water, dried, and recrystallized with ethanol to get **5a–c**.

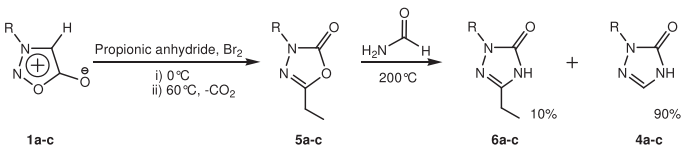
5-Ethyl-3-phenyl-1,3,4-oxadiazol-2(3H)-one (5a). Yield: 76%; mp: 134–136°C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 1.38 (t, 3H, *J* = 7.8 Hz, CH_3), 2.68 (q, 2H, *J* = 7.5 Hz, CH_2), 7.26–7.40 (m, 3H, ArH), 7.80 (d, 2H, *J* = 11.6 Hz, ArH); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 11.50, 33.98, 119.85, 124.96, 129.77, 136.85, 149.75, 155.70; MS (EI): *m/z* 190 (M), 161, 133, 90; *Anal.* Calcd. for $C_{10}H_{10}N_2O_2$ (190.2): C 63.15, H 5.30, N 14.73%. Found: C 63.31, H 5.47, N 14.92%.

3-(4-Chlorophenyl)-5-ethyl-1,3,4-oxadiazol-2(3H)-one (5b). Yield: 72%; mp: 141–143°C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 1.35 (t, 3H, *J* = 7.5 Hz, CH_3), 2.62 (q, 2H, *J* = 7.8 Hz, CH_2), 7.52 (d, 2H, *J* = 9.8 Hz, ArH), 7.88 (d, 2H, *J* = 9.8 Hz, ArH); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 11.32, 33.56, 121.67, 128.38, 129.91, 136.09, 149.69, 155.69; MS (EI): *m/z* 226 (M + 2), 224 (M), 195, 167, 90; *Anal.* Calcd. for $C_{10}H_9N_2O_2Cl$ (224.6): C 53.47, H 4.04, N 12.47%. Found: C 53.71, H 4.24, N 12.52%.

5-Ethyl-3-(4-methoxyphenyl)-1,3,4-oxadiazol-2(3H)-one (5c). Yield: 75%; mp: 138–140°C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 1.36 (t, 3H, *J* = 7.5 Hz, CH_3), 2.64 (q, 2H, *J* = 7.6 Hz, CH_2), 3.76 (s, 3H, CH_3), 6.90 (d, 2H, *J* = 10.2 Hz, ArH), 7.78 (d, 2H, *J* = 10.2 Hz, ArH); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 11.28, 32.19, 55.58, 114.27, 121.81, 131.93, 137.22, 155.38, 158.07; MS (EI): *m/z* 220 (M), 191, 163, 90; *Anal.* Calcd. for $C_{11}H_{12}N_2O_3$ (220.2): C 59.99, H 5.49, N 12.72%. Found: C 60.21, H 5.61, N 12.89%.

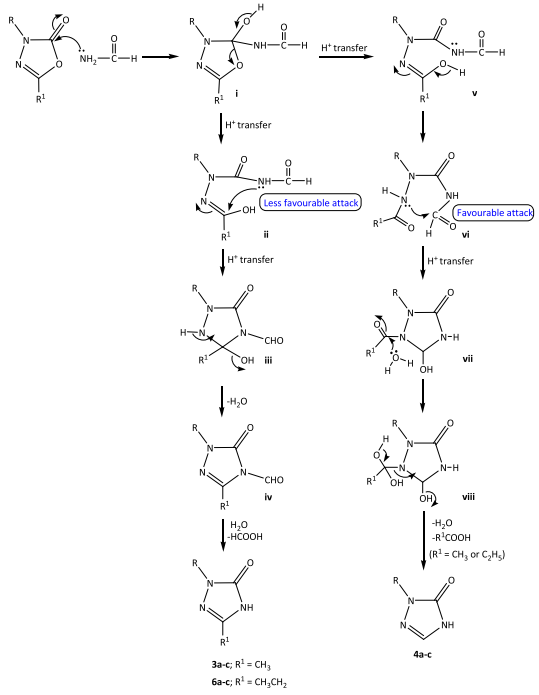
General procedure for the preparation of 2-aryl-2*H*-1,2,4-triazol-3(4*H*)-one (4a-c). 3-Aryl-5-methyl-2-oxo-Δ^4-1,3,4-oxadiazole (**2a–c**, 0.005 M) was refluxed with formamide (10 mL) at 200°C for 6 h. The completion of reaction was monitored by TLC using hexane:ethylacetate

Scheme 3. Synthesis of 2-aryl-2*H* -1,2,4-triazol-3(4*H*)-one **4a-c** also from 5-ethyl-3-aryl-1,3,4-oxadiazol-2(3H)-one **5a-c**.



R = **a**: C_6H_5; **b**: *p*-ClC_6H_4; **c**: *p*-$OCH_3C_6H_4$

Scheme 4. Proposed mechanism for the formation of **3a–c** and **4a–c.** [Color figure can be viewed at wileyonlinelibrary.com]



(6:4) solvent mixture. The reaction mixture was poured into ice cold water. The solid obtained was filtered, dried and passed through silica gel and eluted using hexane: ethylacetate (8:2) solvent mixture to get **4a–c**.

5-Ethyl-2-aryl-2*H*-1,2,4-triazol-3(4*H*)-one **6a–c** was separated by column chromatographic technique using hexane:ethylacetate (8:2) solvent mixture as an eluent.

