Synthesis of 1,2,4-Triazolo[1,5-*d*]-1,2,4-triazine-5-thiones

Majid M. Heravi[a,c,*], Naser Montazeri[a], Mohammad Rahimizadeh[a], Mehdi Bakavoli[a] and Mitra Ghassemzadeh[d]

[a]Department of Chemistry, School of Sciences, Ferdowsi University of Mashhad, Mashhad, Iran;
[b]Department of Chemistry, Azad University, Tonekabon, Iran;
[c]Department of Chemistry, School of Sciences, Azzahra University, Vanak, Tehran, Iran;
[d]Chemistry & Chemical Engineering Research Center of Iran, Tehran, Iran

Received December 20, 2004

In an attempt to discover bicyclic compounds containing the 1,2,4-triazine moiety, 1,2,4-triazolo[1,5-*d*]-1,2,4-triazine-5-thiones from one pot reaction of arylnitriles with 4-amino-1,2,4-triazine-3-thione-5-one in the presence of potassium *tert*-butoxide were synthesized.

J. Heterocyclic Chem., **42**, 1021 (2005).

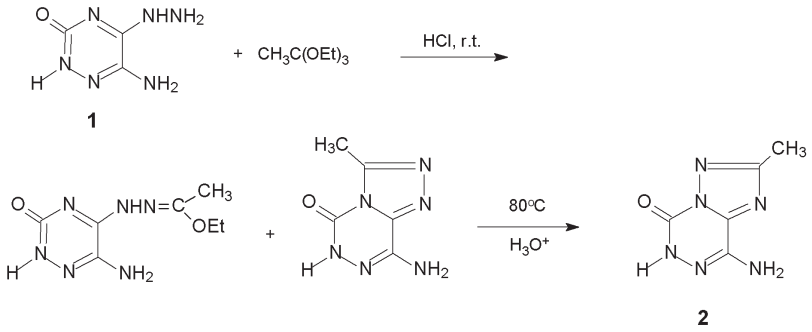
Introduction.

The 1,2,4-triazine ring system is a key component of commercial dyes, herbicides, insecticides and more recently pharmaceutical compositions [1]. Lamotrigine, a sodium channel blocker is the active component of Lamictal, which is in clinical use as an anticonvulsant therapy, contains the 1,2,4-triazine ring [2].

In continuation of our earlier studies on the orientation of cyclization in bicyclic compounds derived from 1,2,4-triazine [3], we now report, in this communication our work on the synthesis of a novel heterocyclic system 1,2,4-triazolo-[1,5-*d*]-1,2,4-triazine-5-thiones.

To the best of our knowledge the only 1,2,4-triazolo[1,5-*d*]1,2,4-triazine **2** has been synthesized through complicated reaction of 5-hydrazino-1,2,4-triazine **1** with triethyl ortho acetate and subsequent heating in concentrated acid [4] (Scheme 1)

Scheme 1



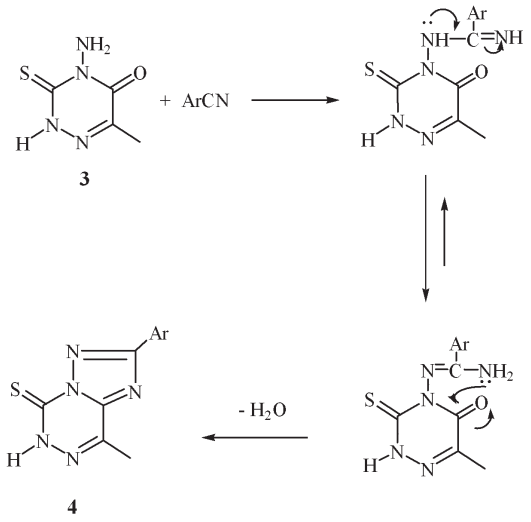
Result and Discussion.

