SYNTHESIS OF 1,3,5-TRIAZINE DERIVATIVES BY THE REACTION OF *S*,*S*'-DIMETHYL *N*-CYANOCARBONIMIDODITHIOATE WITH AMIDES

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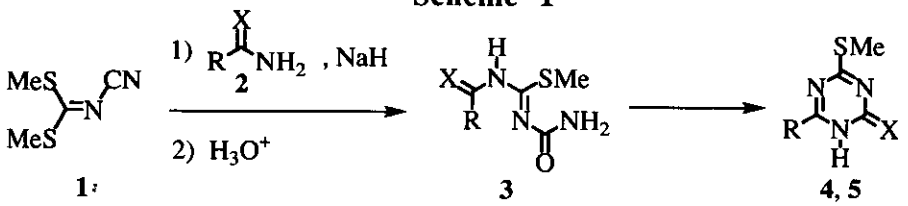
Abstract - *S*,*S*'-Dimethyl *N*-cyanocarbonimidodithioate (**1**) reacted with amides (**2**) in the presence of sodium hydride in a mixture of benzene and *N*,*N*-dimethylacetamide to give the corresponding *N*-acyl-*N*'-carbamoyl-*S*-methylisothioureas (**3**). Refluxing of **3** in methanol gave the corresponding cyclized product, 1,3,5-triazin-2(1*H*)-one derivatives (**4**). Compounds (**4**) were found to be useful intermediates for the synthesis of trisubstituted 1,3,5-triazines.

S,*S*'-Dimethyl *N*-cyanocarbonimidodithioate (**1**),[1] readily prepared by the reaction of cyanamide with carbon disulfide followed by alkylation, is an interesting electrophilic reagent for the introduction of not only an aminomethylene group into amines and active methylene compounds but also a -C=N-C=N- unit in the ring of heterocyclic compounds.[2-7] We report a synthesis of trisubstituted 1,3,5-triazine derivatives using **1** as the starting material.

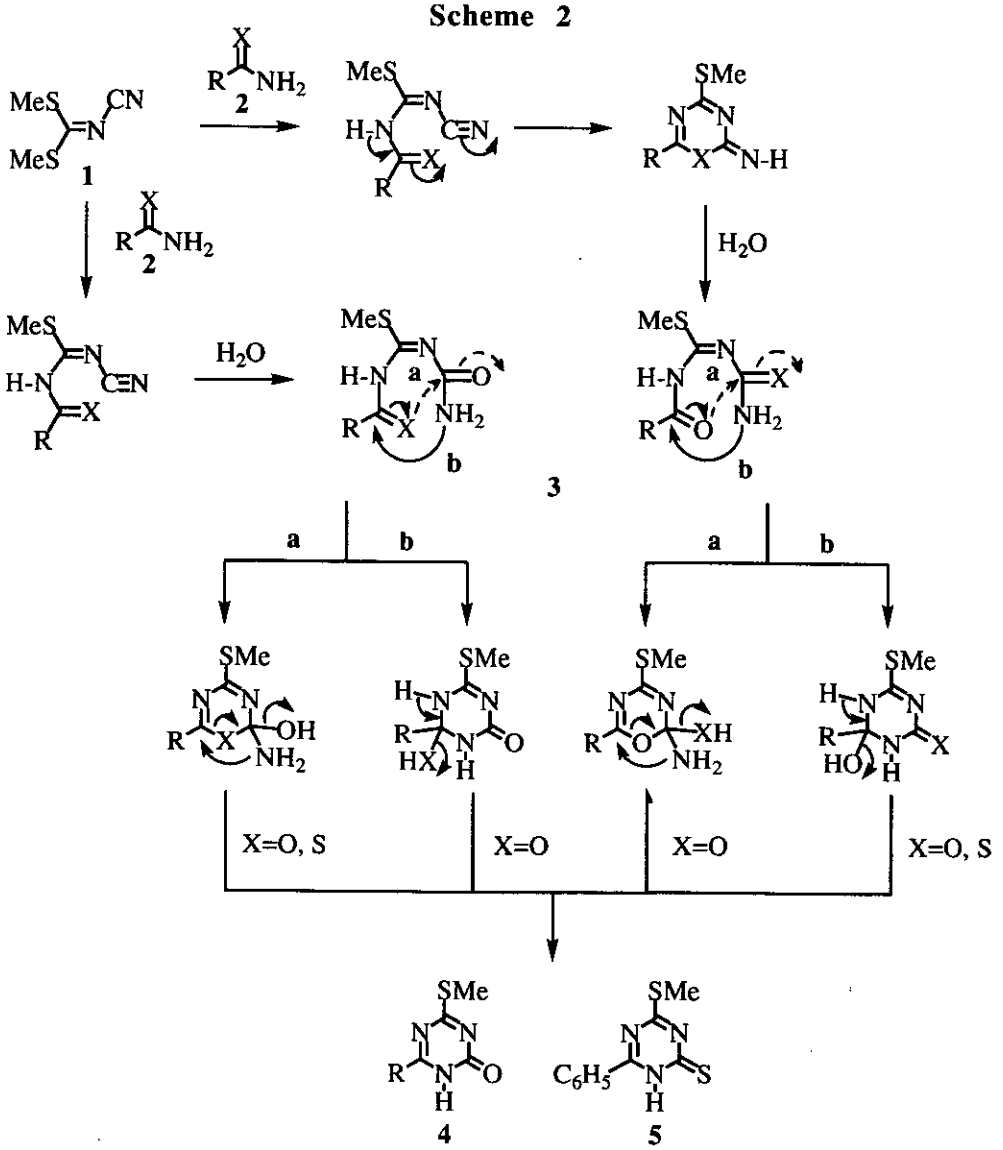
We have previously found that the use of sodium hydride as a base in reactions of ketene dithioacetals with amides gives the satisfactory results.[8] The reaction of **1** with benzamide (**2a**) in the presence of sodium hydride in a mixture of benzene and *N*,*N*-dimethylacetamide at room temperature for 24 h afforded the corresponding conjugate addition-elimination product (**3a**) in 70 % yield. This product was found to be urea derivative, *N*-carbamoyl-*N*'-benzoyl-*S*-methylisothiourea (**3a**), from the elemental analysis and ir, uv, and ^{1}H-nmr spectral