2-Phenyl-2H-1,2,4-triazol-3(4H)-one (4a). Yield: 82%; mp: 214–216°C; ^{1}H-NMR (400 MHz, DMSO-d_6): δ 7.52–7.60 (m, 3H, ArH), 7.85 (d, 2H, *J* = 9.8 Hz, ArH), 8.24 (s, 1H, C5-H),12.10 (bs, 1H, NH); ^{13}C-NMR (100 MHz, DMSO-d_6): δ 119.01, 128.06, 129.27, 136.81, 137.55, 152.35; MS (EI): *m/z* 161 (M), 127, 111, 90; *Anal.* Calcd. for $C_8H_7N_3O$ (161.2): C 59.62, H 4.38, N 26.07%. Found: C 59.93, H 4.80, N 26.41%.

2-(4-Chlorophenyl)-2H-1,2,4-triazol-3(4H)-one (4b). Yield: 85%; mp: 266–268°C; ^{1}H-NMR (400 MHz, DMSO-d_6): δ 7.49 (d, 2H, *J* = 15.2 Hz, ArH), 7.92 (d, 2H, *J* = 15.2 Hz, ArH), 8.12 (s, 1H, C5-H), 12.00 (bs, 1H, NH); ^{13}C-NMR (100 MHz, DMSO-d_6): δ 119.26, 128.77, 128.84, 136.66, 136.72, 152.17; MS (ESI): *m/z* 197 (M + 2), 195 (M), 125, 111, 90; *Anal.* Calcd. for $C_8H_6N_3OCl$ (195.6): C 49.12, H 3.09, N 21.48%. Found: C 49.31, H 3.27, N 21.79%.

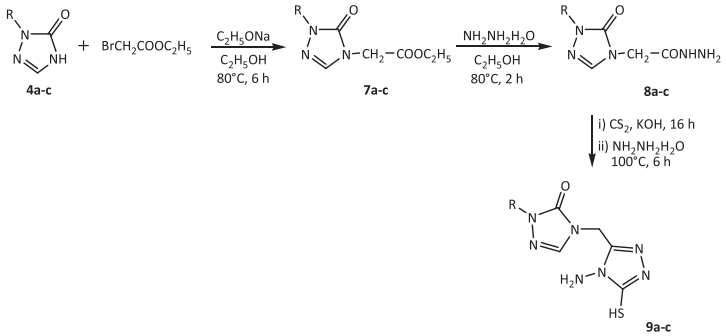
2-(4-Methoxyphenyl)-2H-1,2,4-triazol-3(4H)-one (4c). Yield: 86%; mp: 225–227°C; ^{1}H-NMR (400 MHz, DMSO-d_6): δ 3.78 (s, 3H, CH_3), 6.92 (d, 2H, *J* = 12.2 Hz, ArH), 7.81 (d, 2H, *J* = 12.2 Hz, ArH),12.08 (bs, 1H, NH), 8.19 (s, 1H, C5-H); ^{13}C-NMR (100 MHz, DMSO-d_6, ppm): δ 55.61, 115.47, 121.66, 132.28, 137.22, 151.83,158.26; MS (ESI): *m/z* 191 (M), 127, 113, 90, 55.31; *Anal.* Calcd. for $C_9H_9N_3O_2$ (191.2): C 56.54, H 4.74, N 21.98%. Found: C 56.84, H 4.90, N 22.15%.

5-Ethyl-2-phenyl-2H-1,2,4-triazol-3(4H)-one (6a). Yield: 15%; mp: 175–177°C; ^{1}H-NMR (300 MHz, DMSO-d_6): δ 1.30 (t, 3H, *J* = 7.5 Hz, CH_3), 2.64 (q, 2H, *J* = 7.8 Hz, CH_2), 7.39–7.86 (m, 3H, ArH), 7.91 (d, 2H, *J* = 10.4 Hz, ArH), 11.80 (bs, 1H, NH); ^{13}C-NMR (75 MHz, DMSO-d_6): δ 10.68, 30.10, 120.03, 124.89, 129.14, 137.85, 152.65, 154.10; MS (EI): *m/z* 189 (M), 160, 131, 91; *Anal.* Calcd. for $C_{10}H_{11}N_3O$ (189.2): C 63.48, H 5.86, N 22.21%. Found: C 63.66, H 6.01, N 22.41%.

2-(4-Chlorophenyl)-5-ethyl-2H-1,2,4-triazol-3(4H)-one (6b). Yield: 10%; mp: 180–182°C; ^{1}H-NMR (300 MHz, DMSO-d_6): δ 1.36 (t, 3H, *J* = 7.6 Hz, CH_3), 2.62 (q, 2H, *J* = 7.8 Hz, CH_2), 7.50 (d, 2H, *J* = 11.2 Hz, ArH), 7.90 (d, 2H, *J* = 11.2 Hz, ArH), 12.34 (bs, 1H, NH); ^{13}C-NMR (75 MHz, DMSO-d_6): δ 10.57, 30.21, 121.37, 128.15, 129.94, 135.73, 152.87, 154.06; MS (EI): *m/z* 225 (M + 2), 223 (M), 125, 111, 90; *Anal.* Calcd. for $C_8H_6N_3OCl$ (223.7): C 53.70, H 4.51, N 18.79%. Found: C 53.90, H 4.63, N 18.87%.