6-Methyl-4-amino-1,2,4-triazine-3-thione-5-one **3** was reacted with benzonitrile in the presence of potassium *t*-butoxide in *t*-butyl alcohol at reflux temperature [5]. After cooling the mixture and acidification of the solution, a crystalline compound was obtained in 79% yield. The absence of a band for amide carbonyl group in IR, ^{1}H NMR data, the exact mass measurement and microanalysis suggested that the product should be 8-methyl-2-phenyl-6*H*-1,2,4-triazolo-[1,5-*d*]-1,2,4-triazine-5-thione (**4**, Ar = Ph).

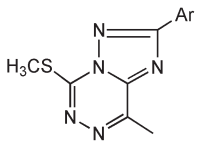
Mechanistically, the formation of **4** could be explained as shown in Scheme 2. Most probably a two step process occurs: first a standard condensation of the amino group with nitrile and the known intramolecular cyclization of nucleophilic the nitrogen moiety to the carbonyl group followed by elimination of water. The unexpected feature of this reaction is selective and preferred attack of nucleophilic nitrogen to the carbonyl group of triazine at the 5 position instead of thione group at the 3 position to afford the expected, 1,2,4-triazolo[5,1-*c*]-1,2,4-triazine **5** (Scheme 3). We have recently reported on the structural elucidation of **3** and found that C=O length is 123.6(3) pm and C=S length is 165.4(3) pm [6]. These data clearly show that C=O bond is stronger than C=S bond and should be cleaved more easily. The only explanation for this reverse attack could be the existence of preferred tautomeric form of triazinone **6** over triazine thione **7**.

In addition, we used semiempirical (AM1) and *ab initio* calculation to estimate that triazinone **8** (-1524.98 au) is more stable than triazine thione **9** (-1508.08 au) and should exist predominantly. In addition, the IR spectrum of compound **3** shows a vibration band for carbonyl group at 1707 cm^{-1}.

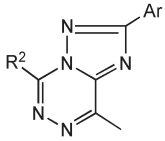
Scheme 2



pound **4** (Ar = Ph) was methylated to give the methylthio derivative **10** (Scheme 4), then the methylthio group was replaced by amines (morpholine) to afford **11a-b**.



10, Ar = Ph

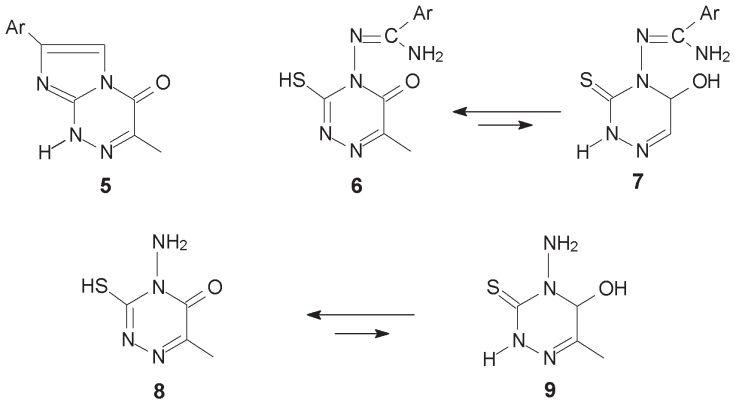


11a, R^2 = O N

11b, R^2 = $PhCH_2NH$-

In conclusion, we have developed a facile and high yielding method for the synthesis of various 1,2,4-triazolo[1,5-*d*]-1,2,4-triazin-5-thiones from readily available starting materials. This method is carried out in a relatively mild condition and does not involve any toxic reagent. The only drawback of this method is that we could not use aliphatic nitriles.

Scheme 3



To establish the generality of the method, various aryl nitriles were efficiently reacted with **3** to obtain **4** in good to high yields (Table 1).