Scheme 1



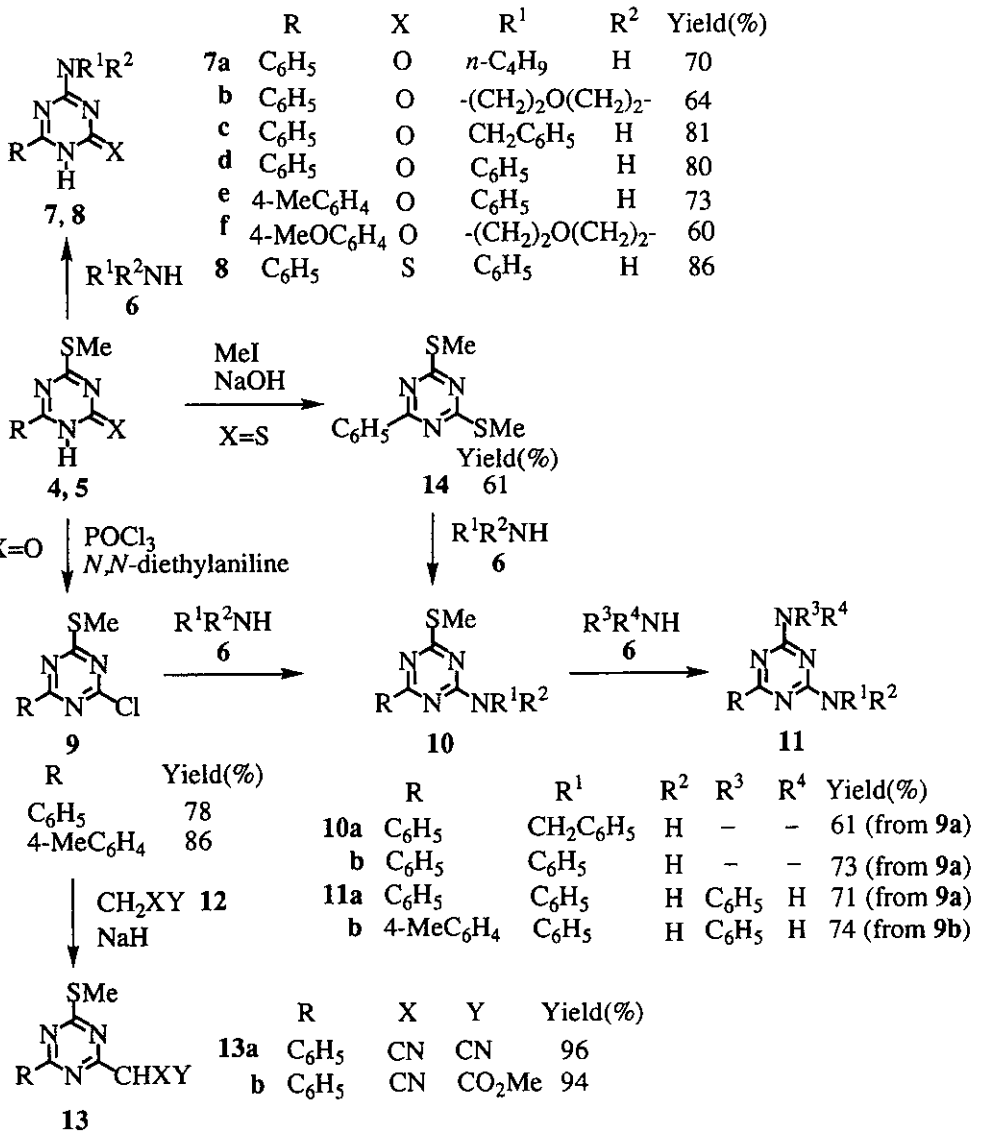
	R	X	Yield(%)		R	X	Yield(%)
3a	C_6H_5	O	70	**4a**	C_6H_5	O	75
b	4-MeC_6H_4	O	70	**b**	4-MeC_6H_4	O	60
c	4-$MeOC_6H_4$	O	58	**c**	4-$MeOC_6H_4$	O	54
d	Me	O	46	**5**	C_6H_5	S	70 (from **1**)