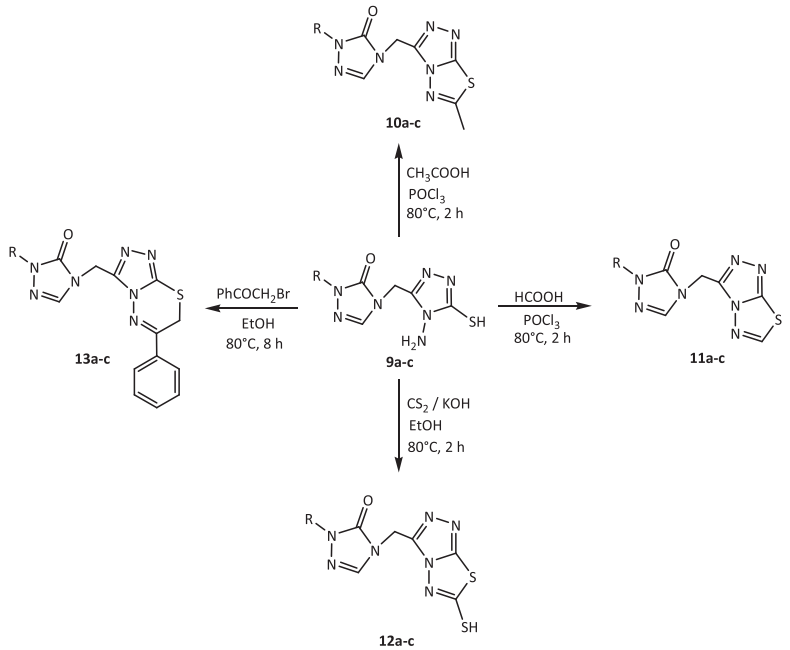
5-Ethyl-2-(4-methoxyphenyl)-2H-1,2,4-triazol-3(4H)-one (6c). Yield: 12%; mp: 164–166°C; ^{1}H-NMR (300 MHz, DMSO-d_6): δ 1.34 (t, 3H, *J* = 7.5 Hz, CH_3), 2.60 (q, 2H, *J* = 7.8 Hz,

Scheme 5. Synthesis of 4-(4-amino-5-mercapto-4*H*-1,2,4-triazol-3-yl)methyl)-2-aryl-2H-1,2,4-triazol-3(4*H*)-one **9a-c**.



R = **a**: C_6H_5; **b**: *p*-ClC_6H_4; **c**: *p*-$OCH_3C_6H_4$

Scheme 6. Synthesis of triazolo[3,4-*b*][1,3,4]thiadiazoles **10**, **11**, **12a-c** and triazolo[3,4-*b*][1,3,4]thiadiazines **12a-c**.



R = **a**: C_6H_5; **b**: *p*-ClC_6H_4; **c**: *p*-$OCH_3C_6H_4$

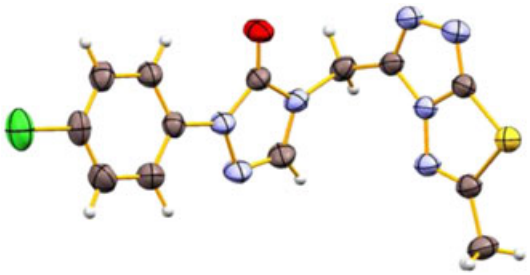


Figure 2. The molecular structure of the compound **10b**. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms are shown as spheres of arbitrary radius. [Color figure can be viewed at wileyonlinelibrary.com]

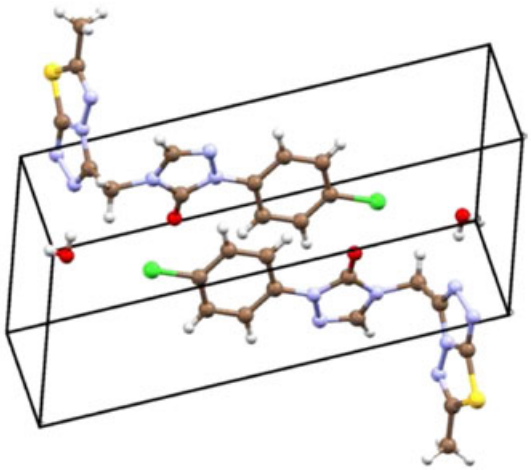


Figure 3. Unit cell packing diagram of the molecules of compound **10b**. [Color figure can be viewed at wileyonlinelibrary.com]

CH_2), 3.76 (s, 3H, CH_3), 6.96 (d, 2H, J = 10.6 Hz, ArH), 7.78 (d, 2H, J = 10.6 Hz, ArH), 12.88 (bs, 1H, NH); ^{13}C-NMR (100 MHz, DMSO-d_6): δ 10.23, 30.31, 55.63, 115.28, 120.59, 132.86, 136.72, 152.43, 153.29, 158.55; MS (EI): *m/z* 219 (M), 189, 161, 91; *Anal.* Calcd. for $C_{11}H_{13}N_3O_2$ (219.2): C 60.26, H 5.98, N 19.17%. Found: C 60.42, H 6.11, N 19.29%.

General procedure for the synthesis of ethyl 2-(5-oxo-1-aryl-1*H*-1,2,4-triazol-4(5*H*)-yl)acetate (7a–c). Compound **4a–c** (0.01 M) was refluxed with equivalent amount of natrium (0.01 M) in absolute ethanol for 2 h. Then, ethylbromoacetate (0.01 M) was added and refluxed for an additional 5 h. The completion of reaction was monitored by TLC using hexane:ethylacetate (7:3) solvent mixture, and solvent was removed under reduced pressure to afford **7a–c**.

Ethyl 2-(5-oxo-1-phenyl-1H-1,2,4-triazol-4(5H)-yl)acetate (7a). Yield: 85%; mp: 94–96°C; ^{1}H-NMR (400 MHz, DMSO-d_6): δ 1.34 (t, 3H, CH_3), 4.20 (q, 2H, CH_2), 4.64 (s, 2H, NCH_2), 7.19–7.57 (m, 3H, ArH), 7.80 (d, 2H, J = 12.8 Hz, ArH), 8.36 (s, 1H, C5-H); ^{13}C-NMR (100 MHz, DMSO-d_6): δ 14.00, 51.37, 60.33, 118.25, 128.63, 129.74, 136.39, 138.28, 152.18, 169.44; MS (EI): *m/z* 247 (M), 209, 153, 125, 111, 90; *Anal.* Calcd. for $C_{12}H_{13}N_3O_3$ (247.2): C 58.29, H 5.30, N 16.99%. Found: C 58.60, H 5.54, N 17.25%.

