JOURNAL OF PHYSICAL ORGANIC CHEMISTRY
J. Phys. Org. Chem. 2004; **17:** 49–55
Published online 12 November 2003 in Wiley InterScience (www.interscience.wiley.com). DOI: 10.1002/poc.686

Regioselective synthesis of 1,2,4-triazin-5-one via gas-phase pyrolysis of 4-arylidenimino-3(2*H*)-thioxo-1,2,4-triazin-5(4*H*)-one. Kinetic and mechanistic study

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Received 21 March 2003; revised 15 June 2003; accepted 17 June 2003

ABSTRACT: 4-Arylidenimino-3(2*H*)-thioxo-1,2,4-triazin-5(4*H*)-ones (**1a–e**) and 4-arylidenimino-3-methylthio-1,2,4-triazin-5(4*H*)-ones (**2a–e**) were synthesized. Pyrolytic deprotection of these substrates were carried out. The kinetic results, product analysis and theoretical studies lend support to a reaction pathway involving a six-membered transition state in which the carbonyl and not thione bond attacks the hydrogen atom of the arylidenimino group. This reaction represents an efficient, clean and general synthetic procedure for the protection and selective synthesis of potential biologically active triazines and their derivatives. Copyright © 2003 John Wiley & Sons, Ltd.

KEYWORDS: 4-arylidenimino-3(2*H*)-thioxo-1,2,4-triazin-5(4*H*)-one; gas-phase pyrolysis

INTRODUCTION

Recently, we have presented the results of kinetic studies and thermal analysis of selective pyrolytic deprotection of 4-arylidenimino-1,2,4-triazol-3(2*H*)-one and their 3(2*H*)-thione derivatives in the gas phase.[1,2] These were shown to give arylnitriles and triazole derivatives (Scheme 1).

In the present investigation, we envisaged the possible utility of the triazines **1a–e** (Fig. 1) and **2a–e** as potential starting materials for the protection of N-4 in the triazines, hoping to assist in regioselective substitution at other nitrogen sites in the triazine ring. A preliminary publication described the utility of this methodology for the synthesis of the biologically important 2-glucosyl derivatives.[3]

RESULTS AND DISCUSSION

The required substrates **1a–e** and **2a–e** were prepared and fully characterized by NMR and mass spectrometry (MS), as described in the Experimental section. Compounds **1a–e** were prepared by refluxing 4-amino-3(2*H*)-thioxo-1,2,4-triazin-5(4*H*)-one with the appropriate aromatic aldehyde for several hours in acetic acid. The *S*-methyl derivatives **2a–e** were prepared by methylation of **1a–e** with methyl iodide in *N*,*N*-dimethylformamide (DMF) and triethylamine at room temperature.

The products of pyrolysis of each substrate were analysed; the constituents of all pyrolysates were ascertained to be arylnitrile together with the 1,2,4-triazine fragment.

For each substrate, first-order rate coefficients were obtained at regular temperature intervals. Each rate constant is the average of at least three independent measurements, in agreement to within $\pm 2\%$. The reactions for which the kinetic data were obtained have been ascertained to be homogeneous, unimolecular, non-catalytic and non-radical processes.[4,5] Arrhenius plots of the data using the first-order rate equation:

$$\log k(\mathrm{s}^{-1}) = \log A - E_\mathrm{a}\left(\mathrm{kJ\,mol}^{-1}\right)(2.303RT)^{-1}$$

were strictly linear over $\geq$95% reaction with correlation coefficients in the range 0.99 ± 0.005. The log A and E_a values and the first order-rate constants of the 10 compounds under investigation are given in Tables 1 and 2. Together with the *cis*-stereochemistry of the elimination, this was taken to indicate a cyclic mechanism involving either transition state (A) or (B) for **1a–e** (Scheme 2).