Scheme 2



data. The resulting (**3a**) was converted to 4-methylthio-6-phenyl-1,3,5-triazin-2(1*H*)-one (**4a**) at reflux in methanol in 75 % yield. Compounds (**3b-d**) and (**4b** and **4c**) were also synthesized by the reaction of **1** with the corresponding carboxamides (*p*-toluamide(**2b**), *p*-anisamide(**2c**), and acetamide(**2d**)) in a similar manner to that described for **3a** and **4a**. An attempt of the cyclization of **3d** was unsuccessful. Reaction of compound (**1**) with thiobenzamide (**2e**) in benzene, followed by cyclization yielded 4-methylthio-6-phenyl-1,3,5-triazin-2(1*H*)-thione (**5**) in good yield. In this case, the corresponding intermadiate, urea derivative, could not be isolated. We have proposed several ring opening-ring closure methanisms for the formation of 1,3,5-triazine ring (Scheme 2).

Scheme 3



The aminolysis of **4a,b,c** and **5** with amines (**6**), such as *n*-butylamine (**6a**), morpholine (**6b**), benzylamine (**6c**) and aniline (**6d**), at 120°C gave 4(or 6)-amino-1,3,5-triazin-2(1*H*)-one (**7a-f**) and 4-phenyl-6-phenylamino-1,3,5-triazin-2(1*H*)-thione (**8**)[9] in 64-86 % yields. Chlorination of **4a** and **4b** with phosphorus oxychloride gave 2-chloro-1,3,5-triazine derivatives (**9a** and **9b**) in 78 and 86 % yields, respectively. Reactions of **9a** with 2 equivalents of amines at 100°C gave the corresponding 2-amino-1,3,5-triazine derivatives (**10a** and **10b**[10]) in good yields. Reactions of **9a** and **9b** with 4 equivalents of aniline (**6d**) at 150°C for 6 h provided bis(phenylamino)-1,3,5-triazines (**11a** and **11b**) in 71 and 74 % yields. 2-Chlorotriazine (**9a**) also reacted with active methylene compounds, such as malononitrile (**12a**) and methyl cyanoacetate (**12b**), in the presence of sodium hydride in DMSO at room temperature for 6 h to give the products (**13a**) and (**13b**) in 96 and 94 % yields. On the other hand, the reaction of 4-methylthio-1,3,5-triazin-2(1*H*)-one (**4a**) with methyl cyanoacetate (**12b**) did not occur under similar conditions. Compound (**5**) was readily converted to 2,4-bis(methylthio)-6-phenyl-1,3,5-triazine (**14**)[11] by methylation with methyl iodide in good yield. The reaction of compound (**14**) with 2 equivalents of aniline (**6d**) at 120°C for 4 h gave **10b** in 70 % yield.

EXPERIMENTAL

All melting points were determined in a capillary tube and are uncorrected. Infrared (ir) spectra were recorded in potassium bromide pellets on a JASCO IRA-2 spectrophotometer and ultraviolet (uv) absorption spectra were determined in 95% ethanol on a Hitachi EP-S2 spectrophotometer. ^{1}H Nuclear magnetic resonance (nmr) spectra were obtained on Varian Gemini-200(200 MHz) and Gemini-300(300 MHz) spectrometers with tetramethylsilane as an internal standard. Mass spectra (ms) were recorded on a JEOL JMS-DX303 mass spectrometer.

Reaction of *S,S'*-Dimethyl *N*-cyanocarbonimidodithioate (1) with amides (2); General Procedure: To a suspension of sodium hydride (60 % in paraffin, 800 mg, 20 mmol) in 40 ml of a mixture of benzene and *N,N*-dimethylacetamide (1:1) was added a mixture of **1** (1.46 g, 10 mmol) and an amide (10 mmol). The resulting mixture was stirred at room temperature for 24 h. The reaction mixture was poured into 200 ml of cold water and acidified with 10% hydrochloric acid. After standing for 1 h, the resulting precipitate was collected by filtration and dried. The crude product was recrystallized from benzene or a mixture of benzene and

hexane.