Ethyl 2-(1-(4-chlorophenyl)-5-oxo-1H-1,2,4-triazol-4(5H)-yl) acetate (7b). Yield: 90%; mp: 77–79°C; ^{1}H-NMR (400 MHz, DMSO-d_6): δ 1.27 (t, 3H, CH_3), 4.09 (q, 2H, CH_2), 4.58 (s, 2H, NCH_2), 7.68 (d, 2H, J = 14.2 Hz,

ArH), 7.90 (d, 2H, *J* = 14.2 Hz, ArH), 8.26 (s, 1H, C5-H); ^{13}C-NMR (100 MHz, DMSO-d_6): δ 14.73, 49.74, 61.62, 119.15, 129.30, 129.99, 137.39, 138.68, 152.29, 168.13; MS (EI): *m/z* 283 (M+2), 281 (M), 209, 153, 125, 111, 90; *Anal.* Calcd. for $C_{12}H_{12}N_3O_3$ (281.7): C 51.16, H 4.29, N 14.92%. Found: C 51.32, H 4.45, N 15.13%.

Ethyl 2-(1-(4-methoxyphenyl)-5-oxo-1H-1,2,4-triazol-4(5H)-yl)acetate (7c). Yield: 90%; mp: 92–94°C; ^{1}H-NMR (400 MHz, DMSO-d_6): δ 1.30 (t, 3H, CH_3), 3.85 (s, 3H, CH_3), 4.11 (q, 2H, CH_2), 4.60 (s, 2H, NCH_2), 6.89 (d, 2H, *J* = 10.8 Hz, ArH), 7.86 (d, 2H, *J* = 10.8 Hz, ArH), 8.28 (s, 1H, C5-H); ^{13}C-NMR (100 MHz, DMSO-d_6): δ 13.92, 50.83, 54.82, 60.97, 115.85, 122.41, 132.78, 138.50, 151.83, 159.00, 167.40; MS (ESI): *m/z* 277 (M), 207, 154, 125, 111, 91; *Anal.* Calcd. for $C_{13}H_{15}N_3O_4$ (277.3): C 56.31, H 5.45, N 15.15%. Found: C 56.77, H 4.68, N 15.26%.

General procedure for the synthesis of 2-(5-oxo-1-aryl-1*H*-1,2,4-triazol-4(5*H*)-yl)acetohydrazide (8a–c). A mixture of compound **7a–c** (0.01 M) and hydrazinehydrate (99%, 0.02 M) in ethanol was refluxed at 80°C for 4 h. After completion of reaction [monitored by TLC using hexane: ethylacetate (7:3) solvent mixture], the solvent was removed under reduced pressure to obtain **8a–c**.

2-(5-Oxo-1-phenyl-1H-1,2,4-triazol-4(5H)-yl)acetohydrazide (8a). Yield: 92%; mp: 186–188°C; ^{1}H-NMR (400 MHz, DMSO-d_6): δ 4.23 (s, 2H, NH_2), 4.45 (s, 2H, NCH_2), 7.35–7.53 (m, 3H, ArH), 7.85 (d, 2H, *J* = 12.0 Hz, ArH), 8.16 (s, 1H, C5-H), 9.54 (bs, 1H, NH); ^{13}C-NMR (100 MHz, DMSO-d_6): δ 45.87, 118.40, 129.13, 129.58, 136.37, 138.28, 151.64, 166.21; MS (EI): *m/z* 233 (M), 208, 179, 153, 125, 111, 90; *Anal.* Calcd. for $C_{10}H_{11}N_5O_2$ (233.2): C 51.50, H 4.75, N 30.03%. Found: C 51.75, H 4.98, N 30.26%.

2-(1-(4-Chlorophenyl)-5-oxo-1H-1,2,4-triazol-4(5H)-yl)acetohydrazide (8b). Yield: 95%; mp: 178–180°C; ^{1}H-NMR (400 MHz, DMSO-d_6): δ 4.42 (s, 2H, NCH_2), 5.01 (s, 2H, NH_2), 7.71 (d, 2H, *J* = 11.8 Hz, ArH), 7.90 (d, 2H, *J* = 11.8 Hz, ArH), 8.20 (s, 1H, C5-H), 9.57 (bs, 1H, NH); ^{13}C-NMR (100 MHz, DMSO-d_6): δ 44.91, 119.36, 129.34, 130.76, 137.21, 138.00, 152.01,165.86; MS (EI): *m/z* 269 (M + 2), 267 (M), 236, 208, 153, 125, 111, 90; *Anal.* Calcd. for $C_{10}H_{10}N_5O_2Cl$ (267.7): C 44.87, H 3.77, N 26.16%. Found: C 45.01, H 4.10, N 26.31%.

2-(1-(4-Methoxyphenyl)-5-oxo-1H-1,2,4-triazol-4(5H)-yl)acetohydrazide (8c). Yield: 92%; mp: 166–168°C; ^{1}H-NMR (400 MHz, DMSO-d_6): δ 3.80 (s, 3H, CH_3), 4.20 (s, 2H, NH_2), 4.48 (s, 2H, NCH_2), 6.91 (d, 2H, *J* = 9.2 Hz, ArH), 7.82 (d, 2H, *J* = 9.2 Hz, ArH), 8.32 (s, 1H, C5-H), 9.60 (bs, 1H, NH); ^{13}C-NMR (100 MHz, DMSO-d_6): δ 47.23, 55.85, 114.65, 121.49, 132.83, 139.46, 151.18, 158.20,166.79; MS (EI): *m/z* 263 (M), 232, 184, 153, 125, 111, 90; *Anal.* Calcd. for $C_{11}H_{13}N_5O_3$ (263.3): C 50.19, H 4.98, N 26.60%. Found: C 50.42, H 5.11, N 26.87%.