It is noteworthy to mention that *p*-aminobenzonitrile and *p*-hydroxybenzonitrile did not react with **3** under the above reaction conditions. However, after protection of amino and hydroxy groups by acetylation, reaction occurred. Deprotection gave the corresponding 1,2,4-triazolo[1,5-*d*]-1,2,4-triazines (enteries **4i** and **4j**). Unreactivity of p-aminobenzonitrile and *p*-hydroxylbenzonitrile may be due to strong electron releasing of amino and hydroxyl group making the nitrile group less electrophilic. Although the present method tolerates substantial variation in aryl nitrile as the substrate (Table 1), alkyl nitriles did not react. We have no explanation for this lack of reactivity and perhaps elucidation of the precise answer to this question needs further investigations.

To prove our structure and open a way to synthesiz various derivatives of 1,2,4-triazolo[1,5-*d*]-1,2,4-triazine, com-

EXPERIMENTAL

The melting points are uncorrected and were obtained by a Kofler Heizbank Reichart type 7841 melting point apparatus. IR spectra were obtained on a 4300 Shimadzu spectrometer. The ^1H NMR spectra were recorded on a Bruker AC 100, unless otherwise stated using TMS as standard reference. Mass spectra scanned on a Varian CH-7 instrument at 70 eV. Microanalyses were performed in Iranian Oil Research Center of Iran, Tehran, Iran.

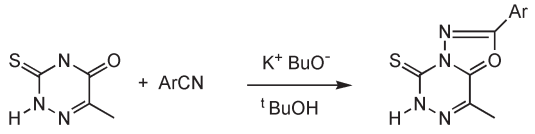
Synthesis of 1,2,4-Triazolo[1,5-*d*]-1,2,4-triazin-5-thiones.

General Procedure.

Potassium (0.195 g, 5 mmol) was dissolved in ^{t}BuOH (30 mL). To this solution compound **3** (0.515 g, 5 mmol) and an appropriate nitrile (5 mmol) were added. This mixture was refluxed for 4 hrs. After cooling, the mixture was filtered and to the filtrate 10% HCl was added dropwise. The resulting solid was collected by filtration and crystallized from a suitable solvent. The products were characterized by spectroscopic and analytical data.

Table

Synthesis of 1,2,4-Triazolo[1,5-*d*]-1,2,4-triazine-5-thiones



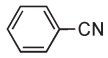
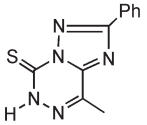
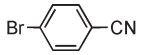
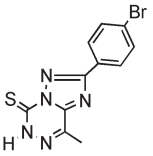
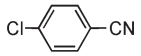
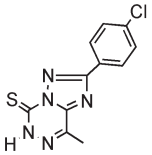
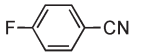
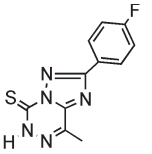
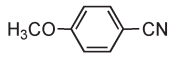
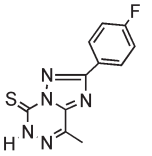
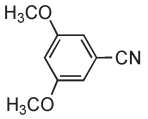
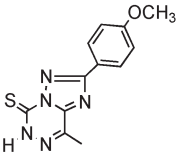
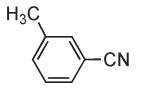
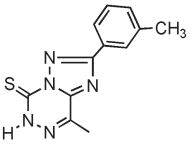
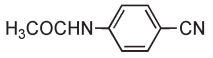
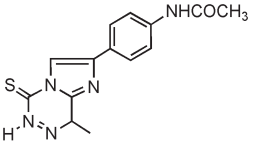
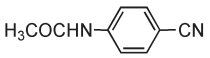
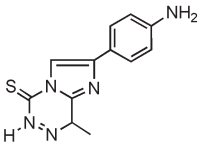
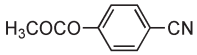
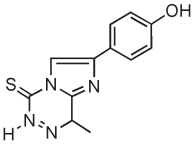
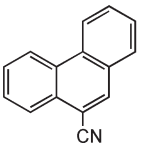
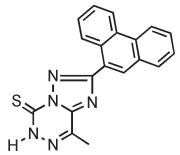
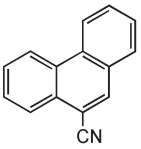
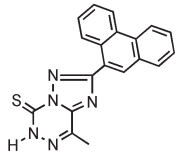
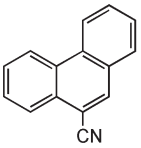
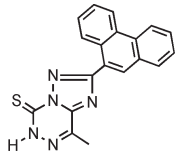
Entry	Arylnitrile	Product	Yield (%)
4a			79
4b			80
4c			82
4d			80
4e			76
4f			85
4g			84
4h			60