***N*-Carbamoyl-*N'*-benzoyl-*S*-methylisothiourea (3a):** yield 70 %; pale yellow needles, mp 141-143°C(benzene); ir (KBr) νmax: 3400, 3340, 1700, 1535 cm^{-1}; uv (EtOH) λmax nm(log ε): 257(4.40), 201(4.36); ^{1}H-nmr ($CDCl_3$) δ: 2.45 (3H, s, SMe), 3.36 (2H, br s, NH_2), 7.07-8.24(5H, m, aromatic-H), 11.86(1H, br s, NH); ms *m/z*(%): 237(M^+,28), 147(23), 105(100), 77(41). Anal. Calcd for $C_{10}H_{11}N_3O_2S$: C, 50.62; H, 4.67; N, 17.71; S, 13.51. Found; C, 50.90; H, 4.62; N, 17.81; S, 13.28.

***N*-Carbamoyl-*N'*-*p*-methylbenzoyl-*S*-methylisothiourea (3b):** yield 70 %; pale yellow needles, mp 143-144°C(benzene); ir (KBr) νmax: 3475, 3190, 1685, 1630, 1560, 1370 cm^{-1}; uv (EtOH) λmax nm(log ε): 262(4.48); ^{1}H-nmr ($CDCl_3$) δ: 2.39 (3H, s, Me), 2.42(3H, s, SMe), 5.12 (1H, br s, NH), 5.52(2H, br s, NH_2), 7,28(2H, d, *J*=8.1 Hz, aromatic-H), 7.85(2H, d, *J*=8.1 Hz, aromatic-H); ms *m/z*(%): 252(M^++1, 4), 251(M^+, 26), 161(12), 119(100), 91(28). Anal. Calcd for $C_{11}H_{13}N_3O_2S$: C, 52.57; H, 5.21; N, 16.72; S, 12.76. Found; C, 52.72; H, 5.09; N, 16.43; S, 13.02.

***N*-Carbamoyl-*N'*-*p*-methoxybenzoyl-*S*-methylisothiourea (3c):** yield 58 %; colorless needles, mp 133-134°C(benzene); ir (KBr) νmax: 3460, 3400, 3200, 1560, 1360, 1235 cm^{-1}; uv (EtOH) λmax nm(log ε): 279(4.45), 220(4.21); ^{1}H-nmr ($CDCl_3$) δ: 2.39 (3H, s, SMe), 3.87 (3H, s, OMe), 5.05(1H, br s, NH), 5.56(2H, br s, NH_2), 6.97(2H, d, *J*=6.8 Hz, aromatic-H), 7.94(2H, d, *J*=6.8 Hz, aromatic-H); ms *m/z*(%): 267(M^+, 21), 138(14), 135(100). Anal. Calcd for $C_{11}H_{13}N_3O_3S$: C, 49.42; H, 4.90; N, 15.72; S, 12.00. Found; C, 49.59; H, 4.83; N, 15.75; S, 12.09.

***N*-Carbamoyl-*N'*-acetyl-*S*-methylisothiourea (3d):** yield 46 %; yellow needles, mp 120-122°C (benzene); ir (KBr) νmax: 3410, 3340, 3275, 3230, 1710, 1660, 1570, 1410, 1360, 1235 cm^{-1}; uv (EtOH) λmax nm(log ε): 261(4.14), 236(4.19); ^{1}H-nmr ($CDCl_3$) δ: 2.18(3H, s, Me), 2.32 (3H, s, SMe), 5.00 (1H, br s NH), 5.40(2H, br s, NH_2); ms *m/z*(%): 175(M^+,35), 160(15), 132(18), 86(51), 42(100). Anal. Calcd for $C_5H_9N_3O_2S$: C, 34.27; H, 5.18; N, 23.98; S, 18.30. Found; C, 34.55; H, 4.92; N, 24.01; S, 18.34.

4-Methylthio-6-phenyl-1,3,5-triazin-2(1*H*)-thione (5): yield 70 %; yellow needles, mp 167-170°C

(benzene); ir (KBr) νmax: 1520, 1218 cm^{-1}; uv (EtOH) λmax nm(log ε): 290(4.47), 258(4.46); ^{1}H-nmr (DMSO-d_6) δ: 2.55(3H, s, SMe), 3.38 (1H, br s, NH), 7.50-7.80(3H, m, aromatic-H), 8.26(2H, d, *J*=8.3 Hz, aromatic-H); ms *m/z*(%): 235(M^+,100), 202(29), 188(11), 147(10), 132(29), 104(52). Anal. Calcd for $C_{10}H_9N_3S_2$: C, 51.04; H, 3.86; N, 17.86; S, 27.25. Found; C, 51.23; H, 3.89; N, 17.79; S, 26.97.

Cyclization of 3; General Procedure: A solution of **3** (5 mmol) in 100 ml of methanol was refluxed for 24 h. After removal of the solvent the residue was recrystallized from benzene-methanol.