General procedure for the preparation of 4-(4-amino-5-mercapto-4*H*-1,2,4-triazol-3-yl)methyl)-2-aryl-2*H*-1,2,4-triazol-3(4*H*)-one (9a–c). To a solution of KOH (0.015 M) in absolute ethanol (10 mL) and compound **8a–c** (0.01 M), carbon disulfide (0.015 M) was added, and the reaction mixture was stirred at room temperature under guard tube conditions for 16 h. It was then diluted with dry ether (30 mL). The solid obtained was filtered and washed with dry ether to get corresponding potassium salt in nearly quantitative yield (98%). A suspension of potassium salt (0.005 M), hydrazinehydrate (85%, 5 mL), and DM water (1 mL) was refluxed with stirring for 6 h. The reaction mixture was then poured into ice cold water and neutralized with conc. HCl to pH = 5. The precipitate obtained was filtered, dried, and recrystallized from ethanol to get **9a–c**.

4-(4-Amino-5-mercapto-4H-1,2,4-triazol-3-yl)methyl)-2-phenyl-2H-1,2,4-triazol-3(4H)-one (9a). Yield: 64%; mp: 220–222°C; ^{1}H-NMR (400 MHz, DMSO-d_6): δ 5.17 (bs, 2H, NH_2), 5.33 (s, 2H, NCH_2), 7.34–7.56 (m, 3H, ArH), 7.90 (d, 2H, *J* = 10.8 Hz, ArH), 8.28 (s, 1H, C5-H),13.82 (bs,1H, SH/NH); ^{13}C-NMR (100 MHz, DMSO-d_6): δ 40.96, 119.57, 129.20, 129.74, 137.41, 138.86, 151.26, 153.38,160.43; MS (EI): *m/z* 289 (M), 261, 195, 153, 125, 111, 90; *Anal.* Calcd. for $C_{11}H_{11}N_7OS$ (289.3): C 45.67, H 3.83, N 33.89%. Found: C 45.92, H 4.06, N 34.11%.

4-(4-Amino-5-mercapto-4H-1,2,4-triazol-3-yl)methyl)-2-(4-chlorophenyl)-2H-1,2,4-triazol-3(4H)-one (9b). Yield: 65%; mp: 216–218°C; ^{1}H-NMR (400 MHz, DMSO-d_6): δ 5.21 (bs, 2H. NH_2), 5.30 (s, 2H, NCH_2), 7.68 (d, 2H, *J* = 11.2 Hz, ArH), 7.95 (d, 2H, *J* = 11.2 Hz, ArH), 8.24 (s, 1H, C5-H),13.76 (bs, 1H, SH/NH); ^{13}C-NMR (100 MHz, DMSO-d_6): δ 40.77, 120.57, 129.09, 130.70, 137.23, 139.56, 151.38, 154.03,162.49; MS (EI): *m/z* 325 (M + 2), 323 (M), 308, 253, 195, 153, 125, 111, 90; *Anal.* Calcd. for $C_{11}H_{10}N_7OSCl$ (323.8): C 40.81, H 3.11, N 30.28%. Found: C 41.15, H 3.34, N 30.54%.

4-(4-Amino-5-mercapto-4H-1,2,4-triazol-3-yl)methyl)-2-(4-methoxyphenyl)-2H-1,2,4-triazol-3(4H)-one (9c). Yield: 60%; mp: 193–195°C; ^{1}H-NMR (400 MHz, DMSO-d_6): δ 3.81 (s, 3H, CH_3), 5.18 (bs, 2H, NH_2), 5.28 (s, 2H, NCH_2), 6.90 (d, 2H, *J* = 11.6 Hz, ArH), 7.80 (d, 2H, *J* = 11.6 Hz, ArH), 8.33 (s, 1H, C5-H),13.80 (bs, 1H, SH/NH); ^{13}C-NMR (100 MHz, DMSO-d_6): δ 38.29, 54.57, 115.37, 122.09, 132.21, 138.28, 151.69, 153.59, 158.81,163.50; MS (EI): *m/z* 319 (M), 308, 291, 195, 153, 125, 111, 90; *Anal.* Calcd. for $C_{12}H_{13}N_7O_2S$ (319.3): C 45.13, H 4.10, N 30.70%. Found: C 45.28, H 4.35, N 31.00%.

General procedure for the preparation of 4-(6-methyl-[1,2,4]triazolo[3,4-*b*][1,3,4]thiadiazol-3-yl)methyl)-2-aryl-2*H*-1,2,4-triazol-3(4*H*)-one (10a–c). A mixture of compound **9a–c** (0.01 M) and acetic acid (0.01 M) in phosphorus oxychloride (10 mL) was refluxed for 2 h at 80°C on water bath. After completion of reaction [monitored by TLC

using hexane:ethylacetate (7:3) solvent mixture], excess of phosphorus oxychloride was expelled out, and the reaction mixture was poured into ice cold water and neutralized using solid sodium bicarbonate. The white solid obtained was filtered, dried, and recrystallized from ethanol.

4-(6-Methyl-[1,2,4]triazolo[3,4-b][1,3,4]thiadiazol-3-yl)methyl)-2-phenyl-2H-1,2,4-triazol-3(4H)-one (10a). Yield: 78%; mp: 201–203°C; ^{1}H-NMR (400 MHz, DMSO-d_6): δ 2.82 (s, 3H, CH_3), 5.31 (s, 2H, CH_2), 7.41–7.55 (m, 3H, ArH), 7.75 (d, 2H, J = 10.8 Hz, ArH), 8.32 (s, 1H, C5-H); ^{13}C-NMR (100 MHz, DMSO-d_6): δ 166.23, 160.24, 155.25, 151.31, 139.08, 136.74, 130.26, 129.52, 118.56, 37.05, 16.34; MS (EI): *m/z* 313 (M), 155, 125, 111, 91; *Anal.* Calcd. for $C_{13}H_{11}N_7OS$ (313.3): C 49.83, H 3.54, N 31.29%. Found: C 50.21, H 3.80, N 31.77%.