The reaction involves elimination of arylnitriles from the substrates **1a–e** and **2a–e**, but this does not indicate whether this proceeds via the attack of the thione or the

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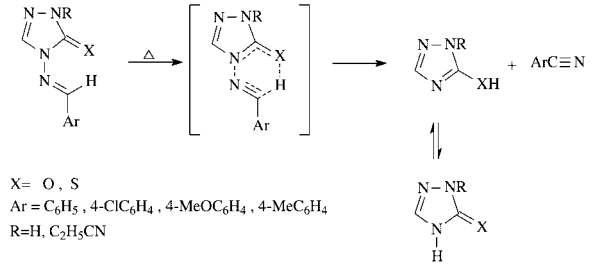
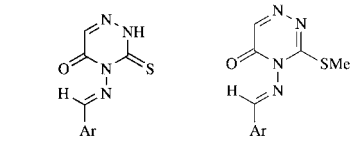
Contract/grant sponsor: University of Kuwait; *Contract/grant number:* SC03/00.
Contract/grant sponsor: Analab/SAF; *Contract/grant numbers:* GS01/01, GS02/01, GS03/01.



Scheme 1



1a-e **2a-e**

	Ar
a	C_6H_5
b	*p*-$NO_2C_6H_4$
c	*p*-ClC_6H_4
d	*p*-$CH_3C_6H_4$
e	*p*-$CH_3OC_6H_4$

Figure 1. Substrates studied

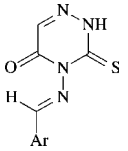
carbonyl group on the hydrogen atom of the arylidenimino group.

To make the choice between (A) and (B) we measured the kinetic effect of replacing C═S in **1a–e** by C—SMe in **2a–e**, in order to engage the π-bond of the thione group in an attempt to force the reaction to proceed via transition state [C] (Fig. 2).

The results of our investigation of the relative reactivity of the thermal elimination of nitriles from 4-arylideneimino-1,2,4-triazol-3(2*H*)ones **3a–e** and their 3(2*H*)-thione analogues **4a–e** and from 4-arylidenimino-2-cyanoethyl-1,2,4-triazol-3(2*H*)-ones **5a–e** and their thione analogues **6a–e** are summarized in Table 3. Substrates **4a–e** are 582–2517 times more reactive than their corresponding oxygen analogues **3a–e**, and **6a–e** are 498–2943 times more reactive than their oxygen analogues **5a–e**. We attribute the reactivity of the thione compounds over their oxygen analogues to the greater protophilicity and lability together with the relative thermodynamic stability and π-bond energy difference of the C═S and C═O bonds.[1,2]

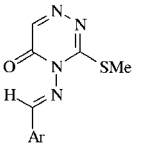
If the same reasoning for this relative rate factor were applied to the triazine system, one would expect that **1a–e** to be much more reactive than **2a–e**. The kinetic data for the pyrolytic reaction of the triazine compounds show that this is not the case. The relative rate factor of

Table 1. Kinetic data for pyrolysis of **1a–e**

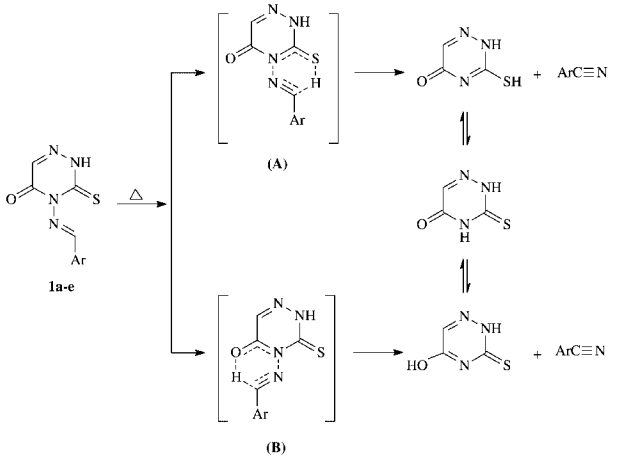


Compound	Ar	*T*(K)	$10^4k(s^{-1})$	Log [*A* (s^{-1})]	E_a(kJ mol^{-1})
1a	C_6H_5	444.10	0.682	9.16	112.8
		454.70	1.792		
		466.40	3.790		
		490.00	14.690		
		501.90	24.04		
1b	*p*-$NO_2C_6H_4$	438.60	3.986	9.91	111.8
		447.70	7.102		
		457.70	13.800		
		467.40	26.50		
		476.50	44.58		
1c	*p*-ClC_6H_4	425.60	1.209	8.48	100.8
		435.20	2.492		
		454.70	9.028		
		465.10	14.23		
		474.50	22.77		
1d	*p*-$CH_3C_6H_4$	447.90	2.159	8.51	104.3
		467.20	7.277		
		477.40	14.04		
		490.00	21.19		
		497.30	34.75		
1e	*p*-$CH_3OC_6H_4$	452.50	0.798	13.7	153.7
		462.30	2.383		
		482.50	11.480		
		492.10	24.46		
		502.90	50.28		