Table (continued)

Entry	Arylnitrile	Product	Yield (%)
4i			62
4j			68
4k			73
4l			75
4m			88

[a] Yields refer to isolated products.

2-Phenyl-8-methyl-6*H*-1,2,4-triazolo[1,5-*d*]1,2,4-triazine-5-one (**4a**).

This compound was obtained in 79% yield, mp: 282-3 °C (EtOH); ^{1}H NMR, (d_6-DMSO): δ 2.61 (s, 3H, CH_3), 7.59 (m, 3H, ArH), 8.23 (m, 2H, ArH), 14.6 (s, broad, 1H, NH); IR (KBr disc) 3250, 1600, 1520, 1480, 1440 cm^{-1}; MS m/z M^+ 243(5), 242(26), 241(70), 240(100), 212(31), 211(46), 185(51), 179(77), 157(31), 143(25).

Anal. Calcd. for $C_{11}H_9N_5S$: C, 54.32; H, 3.70; N, 28.80; S, 13.16. Found C, 55.00; H, 3.60; N, 28.60; S, 12.3.

2-(*p*-Bromophenyl)-8-methyl-6*H*-1,2,4-triazolo[1,5-*d*]1,2,4-triazine-5-one (**4b**).

This compound was obtained in 80% yield, mp: 250-2 °C (benzene); ^{1}H NMR, (d_6-DMSO): δ 2.59 (s, 3H, CH_3), 7.79 (d, *J* = 7.8 Hz, 3H, ArH), 8.16 (d, *J* = 7.8 Hz, 2H, ArH), 14.6 (s, broad, 1H, NH); IR (KBr disc) 3120, 3080, 2980, 1595, 1515, 1440 cm^{-1}; MS m/z M^++2: 324(29), M+1: 323(60), M^+: 322(28), 265(10), 185(82), 184(92), 182(100), 181(86), 114(40), 102(88);

Anal. Calcd. for $C_{11}H_8BrN_5S$: C, 40.99; H, 2.48; N, 21.73. Found: C, 41.03; H, 2.35; N, 21.61.

2-(*p*-Chlorophenyl)-8-methyl-6*H*-1,2,4-triazolo[1,5-*d*]1,2,4-triazine-5-one (**4c**).

This compound was obtained in 82% yield, mp: 216-7 °C (benzene/EtOH, 50/50); ^{1}H NMR, (d_6-DMSO): δ 2.6 (s, 3H, CH_3), 7.64 (d, *J* = 8.4 Hz, 3H, ArH), 8.21 (d, *J* = 8.4 Hz, 2H, ArH), 14.61 (s, broad, 1H, NH); IR (KBr disc) 3150, 3080, 1995, 1520, 1445 cm^{-1}; MS m/z M^+ 277(5), 276(13), 275(73), 273(100), 244(21), 215(34), 139(36), 136(73), 114(56).

Anal. Calcd. for $C_{11}H_8ClN_5S$: C, 47.57; H, 2.90; N, 25.21. Found: C, 47.43; H, 2.86; N, 25.81.

2-(*p*-Flourophenyl)-8-methyl-6*H*-1,2,4-triazolo[1,5-*d*]1,2,4-triazine-5-one (**4d**).