2-(4-Chlorophenyl)-4-(6-methyl-[1,2,4]triazolo[3,4-b][1,3,4]thiadiazol-3-yl)methyl)-2H-1,2,4-triazol-3(4H)-one (10b). Yield: 85%; mp: 222–224°C; ^{1}H-NMR (400 MHz, DMSO-d_6): δ 2.71 (s, 3H, CH_3), 5.35 (s, 2H, CH_2), 7.52 (d, 2H, J = 9.2 Hz, ArH), 7.90 (d, 2H, J = 9.2 Hz, ArH), 8.36 (s, 1H, C5-H); ^{13}C-NMR (100 MHz, DMSO-d_6): δ 17.87, 36.40, 119.31, 129.09, 129.19, 136.38, 138.38, 150.61, 154.69, 161.96, 167.76; MS (EI): *m/z* 349 (M + 2), 347 (M), 153, 125, 111, 84; *Anal.* Calcd. for $C_{13}H_{10}N_7OSCl$ (347.8): C 44.90, H 2.90, N 28.19%. Found: C 45.21, H 3.07, N 28.39%.

2-(4-Methoxyphenyl)-4-(6-methyl-[1,2,4]triazolo[3,4-b][1,3,4]thiadiazol-3-yl)methyl)-2H-1,2,4-triazol-3(4H)-one (10c). Yield: 79%; mp: 195–197°C; ^{1}H-NMR (400 MHz, DMSO-d_6): δ 2.68 (s, 3H, CH_3), 3.84 (s, 3H, CH_3), 5.29 (s, 2H, CH_2), 6.84 (d, 2H, J = 11.6 Hz, ArH), 7.84 (d, 2H, J = 11.6 Hz, ArH), 8.41 (s, 1H, C5-H); ^{13}C-NMR (100 MHz, DMSO-d_6): δ 18.21, 37.08, 55.91, 114.82, 122.55, 131.52, 139.07, 151.67, 155.63, 158.27, 160.70,166.59; MS (EI): *m/z* 343 (M), 312, 156, 125, 111, 91; *Anal.* Calcd. for $C_{14}H_{13}N_7O_2S$ (343.4): C 48.97, H 3.82, N 28.55%. Found: C 49.20, H 4.03, N 28.83%.

General procedure for the preparation of 4-([1,2,4]triazolo[3,4-*b*][1,3,4]thiadiazol-3-yl)methyl)-2-aryl-2*H*-1,2,4-triazol-3(4*H*)-one (11a–c). A mixture of compound **9a–c** (0.01 M) and formic acid (0.01 M) in phosphorus oxychloride (10 mL) was refluxed for 2 h at 80°C on water bath. After completion of reaction [monitored by TLC using hexane:ethylacetate (7:3) solvent mixture], excess of phosphorus oxychloride was expelled out, and the reaction mixture was poured into ice cold water and neutralized using solid sodium bicarbonate. The white solid obtained was filtered, dried, and recrystallized from ethanol.

4-([1,2,4]Triazolo[3,4-b][1,3,4]thiadiazol-3-yl)-methyl)-2-phenyl-2H-1,2,4-triazol-3(4H)-one (11a). Yield: 74%; mp: 225–227°C; ^{1}H-NMR (400 MHz, DMSO-d_6): δ 5.36 (s, 2H, CH_2), 7.38–7.58 (m, 3H, ArH), 7.72 (d, 2H, J = 11.2 Hz, ArH), 8.25 (s, 1H, −N = CH-S-),8.37 (s, 1H, C5-H); ^{13}C-NMR (100 MHz, DMSO-d_6): δ 36.61, 118.47, 129.48, 129.76, 130.51, 138.61, 139.29, 151.37, 152.69, 164.21, 167.07; MS (EI): *m/z* 299 (M), 127, 111, 91; *Anal.* Calcd. for $C_{12}H_9N_7OS$ (299.3): C 48.15, H 3.03, N 32.76%. Found: C 48.39, H 3.21, N 32.97%.

4-([1,2,4]Triazolo[3,4-b][1,3,4]thiadiazol-3-yl)methyl)-2-(4-chlorophenyl)-2H-1,2,4-triazol-3(4H)-one (11b). Yield: 76%; mp: 218–220°C; ^{1}H-NMR (400 MHz, DMSO-d_6): δ 5.39 (s, 2H, CH_2), 7.58 (d, 2H, J = 9.6 Hz, ArH), 7.92 (d, 2H, J = 9.6 Hz, ArH), 8.31 (s, 1H, −N = CH-S-), 8.41 (s, 1H, C5-H); ^{13}C-NMR (100 MHz, DMSO-d_6): δ 37.48, 118.59, 129.17, 129.22, 136.56, 139.42, 151.37, 153.41, 163.89,167.37; MS (EI): *m/z* 335 (M + 2), 333 (M), 254, 123, 113, 91; *Anal.* Calcd. for $C_{12}H_8N_7OSCl$ (333.8): C 43.18, H 2.42, N 29.38%. Found: C 43.31, H 2.77, N 29.81%.

4-([1,2,4]Triazolo[3,4-b][1,3,4]thiadiazol-3-yl)methyl)-2-(4-methoxyphenyl)-2H-1,2,4-triazol-3(4H)-one (11c). Yield: 62%; mp: 196–198°C; ^{1}H-NMR (400 MHz, DMSO-d_6): δ 3.79 (s, 3H, CH_3), 5.30 (s, 2H, CH_2), 6.90 (d, 2H, J = 10.2 Hz, ArH), 7.82 (d, 2H, J = 10.2 Hz, ArH), 8.27 (s, 1H, −N = CH-S-), 8.38 (s, 1H, C5-H); ^{13}C-NMR (100 MHz, DMSO-d_6): δ 36.77, 56.11, 114.73, 121.61, 132.27, 139.24, 151.78, 152.64, 158.31, 164.07, 166.85; MS (EI): *m/z* 329 (M), 197, 125, 111, 90; *Anal.* Calcd. for $C_{13}H_{11}N_7O_2S$ (329.3): C 47.41, H 3.37, N 29.77%. Found: C 47.78, H 3.59, N 29.97%.