Table 2. Kinetic data for pyrolysis of **2a–e**



Compound	Ar	T(K)	$10^4k(s^{-1})$	Log [A (s^{-1})]	E_a (kJ mol^{-1})
2a	C_6H_5	529.50	3.758	10.7	143.1
		539.30	6.768		
		552.40	14.400		
		558.80	19.180		
		563.60	27.550		
		569.40	37.04		
2b	*p*-$NO_2C_6H_4$	489.00	4.505	5.72	84.84
		498.70	7.006		
		508.80	10.010		
		519.60	16.26		
		530.90	23.16		
2c	*p*-ClC_6H_4	524.30	3.707	8.87	123.6
		534.50	6.103		
		548.40	13.130		
		557.30	18.28		
		568.00	33.41		
2d	*p*-$CH_3C_6H_4$	523.60	4.182	8.54	119.4
		533.80	7.263		
		544.30	12.480		
		555.20	20.49		
		566.90	33.95		
2e	*p*-$CH_3OC_6H_4$	524.20	2.692	10.2	137
		534.40	4.336		
		544.70	9.403		
		554.60	14.74		
		565.90	26.27		



Scheme 2

elimination of **1a–e** and **2a–e** at 500 K is 2–99 (Table 4), which is much lower than those obtained for pyrolysis of the corresponding triazoles.

In the absence of theoretical studies and with the aim of further examining and characterizing in detail both mechanistic pathways suggested (Scheme 2), we report in this paper our theoretical study on **1a–e** and **2a–e**.

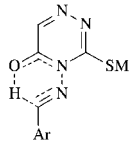


Figure 2. Transaction state [C]

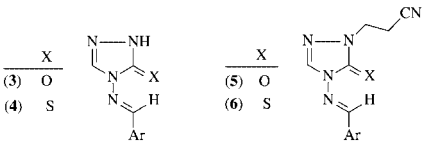
Method of calculation

The total molecular energy as a function of internal rotation around the N(sp^2)—N(sp^3) bond, referred to as the N—N bond, in the **1a** molecule was calculated at the *ab initio* MO SCF level with the Titan molecular modeling program[6] and the Gaussian package.[7]

All the *ab initio* calculations were performed with the 3–21G* basis set and full molecular relaxation at fixed values of the rotational coordinates Φ.

First, the structure of the molecule was built using the Titan molecular modeling program, and RHF calculations were performed to the optimize the molecular geometry with the polarization 3–21G* basis set. The geometry of the molecule was re-optimized using Gaussian

Table 3. Rate constants at 500 K and k_{rel} for triazoles **3–6**



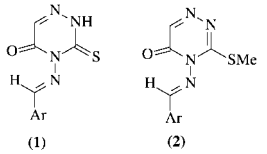
Ar	**3** $10^6k(s^{-1})$	**4** $10^3k(s^{-1})$	k_{rel} (**4/3**)	**5** $10^6k(s^{-1})$	**6** $10^3k(s^{-1})$	k_{rel} (**6/5**)
(**a**) C_6H_5	2.35	4.83	2055	5.08	5.44	1070
(**b**) 4-$NO_2C_6H_4$	—	—	—	4.29	2.14	498
(**c**) 4-ClC_6H_4	2.19	5.2	2374	1.26	3.33	2643
(**d**) 4-$CH_3C_6H_4$	2.8	7.05	2517	2.29	5.68	2480
(**e**) 4-$CH_3OC_6H_4$	8.15	4.75	582	1.75	5.15	2943

98 under the assumption of *C*1 symmetry with the 3–21G* basis set. A complete set of 6–31G* calculations were also carried out for comparison purposes. The most significant bond lengths (Å), bond angles (°) and dihedral angles (°) for the compound referring to relaxed geometries at the 3–21G* and 6–31G* levels are listed in Table 5. Among the listed geometric parameters, the dihedral angle C_{12}—N_{11}—N_8—C_4 shows a strong dependence on the level of calculations.