This compound was obtained in 80% yield, mp: 264-5 °C (EtOH); ^{1}H NMR, (d_6-DMSO): δ2.6 (s, 3H, CH_3), 7.41 (t, *J* = 8.8 Hz, 2H, ArH), 8.25 (q, *J* = 7.6 Hz, 2H, ArH), 14.25 (s, broad, 1H, NH); IR (KBr disc) 3230, 3070, 1610, 1515, 1495 cm^{-1}; MS m/z M^+ 261(6), 260(23), 259(60), 258(100), 195(22), 193(24), 157(16), 156(15), 155(14).

Anal. Calcd. for $C_{11}H_8FN_5S$: C, 50.56; H, 3.08; N, 26.80. Found: C, 50.45; H, 2.99; N, 27.00.

2-(*p*-Methoxyphenyl)-8-methyl-6*H*-1,2,4-triazolo[1,5-*d*]1,2,4-triazine-5-one (**4e**).

This compound was obtained in 76% yield, mp: 223-4 °C (EtOH); ^{1}H NMR, (d_6-DMSO): δ 2.59 (s, 3H, CH_3), 3.8 (s, 3H, OCH_3), 7.12 (d, *J* = 8.82 Hz, 2H, ArH), 8.11 (d, *J* = 8.82 Hz, 2H, ArH), 14.55 (s, broad, 1H, NH); IR (KBr disc) 2980, 2910, 1585, 1530, 1490, 1440 cm^{-1}; MS m/z M^+ 273(4), 271(20), 269(6), 267(100), 223(19), 109(87), 133(70), 132(73), 119(31).

Anal. Calcd. for $C_{12}H_{11}N_5OS$: C, 52.73; H, 4.05; N, 25.62. Found: C, 52.68; H, 4.00; N, 25.70.

2-(2,3-Dimethoxyphenyl)-8-methyl-6*H*-1,2,4-triazolo[1,5-*d*]-1,2,4-triazine-5-one (**4f**).

This compound was obtained in 85% yield, mp: 355-6 °C (benzene); ^{1}H NMR, (d_6-DMSO): δ 2.60 (s, 3H, CH_3), 3.85 (s, 6H, 2 CH_3-O), 6.7 (d, *J* = 2.14 Hz, 1H, Ar-H), 7.32 (d, *J* = 2.14 Hz, 2H, Ar-H), 14.58 (s, broad, 1H, NH); IR (KBr disc) 3250, 3020, 1600, 1520, 1460, 1415, 1330 cm^{-1}; MS m/z M^+ 303(30), 231(6), 230(11), 165(100), 163(35), 134(5).

Anal. Calcd. for $C_{13}H_{13}N_5O_2S$: C, 51.48; H, 4.29; N, 23.10. Found: C, 51.32; H, 4.27; N, 22.98.

2-(*m*-Methylphenyl)-8-methyl-6*H*-1,2,4-triazolo[1,5-*d*]1,2,4-triazine-5-one (**4g**).

This compound was obtained in 84% yield, mp: 234-5 °C (EtOH); ^{1}HNMR, (d_6-DMSO): δ 2.48 (s, 3H, CH_3), 2.6 (s, 3H, CH_3), 7.48 (m, 2H, Ar-H), 8.0 (m, 2H, Ar-H), 14.6 (s, broad, 1H, NH); IR (KBr disc) 3140, 3070, 1595, 1515, 1450, 1355 cm^{-1}; MS m/z M^+ 257(6), 256(34), 255(52), 254(88), 224(38), 223(46), 194(55), 132(20), 115(80).

Anal. Calcd. for $C_{12}H_{11}N_5S$: C, 56.01; H, 4.30; N, 27.21. Found: C, 55.97; H, 4.25; N, 26.98.

2-(*p*-Acetanilide)-8-methyl-6*H*-1,2,4-triazolo[1,5-*d*]1,2,4-triazine-5-one (**4h**).