General procedure for the preparation of 4-(6-mercapto-[1,2,4]triazolo[3,4-*b*][1,3,4]thiadiazol-3-yl)methyl)-2-aryl-2*H*-1,2,4-triazol-3(4*H*)-one (12a–c). To a solution of KOH (0.015 M) in absolute ethanol (10 ml) and compound **9a–c** (0.01 M), carbon disulfide (0.015 M) was added, and the reaction mixture was refluxed for 2 h. After completion of reaction [monitored by TLC using hexane: ethylacetate (7:3) solvent mixture], the volume of solvent was reduced under pressure and poured into ice cold water. The white solid obtained was filtered, dried, and recrystallized from ethanol.

4-(6-Mercapto-[1,2,4]triazolo[3,4-b][1,3,4]thiadiazol-3-yl)methyl)-2-phenyl-2H-1,2,4-triazol-3(4H)-one (12a). Yield: 72%; mp: 184–186°C; ^{1}H-NMR (400 MHz, DMSO-d_6): δ 5.36 (s, 2H, CH_2), 7.39–7.60 (m, 3H, ArH), 7.81 (d, 2H, J = 9.8 Hz, ArH), 8.42 (s, 1H, C5-H),13.48 (s, 1H, SH); ^{13}C-NMR (100 MHz, DMSO-d_6): δ 36.28, 118.71, 129.19, 129.24, 130.67, 137.35, 138.39, 151.87, 154.77, 161.20, 167.83; MS (EI): *m/z* 331 (M), 179, 127, 111, 91; *Anal.* Calcd. for $C_{12}H_9N_7OS_2$ (331.4): C 43.49, H 2.74, N 29.59%. Found: C 43.86, H 2.93, N 29.87%.

2-(4-Chlorophenyl)-4-(6-mercapto-[1,2,4]triazolo[3,4-b][1,3,4]thiadiazol-3-yl)methyl)-2H-1,2,4-triazol-3(4H)-one (12b). Yield: 78%; mp: 200–202°C; ^{1}H-NMR (400 MHz, DMSO-d_6): δ 5.42 (s, 2H, CH_2), 7.62 (d, 2H, J = 10.2 Hz, ArH), 7.90 (d, 2H, J = 10.2 Hz, ArH), 8.32 (s, 1H, C5-H), 13.50 (s, 1H, SH); ^{13}C-NMR (100 MHz, DMSO-d_6): δ 37.05, 118.31, 129.40, 129.79, 136.39, 139.27, 151.67, 153.51, 162.57, 166.94; MS (EI): *m/z* 367 (M + 2), 365

(M), 184, 125, 111, 90; *Anal.* Calcd. for $C_{12}H_8N_7OS_2Cl$ (365.8): C 39.40, H 2.20, N 26.80%. Found: C 39.57, H 2.62, N 26.98%.

4-(6-Mercapto-[1,2,4]triazolo[3,4-b][1,3,4]thiadiazol-3-yl)methyl)-2-(4-methoxyphenyl)-2H-1,2,4-triazol-3(4H)-one (12c). Yield: 70%; mp: 194–196°C; ^{1}H-NMR (400 MHz, DMSO-d_6): δ 3.82 (s, 3H, CH_3), 5.41 (s, 2H, CH_2), 6.88 (d, 2H, J = 10.6 Hz, ArH), 7.85 (d, 2H, J = 10.6 Hz, ArH), 8.40 (s, 1H, C5-H), 13.42 (s, 1H, SH); ^{13}C-NMR (100 MHz, DMSO-d_6): δ 37.16, 57.28, 115.61, 122.37, 132.53, 139.21, 151.14, 152.71, 158.34, 163.50, 167.24; MS (EI): *m/z* 361 (M), 274, 127, 113, 90; *Anal.* Calcd. for $C_{13}H_{11}N_7O_2S_2$ (361.4): C 43.20, H 3.07, N 27.13%. Found: C 43.66, H 3.39, N 27.55%.

General procedure for the preparation of 2-aryl-4-(6-phenyl-7*H*-[1,2,4]triazolo[3,4-*b*][1,3,4]thiadiazin-3-yl)methyl)-2*H*-1,2,4-triazol-3(4*H*)-one (13a–c). A mixture of compound **9a–c** (0.01 M) and phenacylbromide (0.01 M) in absolute ethanol (10 ml) is refluxed at 80°C for 8 h. The completion of reaction was monitored by TLC using hexane:ethylacetate (7:3) solvent mixture. The solvent was removed under reduced pressure to get **11a–c** which was recrystallized from ethanol.

2-Phenyl-4-(6-phenyl-7H-[1,2,4]triazolo[3,4-b][1,3,4]thiadiazin-3-yl)methyl)-2H-1,2,4-triazol-3(4H)-one (13a). Yield: 76%; mp: 226–228°C; ^{1}H-NMR (400 MHz, DMSO-d_6): δ 3.44 (s, 2H, $-SCH_2$), 5.40 (s, 2H, CH_2), 7.36–7.58 (m, 6H, ArH), 7.72 (d, 2H, J = 12.8 Hz, ArH), 7.84 (d, 2H, J = 10.4 Hz, ArH), 8.43 (s, 1H, C5-H); ^{13}C-NMR (100 MHz, DMSO-d_6): δ 33.97, 35.28, 118.59, 125.09, 128.06, 128.61, 129.41, 131.73, 134.23, 137.58, 139.47, 151.46, 154.21, 162.62, 166.37; MS (EI): *m/z* 389 (M), 127, 113, 91; *Anal.* Calcd. for $C_{19}H_{15}N_7OS$ (389.4): C 58.60, H 3.88, N 25.18%. Found: C 58.80, H 4.02, N 27.30%.