Additional energy values were calculated using 3–21G* for the molecule by freezing the coordinate for internal rotation Φ (dihedral angle C_{12}—N_{11}—N_8—C_4) and relaxing all the other structural variables in order to define potential energy profiles. These energy values were calculated in the Φ interval between 0 and 360.0°. Table 6 and Fig. 3 summarize the results obtained. It appears that minimum energy is obtained when $\Phi = 60.0°$.

The calculations shows that the molecular energy of the molecule changes with change in Φ. Calculations also shows symmetrical results on going from $\Phi = 0.0$ to 360.0°. This means that the energy of the molecule changes on going from $\Phi = 0.0$ to 180.0°, then on going to, for example, $\Phi = 210.0°$ we obtained the same result as for $\Phi = 150.0°$, and so on. The minimum energy is obtained with $\Phi = 60.0°$. This result should be used to confirm that the bonding to form the transition state will be by the formation of O···H-bond, H-bonds which is highly favored by the geometry obtained that gives the minimum energy with $\Phi = 60.0°$ (Fig. 4).

Table 4. Rate constants at 500 K and relative k_{rel} for triazines **1a–e** and **2a–e**



Ar	**1** $10^3k(s^{-1})$	**2** $10^3k(s^{-1})$	k_{rel} (**1/2**)
(**a**) C_6H_5	2.41	0.05	48
(**b**) 4-$NO_2C_6H_4$	16.84	7.21	2
(**c**) 4-ClC_6H_4	8.93	0.09	99
(**d**) 4-$CH_3C_6H_4$	4.12	0.17	24
(**e**) 4-$CH_3OC_6H_4$	4.29	0.06	71

CONCLUSIONS

Product analysis together with the kinetic results are in accord with a reaction pathway involving a cyclic six-membered transition state (A) or (B) (Scheme 2).

Table 5. Significant bond lengths, bond angles and dihedral angles referring to relaxed geometries in molecule **1a**, calculated at the HF/3–21G* and HF/6–31G* levels

Parameter	HF/3–21G*	HF/6–31G*
Bond length (Å)		
C_4—C_3	1.467	1.475
C_5—N_2	1.363	1.352
N_8—C_4	1.397	1.392
S_9—C_5	1.649	1.657
O_{10}— C_4	1.207	1.189
N_{11}—N_8	1.441	1.400
C_{12}—N_{11}	1.266	1.259
H_{13}—C_{12}	1.072	1.079
Bond angle (°)		
C_4—C_3—N_1	123.8	123.2
C_5—N_2—N_1	126.6	127.5
N_8—C_4—C_3	113.7	113.8
S_9—C_5—N_2	120.5	120.3
O_{10}—C_4—N_8	123.4	123.0
N_{11}—N_8—C_4	119.1	118.0
C_{12}—N_{11}—N_8	115.7	114.3
H_{13}—C_{12}—N_{11}	123.2	121.6
Dihedral angles (°)		
C_4—C_3—N_1—N_2	0.0	0.0
C_5—N_2—N_1—C_3	1.521	−1.291
N_8—C_4—C_3—N_1	−0.954	0.068
S_9—C_5—N_2—N_1	179.4	−179.2
O_{10}—C_4—C_3—N_8	179.4	−179.1
N_{11}—N_8—C_4—C_3	−167.0	168.1
C_{12}—N_{11}—N_8—C_4	−59.17	72.03
H_{13}—C_{12}—N_{11}—N_8	−0.620	1.420
Total energy (hartree)	−1067.8041121	−1073.44718

Table 6. Rotational angle Φ versus the calculated molecular energy using the 3–21G* basis set, with parameters obtained from full optimization of molecule **1a**, with freezing of the C_{12}—N_{11}—N_8—C_4 dihedral angle

Φ(°)	Energy (hartree)
0.0	−1067.8040202
30.0	−1067.8038029
60.0	−1067.8041109
90.0	−1067.8033463
105.0	−1067.8029976
120.0	−1067.802591
150.0	−1067.7992056
180.0	−1067.7967985
210.0	−1067.7992055
240.0	−1067.802591
255.0	−1067.8029976
270.0	−1067.8033463
300.0	−1067.8041112
330.0	−1067.8038029
360.0	−1067.8040202