This compound was obtained in 60% yield, mp: 301-3 °C (EtOH); ^{1}H NMR, (d_6-DMSO): δ 2.09 (s, 3H, CH_3), 2.6 (s, 3H, CH_3), 7.75 (d, *J* = 8.54 Hz, 2H, Ar-H), 8.2 (d, *J* = 8.54 Hz, 2H, Ar-H), 10.22 (s, 1H, NH), 14.58 (s, broad, 1H, NH); IR (KBr disc) 3300, 31501670, 1600, 1525, 1455, 1320 cm^{-1}; MS m/z M^+ 300(6), 299(67), 298(67), 297(100), 254(25), 253(65), 198(44), 183(26), 182(82), 156(38), 130(20).

Anal. Calcd. for $C_{14}H_{13}N_5OS$: C, 52.00; H, 4.00; N, 28.00. Found: C, 52.30; H, 4.07; N, 27.86.

2-(*p*-Aminophenyl)-8-methyl-6*H*-1,2,4-triazolo[1,5-*d*]1,2,4-triazine-5-one (**4i**).

This compound was obtained in 62% yield, mp: 323-4 °C (acetone); ^{1}H NMR, (d_6-DMSO): δ 2.45 (s, 3H, CH_3), 5.55 (s, broad, 2H, NH_2), 6.65 (d, *J* = 7.85 Hz, 2H, Ar-H), 7.72 (d, *J* = 7.85 Hz, 2H, Ar-H), 14.21 (s, broad, 1H, NH); IR (KBr disc) 3420, 3350, 2985, 1615, 1495, 1440, 1300 cm^{-1}; MS m/z M^+ 258(2), 257(4), 255(57), 237(15), 214(26), 210(100), 183(35), 158(34), 118(36), 116(92).

Anal. Calcd. for $C_{12}H_{11}N_5S$: C, 56.01; H, 4.30; N, 27.21. Found: C, 56.28; H, 4.09; N, 26.91..

2-(*p*-Hydroxyphenyl)-8-methyl-6*H*-1,2,4-triazolo[1,5-*d*]1,2,4-triazine-5-one (**4j**).

This compound was obtained in 68% yield, mp: 331-2 °C (EtOH); ^{1}H NMR, (d_6-DMSO): δ 2.58 (s, 3H, CH_3), 6.94 (d, *J* = 8.27 Hz, 2H, Ar-H), 8.05 (d, *J* = 8.27 Hz, 2H, Ar-H), 10.13 (s, broad, 1H, OH), 14.6 (s, broad, 1H, NH); IR (KBr disc) 3400, 3150, 1605, 1500, 1435, 1320 cm^{-1}; MS m/z M^+ 259(4), 258(33), 257(84), 256(100), 225(31), 224(39), 196(4), 195(75), 166(24), 153(21), 135(31), 103(51).

Anal. Calcd. for $C_{12}H_{10}N_4OS$: C, 50.96; H, 3.47; N, 27.02. Found: C, 49.88; H, 3.90; N, 26.03.

2-(9-Phenanthrenyl)-8-methyl-6*H*-1,2,4-triazolo[1,5-*d*]1,2,4-triazine-5-one (**4k**).

This compound was obtained in 73% yield, mp: 302-3 °C (EtOH/ DMAc); ^{1}H NMR, (d_6-DMSO): δ 2.66 (s, 3H, CH_3), 7.72 – 9.18 (m, 9H, Ar-H), 14.68 (s, broad, 1H, NH); IR (KBr disc) 3420, 3350, 2985, 1615, 1495, 1440, 1300 cm^{-1}; MS m/z M^+ 343(4), 342(14), 341(48), 340(100), 280(15), 279(60), 265(38), 199(69), 186(15), 174(12).

Anal. Calcd. for $C_{19}H_{13}N_5S$: C, 66.47; H, 3.82; N, 20.40. Found: C, 66.75; H, 3.82; N, 20.34.