2-(4-Chlorophenyl)-4-(6-phenyl-7H-[1,2,4]triazolo[3,4-b][1,3,4]thiadiazin-3-yl)methyl)-2H-1,2,4-triazol-3(4H)-one (13b). Yield: 75%; mp: 230–232°C; ^{1}H-NMR (400 MHz, DMSO-d_6): δ 3.42 (s, 2H, $-SCH_2$), 5.45 (s, 2H, CH_2), 7.44–7.52 (m, 3H, ArH), 7.62 (d, 2H, J = 11.8 Hz, ArH), 7.68 (d, 2H, J = 10.2 Hz, ArH), 7.94 (d, 2H, J = 11.8 Hz, ArH), 8.44 (s, 1H, C5-H); ^{13}C-NMR (100 MHz, DMSO-d_6): δ 34.07, 36.56, 119.65, 128.72, 128.84, 129.08, 129.61, 132.98, 134.40, 138.19, 138.53, 150.75, 155.63, 163.49,167.05; MS (EI): *m/z* 425 (M + 2), 423 (M), 215, 195, 125, 111, 84; *Anal.* Calcd. for $C_{19}H_{14}N_7OSCl$ (423.9): C 53.84, H 3.33, N 23.13%. Found: C 54.01, H 3.49, N 23.27%.

2-(4-Methoxyphenyl)-4-(6-phenyl-7H-[1,2,4]triazolo[3,4-b][1,3,4]thiadiazin-3-yl)methyl)-2H-1,2,4-triazol-3(4H)-one (13c). Yield: 70%; mp: 198–200°C; ^{1}H-NMR (400 MHz, DMSO-d_6): δ 3.38 (s, 2H, $-SCH_2$), 3.80 (s, 3H, CH_3), 5.37 (s, 2H, CH_2), 6.85 (d, 2H, J = 12.2 Hz, ArH), 7.48–7.53 (m, 3H, ArH), 7.72 (d, 2H, J = 11.2 Hz, ArH), 7.88 (d, 2H, J = 12.2 Hz, ArH), 8.30 (s, 1H, C5-H); ^{13}C-NMR (100 MHz, DMSO-d_6): δ 33.75, 35.27, 56.43, 114.79, 121.32, 128.45, 129.37, 130.52, 132.25, 134.38, 139.47, 151.76, 158.41, 162.22, 155.11, 167.08; MS (EI): *m/z* 419 (M), 289, 125, 111, 91; *Anal.* Calcd. for $C_{20}H_{17}N_7O_2S$ (419.5): C 57.27, H 4.09, N 23.37%. Found: C 57.57, H 4.33, N 23.62%.

CONCLUSION

We herein report the C5-dealkylation of 3-aryl-5-alkyl-2-oxo-Δ^4-1,3,4-oxadiazoles when reacted with formamide at higher temperature affording 2-aryl-2*H*-1,2,4-triazol-3(4*H*)-ones as major product which served as a useful precursors in the synthesis of triazolo[3,4-*b*][1,3,4] thiadiazole and triazolo[3,4-*b*][1,3,4]thiadiazine derivatives.

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REFERENCES AND NOTES

[1] Pace, A.; Pibiri, I.; Buscemi, S.; Vivona, N. Heterocycles 2004, 63, 2627

[2] Malbec, F.; Milcent, R.; Vicart, P.; Bure, A.M. J Heterocyclic Chem 1984, 21, 1769.

[3] Yongwei, J.; Yongbin, C.; Jun, Z.; Yan, Z.; Xiaoyun, C.; Honggang, H.; Qingjie, Z.; Qiuye, W.; Dazhi, Z.; Yuanying, Z.; Qingyan, S. Eur J Med Chem, 2011, 46, 3135.

[4] Mullican, M. D.; Wilson, M. W.; Connor, D. T.; Kostlan, C. R.; Schrier, D. J.; Dyer, D. D. J Med Chem 1993, 36, 1090.

[5] Zuo, Y.; Yang, S.-Y.; Luo, P.-P.; Tan, Y.; Hao, G.-F.; Wu, Q.-Y.; Xi, Z.; Yang, G.-F. Bioorg Med Chem 2013, 21, 3245.

[6] Neslihan, D.; Reyhan, U.; Ahmet, D. Bioorg Med Chem 2002, 10, 3717.

[7] Pramod, P. K.; Ravindra, R. K.; Mahadevappa, Y. K.; Atukuri, D.; Raveendra, R. K. Eur J Med Chem 2013, 62, 232.

[8] Kattimani, P. P.; Raikar, S. V.; Kamble R. R.; Karidurganavar, M. Y.; Hunnur, R. K. Main Group Chem 2011, 10, 165.

[9] Atukuri, D.; Ravindra R. K.; Pramod P. K. Lett Org Chem 2013, 10, 510.

[10] Mallur, S. G.; Badami, B. V. Farmaco 2000, 55, 65.

[11] Browne, D. L.; Harrity, J. P. A. Tetrahedron 2010, 66, 553.

[12] Wu, C.; Fang, Y.; Larock, R. C.; Shi, F. Org Lett 2010, 12, 2234.

[13] Angadiyavar, C. S.; George, M. V. J Org Chem 1971, 36, 1589.

[14] Imtiaz, K.; Aliya, I.; Naeem, A. Eur J Med Chem 2013, 63, 854.

[15] Thamotharan, S.; Parthasarathi, V.; Hunnur, R. K.; Badami, B. V.; Linden, A. Acta Cryst 2003, E59, o225.

[16] Kattimani, P. P.; Kamble, R. R.; Kumbar, M. N.; Arunkashi, H. K.; Devarajegowda, H. C. Acta Cryst 2014, E70, o499.