4-Methylthio-6-phenyl-1,3,5-triazin-2(1*H*)-one (4a): yield 75 %; colorless needles, mp 275-278°C (benzene-methanol); ir (KBr) νmax: 1685, 1535, 1265 cm^{-1}; uv (EtOH) λmax nm(log ε): 257(4.24), 251(4.29), 230(4.19); ^{1}H-nmr (DMSO-d_6) δ: 2.51 (3H, s, SMe), 7.07-8.24(5H, m, aromatic-H), 11.86(1H, br s, NH); ms *m/z*(%): 219(M^+, 100), 186(20), 116(31), 105(28), 104(76). Anal. Calcd for $C_{10}H_9N_3OS$: C, 54.78; H, 4.14; N, 19.16; S, 14.62. Found; C, 54.78; H, 4.28; N, 18.97; S, 14.35.

4-(4-Methylphenyl)-6-methylthio-1,3,5-triazin-2(3*H*)-one (4b): yield 60 %; pale yellow needles, mp 290-291°C(benzene-methanol); ir (KBr) νmax: 1680, 1535, 1502, 1268 cm^{-1}; uv (EtOH) λmax nm(log ε): 262(4.33), 201(4.42); ^{1}H-nmr (DMSO-d_6) δ: 2.49 (3H, s, Me), 2.58(3H, s, SMe), 7.38(2H, d, *J*=8.0 Hz, aromatic-H), 8.11(2H, d, *J*=8.0 Hz, aromatic-H), 12.45(1H, br s, NH); ms *m/z*(%): 233(M^+,100), 218(14), 200(17), 118(74), 116(36). Anal. Calcd for $C_{11}H_{11}N_3OS$: C, 56.63; H, 4.75; N, 18.01; S, 13.74. Found; C, 56.50; H, 4.75; N, 17.88; S, 13.83.

4-(4-Methoxyphenyl)-6-methylthio-1,3,5-triazin-2(3*H*)-one (4c): yield 54 %; colorless needles, mp 258-263°C(benzene-methanol); ir (KBr) νmax: 2925, 1680, 1600, 1585, 1500, 1255, 1160 cm^{-1}; uv (EtOH) λmax nm(log ε): 308(insufficient solubility); ^{1}H-nmr (DMSO-d_6) δ: 2.50 (3H, s, SMe), 3.86(3H, s, OMe), 7.38(2H, d, *J*=8.0 Hz, aromatic-H), 8.11(2H, d, *J*=8.0 Hz, aromatic-H), 10.60(1H, br s, NH); ms *m/z*(%): 249(M^+, 100), 234(17), 202(16), 134(67), 116(23). HR-ms Calcd for $C_{11}H_{11}N_3O_2S$ *m/z*: 249.0572. Found *m/z*: 249.0576.

Chlorination of 4; General Procedure: A mixture of **4** (10 mmol), 20 ml(ca. 210 mmol) of phosphorus

oxychloride and 2 ml (ca. 13 mmol) of *N*,*N*-diethylaniline was refluxed for 1 h. After removal of excess of phosphorus oxychloride, the residue was treated with 300 ml of cold water. The resulting precipitates was collected by filtration and dried. The crude product was recrystallized from hexane.

2-Chloro-4-methylthio-6-phenyl-1,3,5-triazine (9a): yield 78 %; pale yellow needles, mp 88-89°C(hexane); ir (KBr) νmax: 1520, 1480, 1380, 1240 cm^{-1}; uv (EtOH) λmax nm(log ε): 270(4.64); ^{1}H-nmr ($CDCl_3$) δ: 2.66 (3H, s, SMe), 7.44-7.68(3H, m, aromatic-H), 8.48(2H, dd, *J*=4.9 and 1.4 Hz, aromatic-H); ms *m/z*(%): 239(M^++2, 12), 238(M^++1, 5), 237(M^+, 27), 169(18), 149(11), 104(25). Anal. Calcd for $C_{10}H_8N_3SCl$: C, 50.53; H, 3.39; N, 17.68; S, 13.49; Cl, 14.92. Found; C, 50.72; H, 3.45; N, 17.57; S, 13.24; Cl, 14.88.

2-Chloro-4-(4-methylphenyl)-6-methylthio-1,3,5-triazine (9b): yield 86 %; orange needles, mp 107-108°C(hexane); ir (KBr) νmax: 1610, 1520, 1470, 1385, 1315, 1240 cm^{-1}; uv (EtOH) λmax nm(log ε): 281(4.62); ^{1}H-nmr ($CDCl_3$) δ: 2.44 (3H, s, Me), 2.65(3H, s, SMe), 7.30(2H, d, *J*=8.0 Hz, aromatic-H), 8.36(2H, d, *J*=8.0 Hz, aromatic-H); ms *m/z*(%): 253(M^++2, 38), 252(M^++1, 16), 251(M^+,100), 118(89), 117(14), 116(13). Anal. Calcd for $C_{11}H_{10}N_3SCl$: C, 52.48; H, 4.00; N, 16.69; S, 12.74; Cl, 14.08. Found; C, 52.62; H, 4.01; N, 16.66; S, 12.52; Cl, 13.80.