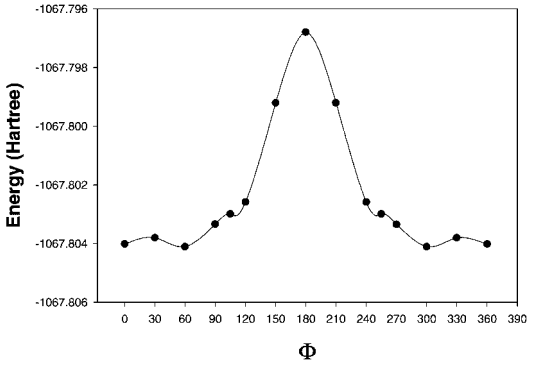


Figure 3. Graph of the calculated molecular energy as a function of the rotational angle Φ for molecule **1a**, calculated by using Gaussian 98 at the 3–21G* level with freezing of the C_{12}—N_{11}—N_8—C_4 dihedral angle

Theoretical study of the gas-phase elimination of arylnitrile from **1a–e** confirms that the reaction pathway involves transition state (B), which means that it involves the attack of the C═O bond and not the C═S bond on the hydrogen atom.

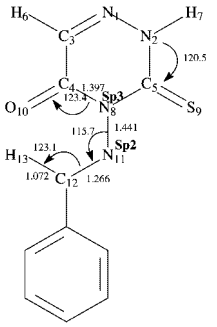


Figure 4. Schematic representation of the structure of molecule **1a**, obtained using the 3–21G* basis set with a C_{12}—N_{11}—N_8—C_4 dihedral angle = 60.0°

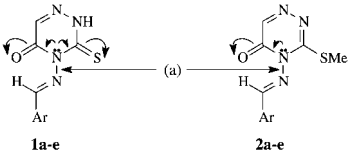


Figure 5. The delocalization of the lone pair of electrons on the nitrogen atom in **1a–e** and **2a–e**

The relative reactivities of 2–99 for **1a–e** over those of **2a–e** could be attributed to the fact that the lone pair of electrons on the nitrogen atom in **1a–e** is effectively delocalized by cross-conjugation on to the carbonyl oxygen and thione sulfur whereas in **2a–e** this delocalization is limited to the carbonyl oxygen only (Fig. 5), which will result in a greater polarity of the N—N bond (a) involved in the transition state for **1a–e** over those of **2a–e**. Consequently, this would facilitate cleavage of this particular bond and hence accelerate the reaction rate.

EXPERIMENTAL

Kinetic measurements

Procedures for the kinetic measurements have been detailed in earlier papers.[1,5]

Syntheses

Preparation of 4-arylidenamino-3(2*H*)-thioxo-1,2,4-triazin-5(4*H*)-ones (1a–e). A solution of 4-amino-3(2*H*)-thioxo-1,2,4-triazin-5(4*H*)-one (1 g, 7.8 mmol), the appropriate aromatic aldehyde (7.8 mmol) and anhydrous sodium acetate (1 g) in acetic acid (10 ml) was heated under reflux: for benzaldehyde 8 h, *p*-nitrobenzaldehyde 24 h, *p*-chlorobenzaldehyde 18 h, *p*-methylbenzaldehyde 6 h and *p*-methoxylbenzaldehyde (4 h).

*4-Benzylidenamino-3(2H)-thioxo-1,2,4-triazin-5(4H)-one (**1a**).* Yellow crystals, yield 66%, m.p. 194–195 °C. MS: *m/z* 232 (M^+, 40%). IR: 3439, 3132, 3054, 2959, 1690 cm^{-1}. ^1H NMR (DMSO-d_6): δ 7.58 (t, 2H, $J = 7.5$ Hz, ArH), 7.67 (t, 1H, $J = 7.5$ Hz, ArH), 7.91 (d, 2H, $J = 7.5$ Hz, ArH), 7.93 (s, 1H, triazine H), 8.68 (s, 1H, CH═N), 13.95 (s, 1H, NH). ^{13}C NMR: δ 128.9, 129.4, 131.1, 131.9, 148.9, 162.9, 171.3, 172.2. Anal. Calcd for $C_{10}H_8N_4OS$ (232.27): C, 51.71; H, 3.47; N, 24.12; S, 13.80. Found: C, 51.97; H, 3.50; N, 23.78; S, 13.82%.