2-(2-Thiophenyl)-8-methyl-6*H*-1,2,4-triazolo[1,5-*d*]1,2,4-triazine-5-one (**4l**).

This compound was obtained in 75% yield, mp: 277-8 °C (EtOH); ^{1}H NMR, (d_6-DMSO): δ 2.59 (s, 3H, CH_3), 7.27 (dd, *J* = 4.9 Hz, 1H, Ar-H), 7.9 (dd, *J* = 4.3 Hz, 2H, Ar-H), 14.6 (s, broad, 1H, NH); IR (KBr disc) 3240, 3080, 1595, 1560, 1470, 1410 cm^{-1}; MS m/z M^+ 249(3), 246(4), 247(12), 245(100), 216(11), 214(30), 186(95), 170(42), 157(16), 148(22), 124(49), 119(48), 108(91).

Anal. Calcd. for $C_9H_7N_5S_2$: C, 66.47; H, 3.79; N, 20.40. Found: C, 66.75; H, 3.82; N, 20.34.

2-(4-Pyridinyl)-8-methyl-6*H*-1,2,4-triazolo[1,5-*d*]1,2,4-triazine-5-one (**4m**).

This compound was obtained in 88% yield, mp: 363-4 °C (EtOH/ DMAc); ^{1}H NMR, (d_6-DMSO): δ 2.62 (s, 3H, CH_3), 7.1 (d, *J* = 4.86 Hz, 2H, Ar-H), 8.8 (d, *J* = 4.86 Hz, 2H, Ar-H), 14.62 (s, broad, 1H, NH); IR (KBr disc) 3250, 3070, 1600, 1510, 1450, 1385 cm^{-1}; MS m/z M^+ 244(5), 243(7), 242(100), 241(22), 181(25), 104(33), 120(27), 82(23), 54(5), 51(3), 50(7).

Anal. Calcd. for $C_{10}H_8N_6S$: C, 49.18; H, 3.27; N, 34.42. Found: C, 48.98; H, 3.43; N, 34.01.

8-Methyl-5-methylthio-2-phenyl-6*H*-1,2,4-triazolo[1,5-*d*]-1,2,4-triazine (**10**).

Compound **4a** (1.215 g, 0.005 mol) was dissolved in 0.5 *N* sodium hydroxide solution (15 mL). To this solution methyl iodide (0.44 mL, 0.005 mol) was added dropwise at room temperature. This mixture was stirred for 4 hrs at ambient temperature. The precipitated solid was collected by filtration, washed with water and crystallized from EtOH to afford the titled compound. This compound was obtained in 67% yield, mp: 157-8 °C (EtOH); ^{1}H NMR, ($CDCl_3$): δ 2.86 (s, 3H, CH_3), 2.96 (s, 3H, -SCH_3), 7.5 (m, 3H, Ar-H), 8.32 (m, 2H, Ar-H); IR (KBr disc) 3050, 1520, 1440, 1395, 1320 cm^{-1}, MS m/z M^+ 257(4), 256(32), 254(100), 185(37), 169(44), 143(42), 108(82), 107(28), 81(19), 71(12).

Anal. Calcd. for $C_{12}H_{11}N_5S$ C, 56.03; H 4.28; N, 27.23. Found: C, 56.28; H, 4.09; N, 26.91.

8-Methyl-5-morpholino-2*H*-phenyl-6*H*-1,2,4-triazolo[1,5-*d*]-1,2,4-triazine (**11a**).