2,4-Bis(methylthio)-6-phenyl-1,3,5-triazine (14): To a solution of **5** (1.0 g, 4.25 mmol) and a sodium hydroxide solution (sodium hydroxide 500 mg, 12.5 mmol + water 1 ml) in 15 ml of dimethyl sulfoxide, methyl iodide (1.28 g, 9 mmol) was added portionwise under stirring at room temperature. After stirring for 8 h, the reaction mixture was poured into 100 ml of cold water and the resulting precipitates were collected by filtration to give 0.65 g (61 %) of colorless solid, mp 91-93°C. An analytical sample was recrystallized from ethanol to give colorless needles, mp 93-94°C[lit., [11] mp 97°C].

Reaction of 4,5,9, and 14 with amines (6); General Procedure: A mixture of **4** (or **5**, **9**, **14**) (2 mmol) and an amine (4-8 mmol) was heated at 120°C for 4 h or 150°C for 6 h. After cooling, 3 ml of methanol was added to the residue and the resulting precipitate was collected by filtration. An analytical sample was recrystallized with ethanol, methanol or benzene-methanol.

4-Butylamino-6-phenyl-1,3,5-triazin-2(1*H*)-one (7a): yield 70 %; colorless needles, mp 260-262°C

(benzene-methanol); ir (KBr) νmax: 1610, 1560, 1490 cm^{-1}; uv (EtOH) λmax nm(log ε): 246(4.25); ^{1}H-nmr (DMSO-d_6) δ: 0.89(3H, t, *J*=7.4 Hz, Me), 1.20-1.62(4H, m, $(CH_2)_2$), 3.15-3.30 (2H, m, CH_2), 3.30-3.49(1H. m, NH), 7.42-8.30(5H, m, aromatic-H), 11.80(1H, br s, NH); ms *m/z*(%): 245(M^++1, 17), 244(M^+, 95), 229(21), 215(42), 202(100), 201(70), 188(66), 187(22), 147(19). Anal. Calcd for $C_{13}H_{16}N_4O$: C, 63.91; H, 6.60; N, 22.94. Found; C, 64.12; H, 6.61; N, 22.81.

4-Morpholino-6-phenyl-1,3,5-triazin-2(1*H*)-one (7b): yield 64 %; colorless needles, mp 295-298°C (benzene-methanol); ir (KBr) νmax: 1650, 1610, 1541, 1490 cm^{-1}; uv (EtOH) λmax nm(log ε): 270(4.17), 241(4.34), 226(4.39), 202(4.52); ^{1}H-nmr (DMSO-d_6) δ: 3.50-4.08 (8H, m, -$(CH_2)_2O(CH_2)_2$-), 7.50-7.77(3H, m, aromatic-H), 8.19(2H, d, *J*=7.0 Hz, aromatic-H); ms *m/z*(%): 258(M^+,100), 228(38), 227(49), 213(40), 201(47). Anal. Calcd for $C_{13}H_{14}N_4O_2$: C, 60.45; H, 5.46; N, 21.70. Found; C, 60.37; H, 5.47; N, 21.67.

4-Benzylamino-6-phenyl-1,3,5-triazin-2(1*H*)-one (7c): yield 81 %; colorless needles, mp 316-319°C (benzene-methanol); ir (KBr) νmax: 3080, 3020, 2945, 1670, 1610, 1560, 1498, 1488 cm^{-1}; uv (EtOH) λmax nm(log ε): 249(insufficient solubility); ^{1}H-nmr (DMSO-d_6) δ: 4.44-4.70(2H, m, CH_2), 7.16-7.67(8H, m, aromatic-H), 8.12(2H, d, *J*=7.0 Hz, aromatic-H), 8.20(1H, br s, NH), 8.45-8.60(1H, m, NH); ms *m/z*(%): 278(M^+,100), 193(33), 106(43), 104(33). Anal. Calcd for $C_{16}H_{14}N_4O$: C, 69.05; H, 5.07; N, 20.13. Found; C, 69.31; H, 5.19; N, 19.90.

4-Phenyl-6-phenylamino-1,3,5-triazin-2(3*H*)-one (7d): yield 80 %; colorless needles, mp 331-335°C (benzene-methanol); ir (KBr) νmax: 3290, 1665, 1600, 1540, 1445 cm^{-1}; uv (EtOH) λmax nm(log ε): 253(4.31); ^{1}H-nmr (DMSO-d_6) δ: 7.09(1H, t, *J*=7.0 Hz, aromatic-H), 7.36(2H, t, *J*=7.5 Hz, aromatic-H), 7.50-7.95(5H, m, aromatic-H), 8.19(2H, d, *J*=8.0 Hz, aromatic-H), 10.05-10.25(1H, m, NH); ms *m/z*(%): 264(M^+,100), 263(M^+-1, 96), 160(20), 147(15), 119(18), 118(27), 104(39). Anal. Calcd for $C_{15}H_{12}N_4O$: C, 68.17; H, 4.58; N, 21.20. Found; C, 68.20; H, 4.74; N, 21.29.