*4-p-Nitrobenzylidenamino-3(2H)-thioxo-1,2,4-triazin-5(4H)-one (**1b**).* Yellow crystals, yield 80%, m.p. 205–206 °C. MS: *m/z* 277 (M^+, 45%). IR: 3438, 3275, 3072, 1681 cm^{-1}. ^1H NMR (DMSO-d_6): δ 8.12 (d, 2H, $J = 8.8$ Hz, ArH), 8.34 (d, 2H, $J = 8.8$ Hz, ArH) 7.90

(s, 1H, triazine H), 8.83 (s, 1H, CH═N), 13.95 (s, 1H, NH). ^{13}C NMR: δ 125.2, 130.9, 138.1, 139.8, 149.8, 150.8, 171.7, 172.1. Anal. Calcd for $C_{10}H_7N_5O_3S$ (277.26): C, 43.32; H, 2.54; N, 25.26; S, 11.56. Found: C, 42.95; H, 2.69; N, 24.79; S, 12.51%.

*4-p-Chlorobenzylidenamino-3(2H)-thioxo-1,2,4-triazin-5(4H)-one (**1c**).* Yellow crystals, yield 90%, m.p. 188 °C. MS: *m/z* 266 (M^+, 20%), 268 (M + 2, 7%). IR: 3437, 3220, 3077, 1690 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.02 (d, 2H, J = 8.4 Hz, ArH), 7.85 (d, 2H, J = 8.4 Hz, ArH), 8.37 (s, 1H, triazine H), 9.20 (s, 1H, CH═N), 10.66 (s, 1H, NH). ^{13}C NMR: δ 129.3, 129.6, 130.4, 130.6, 139.7, 148.9, 170.7, 171.2. Anal. Calcd for $C_{10}H_7N_4OSCl$ (266.7): C, 45.03; H, 2.65; N, 21.01; S, 12.02. Found: C, 45.13; H, 2.85; N, 21.06; S, 12.00%.

*4-p-Methylbenzylidenamino-3(2H)-thioxo-1,2,4-triazin-5(4H)-one (**1d**).* Yellow crystals, yield 60%, m.p. 197 °C. MS: *m/z* 246 (M^+, 45%). IR: 3439, 3085, 3054, 2959,1712 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 2.46 (s, 3H, CH_3), 7.32 (d, 2H, J = 8.0 Hz, ArH), 7.83 (d, 2H, J = 8.0 Hz, ArH), 7.69 (s,1H, triazine H), 8.43 (s, 1H, CH═N), 10.87 (s, 1H, NH). ^{13}C NMR: δ 21.8, 128.5, 129.5, 129.7, 138.0, 144.53, 149.2, 171.5, 172.2. Anal. Calcd for $C_{11}H_{10}N_4OS$ (246.29): C, 53.65; H, 4.09; N, 22.75; S, 13.02. Found: C, 53.44; H, 4.09; N, 22.70; S, 13.15%.

*4-p-Methoxybenzylidenamino-3(2H)-thioxo-1,2,4-triazin-5(4H)-one (**1e**).* Yellow crystals, yield 67%, m.p. 165–167 °C. MS: *m/z* 262 (M^+, 80%). IR: 3157, 3051, 2971, 1712 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 3.92 (s, 3H, OCH_3), 7.01 (d, 2H, J = 8.8 Hz, ArH), 7.90 (d, 2H, J = 8.8 Hz, ArH), 7.68 (s, 1H, triazine H), 8.38 (s, 1H, CH═N), 10.60 (s, 1H, NH). ^{13}C NMR: δ 55.6, 114.5, 123.9, 131.6, 137.9, 149.3, 163.9, 171.5, 171.7. Anal. Calcd for $C_{11}H_{10}N_4O_2S$ (262.2): C, 50.37; H, 3.84; N, 21.36; S, 12.23. Found: C, 50.63; H, 3.84; N, 21.28; S, 12.75%.