Compound **10** (0.257 g, 0.001 mol) and morpholine (0.174 g, 0.002 mol) in ethanol (5 mL) were refluxed for 8 hrs. The mixture was cooled to room temperature and the precipitated solid was collected by filtration, washed with water and crystallized from EtOH to afford the titled compound. This compound was obtained in 81% yield, mp: 196-7 °C (EtOH); ^{1}H NMR, (d_6-DMSO): δ 2.75 (s, 3H, CH_3), 3.91 (d, *J* = 3.8 Hz, 8H, morpholine-H), 7.58 (m, 3H, Ar-H), 8.23 (m, 2H, Ar-H); IR (KBr disc) 2980, 2910, 1585, 1530, 1490, 1440 cm^{-1}; MS m/z M^+ 273(4), 271(20), 269(6), 267(100), 223(19), 209(87), 133(70), 132(73), 119(31).

Anal. Calcd. for $C_{15}H_{16}N_6O$: C, 40.99; H, 2.48; N, 21.73. Found: C, 41.03; H, 2.35; N, 21.61.

8-Methyl-5-benzylamino-2-phenyl-6*H*-1,2,4-triazolo[1,5-*d*]-1,2,4-triazine (**11b**).

Compound **10** (0.257 g, 0.001 mol) and benzylamine (0.214 g, 0.002 mol) in ethanol (5 mL) were refluxed for 8 hrs. The reaction mixture was cooled down to room temperature and the precipitated solid was collected by filtration, washed with water and crystallized from EtOH to afford the titled compound. This compound was obtained in 73% yield, mp: 166-8 °C (EtOH); ^{1}H NMR, ($CDCl_3$): δ 2.87 (s, 3H, CH_3), 4.96 (d, 2H, CH_2), 6.14 (t, 1H, NH), 7.46 (m, 8H, 2 Ar-H), 8.26 (m, 2H, 2 Ar-H); IR (KBr disc) 3200, 3040, 2920, 1610, 1465 cm^{-1}; MS m/z M^+ 316(5), 315(27), 314(68), 284(51), 141(82), 140(64), 129(63), 113(53), 102(79), 90(100), 88(37).

Anal. Calcd. for $C_{18}H_{16}N_6$: C, 68.33; H, 5.97; N, 26.56. Found: C, 67.99; H, 5.89; N, 26.61.

REFERENCES AND NOTES

[1a] D. T. Hurst, *Prog. Heterocyclic Chem.*, **7**, 244 (1995); [b] H. Groger, J. Sans and T. Gunther, *Chim. Oggi*, **18**, 12 (2000).

[2] F. M. Adam, A. J. Burton, K. S. Cardwell, R. A. Cox, R. A. Henson, K. Mills, J. C. Prodger, M. B. Shilling and D. T. Tape, *Tetrahedron Lett.*, **44**, 5657 (2003).

[3a] M. M. Heravi and M. Bakavoli, *J. Chem. Res.*, **11**, 480 (1995); [b] M. M. Heravi, K. Aghapoor and M. A. Nooshabadi, *Synth. Commun.*, **28**, 233 (1998); [c] M. M. Heravi, K. Aghapoor, M. A. Nooshabadi and M. M. Mojtahedi, *Monatsh. Chem.*, **128**, 1143 (1997); [d] M. M. Heravi, A. Kivanloo, M. Rahimizadeh, M. Bakavoli and M. Ghassemzadeh, *Phosphorus, Sulfur and Silicon*, **177**, 249 (2002); [e] M. M. Heravi, A. Kivanloo, M. Rahimzadeh, M. Bakavoli and M. Ghassemzadeh, *Tetrahedron Lett*., **45**, 5747 (2004); [f] M. M. Heravi, A. Kivanloo, M. Rahimzadeh, M. Bakavoli, M. Ghassemzadeh and B. Neumüller, *Tetrahedron Lett*., **46**, 1607 (2005).

[4 C. A. Lovelette and K. Geagon, *J. Heterocyclic Chem.*, **19**, 1345 (1982).

[5] A. Dornow, H. Menzel and P. Marx, *Ber.*, 2179 (1964).

[6] M. Ghassemzadeh, K. Aghapoor, M. M. Heravi and B. Neumüller, *Z. Anorg. Allg. Chem.*, **624**, 1969 (1998).