4-(4-Methylphenyl)amino-6-phenyl-1,3,5-triazin-2(1*H*)-one (7e): yield 73 %; yellow needles, mp

350°C(decomp.) (benzene-methanol); ir (KBr) νmax: 3260, 3050, 1650, 1600, 1545, 1500, 1435, 1355 cm^{-1}; uv (EtOH) λmax nm(log ε): 259(4.25); ^{1}H-nmr (DMSO-d_6) δ: 2.41(3H, s, Me), 7.07(1H, t, *J*=7.0 Hz, aromatic-H), 7.31(2H, t, *J*=7.0 Hz, aromatic-H), 7.39(2H, d, *J*=8.0 Hz, aromatic-H), 7.83(2H, m, aromatic-H). 8.09(2H, d, *J*=8.0 Hz, aromatic-H), 10.09(1H, br s, NH); ms *m/z*(%): 278(M^+, 90), 277(M^+-1, 85), 43(100). Anal. Calcd for $C_{16}H_{14}N_4O$: C, 69.05 H, 5.07; N, 20.13. Found; C, 68.82; H, 5.19; N, 19.88.

4-(4-Methoxyphenyl)amino-6-morpholino-1,3,5-triazin-2(3*H*)-one (7f): yield 60 %; colorless needles, mp 298-305°C (decomp.) (benzene-methanol); ir (KBr) νmax: 2960, 2850, 1675, 1600, 1550, 1505, 1595, 1440, 1260 cm^{-1}; uv (EtOH) λmax nm(log ε): 294(4.43), 221(4.48); ^{1}H-nmr (DMSO-d_6) δ: 3.50-4.00(8H, m, -$(CH_2)_2O(CH_2)_2$-), 3.85(3H, s, OMe), 7.07(2H, d, *J*=8.9 Hz, aromatic-H), 8.20(2H, d, *J*=8.9 Hz, aromatic-H), 11.89(1H, br s, NH); ms *m/z*(%): 288(M^+,100), 258(42), 257(51), 243(43), 231(50), 228(38), 134(79). Anal. Calcd for $C_{14}H_{16}N_4O_3$: C, 58.32; H, 5.59; N, 19.43. Found; C, 58.07; H, 5.43; N, 19.17.

4-Phenyl-6-phenylamino-1,3,5-triazin-2(1*H*)-thione (8): yield 86 %; pale yellow plates, mp 238-241°C (ethanol)[lit.,[9] mp 247°C].

2-Benzylamino-4-methylthio-6-phenyl-1,3,5-triazine (10a): yield 61 %; pale yellow needles, mp 128-131°C(benzene-methanol); ir (KBr) νmax: 3250, 1600, 1530, 1425, 1350 cm^{-1}; uv (EtOH) λmax nm(log ε): 245(4.62); ^{1}H-nmr (DMSO-d_6) δ: 2.57 (3H, s, SMe), 4.74(2H, dd, *J*=16.0 and 6.0 Hz, CH_2), 5.75(1H, br s, NH), 7.25-7.60(8H, m, aromatic-H), 8.40(2H, dd, *J*=16.0 and 6.0 Hz, aromatic-H); ms *m/z*(%): 309(M^++1, 21), 308(M^+, 100), 106(33). Anal. Calcd for $C_{17}H_{16}N_4S$: C, 66.20; H, 5.23; N, 18.17; S, 10.40. Found; C, 66.32; H, 5.34; N, 17.98; S, 10.16.

2-Methylthio-4-phenyl-6-phenylamino-1,3,5-triazine (10b): yield 73 %; pale yellow plates, mp 133-135°C(methanol)[lit.,[10] mp 135°C].

2,4-Bis(phenylamino)-6-phenyl-1,3,5-triazine (11a): yield 71 %; pale yellow needles, mp 216-218°C (benzene-methanol); ir (KBr) νmax: 3240, 1605, 1570, 1510, 1440 cm^{-1}; uv (EtOH) λmax nm(log ε):

266(4.78); ^{1}H-nmr (DMSO-d_6) δ: 7.12(3H, t, *J*=7.0 Hz, aromatic-H), 7.20(2H, br s, 2xNH), 7.39(3H, t, *J*=8.0 Hz, aromatic-H), 7.46-7.59(3H, m, aromatic-H), 7.68(4H, d, *J*=8.0 Hz, aromatic-H), 8.42(2H, dd, *J*=8.0 and 2.0 Hz, aromatic-H); ms *m/z*(%): 340(M^++1, 24), 339(M^+,100), 338(M^+-1, 42), 235(14). Anal. Calcd for $C_{21}H_{17}N_5$: C, 74.31; H, 5.05; N, 20.64. Found; C, 74.31; H, 5.19; N, 20.35.

2,4-Bis(phenylamino)-6-(4-methylphenyl)-1,3,5-triazine (11b): yield 74 %; colorless needles, mp 211-213°C(benzene-methanol); ir (KBr) νmax: 3250, 3100, 1610, 1575, 1505, 1430, 810, 755 cm^{-1}; uv (EtOH) λmax nm(log ε): 202(4.80), 270(4.86); ^{1}H-nmr (DMSO-d_6) δ: 2.50(3H, s, Me), 7.04(2H, t, *J*=7.0 Hz, aromatic-H), 7.22-7.45(6H, m, aromatic-H), 7.66-8.00(4H, m, aromatic-H), 8.28(2H, d, *J*=8.0 Hz, aromatic-H), 9.79(2H, br s, 2xNH); ms *m/z*(%): 354(M^++1, 26), 353(M^+,100), 352(M^+-1, 39), 118(19). Anal. Calcd for $C_{22}H_{19}N_5$: C, 74.76; H, 5.42; N, 19.82. Found; C, 74.68; H, 5.52; N, 19.59.

Reaction of 9a with active methylene compounds (12); General Procedure: A mixture of **9a** (475 mg, 2 mmol), an active methylene compound (**12**) (4 mmol), sodium hydride (60 % in paraffin, 160 mg, 4 mmol), and 15 ml of dimethyl sulfoxide was stirred at room temperature for 6 h. The reaction mixture was poured into 300 ml of cold water and acidified with 10 % hydrochloric acid. The precipitate was collected by filtration and recrystallized from methanol or benzene-methanol.

(2-Methylthio-4-phenyl-1,3,5-triazin-6-yl)malononitrile (13a): yield 96 %; lemon yellow needles, mp 273°C(decomp.) (methanol); ir (KBr) νmax: 2200, 1600, 1580, 1520 cm^{-1}; uv (EtOH) λmax nm(log ε): 306(4.52), 254(4.49); ^{1}H-nmr (DMSO-d_6) δ: 2.51 (3H, s, SMe), 4.60-5.30 (2H, m, NH and CH), 7.43-7.64(3H, m, aromatic-H), 8.26(2H, d, *J*=7.5 Hz, aromatic-H); ms *m/z*(%): 268(M^++1, 17), 267(M^+, 93), 240(10), 104(100). Anal. Calcd for $C_{13}H_9N_5S$: C, 58.41; H, 3.39; N, 26.20; S, 12.00. Found; C, 58.69; H, 3.52; N, 26.13; S, 11.77.

Methyl (2-methylthio-4-phenyl-1,3,5-triazin-6-yl)cyanoacetate (13b): yield 94 %; yellow needles, mp 210-213°C(benzene-methanol); ir (KBr) νmax: 2200, 1660, 1600, 1530, 1500, 1480, 1360, 1285 cm^{-1}; uv (EtOH) λmax nm(log ε): 308(4.58), 260(4.38), 201(4.44); ^{1}H-nmr (DMSO-d_6) δ: 2.50 (3H, s, SMe), 3.39(1H, br s, NH or CH), 3.80(3H, s, OMe), 7.65-7.89(3H, m, aromatic-H), 8.08(2H, d, *J*=7.5 Hz, aromatic-H),

8.40(1H, br s, NH or CH); ms *m/z* (%): 300(M^+,100), 269(30), 268(40), 104(82), 77(25), 74(37). Anal. Calcd for $C_{14}H_{12}N_4O_2S$: C, 55.98; H, 4.03; N, 18.66; S, 10.68. Found; C, 56.28; H, 4.06; N, 18.63; S, 10.44.

REFERENCES

1. R. Gompper, M. Gang, and F. Saygin, *Tetrahedron Lett.*, **1987**, 1885.
2. K. Dewald, P. Blauschmidt, and R. Mayer, *J. Pract. Chem.*, 1967, **35**, 97.
3. R. J. Timmons and L. S. Wittenbrook, *J. Org. Chem.*, 1967, **32**, 1566.
4. H. Kristinsson, *J. Chem. Soc., Chem. Commun.*, **1974**, 350.
5. L. S. Wittenbrook, *J. Heterocycl. Chem.*, 1974, **12**, 37.
6. J. Reiter, L. Pongs, T. Somorai, and P. Dvortsak, *J. Heterocycl. Chem.*, 1986, **23**, 401.
7. Y. Tominaga, S. Ohno, S. Kohra, H. Fujito, and H. Mazume, *J. Heterocycl. Chem.*, 1991, **28**, 1039.
8. S. Kohra, Y. Tominaga, and A. Hosomi, *J. Heterocycl. Chem.*, 1988, **25**, 959.
9. C. P. Joshua and V. P. Rajan, *Aust. J. Chem.*, 1974, **27**, 2627.
10. J. Neuffer and J. Goerdeler, *Chem. Ber.*, 1971, **104**, 3498.
11. C. Grunclmann, H. Ulrick, and A. Kreutzerger, *Chem. Ber.*, 1953, **86**, 181.

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