Preparation of 4-arylidenamino-3-methylthio-1,2,4-triazin-5(4H)- ones (2a–e). A mixture of each of **1a–e** (10 mmol) and methyl iodide (10 mmol) in DMF (5 ml) and triethylamine (10 mmol) was stirred at room temperature overnight. After dilution with water, the precipitate was collected, washed with water several times and recrystallized from ethanol to give crystals of compounds **2a–e**.

*4-Benzylidenamino-3-methylthio-1,2,4-triazin-5(4H)-one (**2a**).* Yellow crystals, yield 75%, m.p. 111–112 °C. MS: *m/z* 246 (M^+, 45%). IR: 3157, 3051, 2971, 1712 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 2.58 (s, 3H, SCH_3), 7.46 (t, 2H, J = 7.6 Hz, ArH), 7.54 (t, 1H, J = 7.6 Hz, ArH), 7.83 (d, 2H, J = 7.6 Hz, ArH), 8.31 (s, 1H, triazine H), 9.33 (s, 1H, CH═N). ^{13}C NMR: δ 15.1, 129.3, 129.5, 132.3, 133.6, 147.6, 149.9, 161.3, 166.0. Anal. Calcd for $C_{11}H_{10}N_4OS$ (246.29): C, 53.65; H, 4.09; N, 22.75; S, 13.02. Found: C, 53.95; H, 4.20; N, 22.79; S, 13.37%.

*4-p-Nitrobenzylidenamino-3-methylthio-1,2,4-triazin-5(4H)-one (**2b**).* Yellow crystals, yield 75%, m.p. 212–213 °C. MS: *m/z* 291 (M^+, 72%). IR: 3436, 3116, 2363, 1689 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 2.68 (s, 3H, SCH_3), 8.08 (d, 2H, J = 8.8 Hz, ArH), 8.38 (d, 2H, J = 8.8 Hz, ArH) 8.40 (s, 1H, triazine H), 9.80 (s, 1H, CH═N). ^{13}C NMR: δ 15.2, 124.5, 130.1, 138.2, 147.9, 150.2, 150.5, 161.3, 161.4. Anal. Calcd. for $C_{11}H_9N_5O_3S$ (291.28): C, 45.36; H, 3.11; N, 24.04; S, 11.01. Found: C, 45.33; H, 3.21; N, 23.96; S, 11.11%.

*4-p-Chlorobenzylidenamino-3-methylthio-1,2,4-triazin-5(4H)-one (**2c**).* Yellow crystals, yield 72%, m.p. 155–156 °C. MS: *m/z* 280 (M^+, 8%), 282 (M + 2, 22%). IR: 3436, 1680, 1605, 1592 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 2.59 (s, 3H, SCH_3), 7.44 (d, 2H, J = 8.5 Hz, ArH), 7.76 (d, 2H, J = 8.5 Hz, ArH) 8.31 (s, 1H, triazine H), 9.38 (s, 1H, CH═N). ^{13}C NMR: δ 15.1, 129.8, 130.6, 130.9, 139.8, 147.6, 150.0, 161.2, 164.1. Anal. Calcd. for $C_{11}H_9N_4OSCl$ (280.73): C, 47.06; H, 3.23; N, 19.96; S, 11.42. Found: C, 47.03; H, 3.36; N, 19.80; S, 11.43%.

*4-p-Methylbenzylidenamino-3-methylthio-1,2,4-triazin-5(4H)-one (**2d**).* Yellow crystals, yield 83%, m.p. 129 °C. MS: *m/z* 260 (M^+, 80%). IR: 3354, 3057, 3015, 2928, 1682 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 2.38 (s, 3H, CH_3), 2.57 (s, 3H, SCH_3), 7.22 (d, 2H, J = 8 Hz, ArH), 7.70 (d, 2H, J = 8 Hz, ArH) 8.29 (s, 1H, triazine H), 9.22 (s, 1H, CH═N). ^{13}C NMR: δ 14.8, 21.8, 129.3, 129.4, 129.8, 144.3, 147.3, 149.7, 161.0, 166.0. Anal. Calcd for $C_{12}H_{12}N_4OS$ (260.31): C, 55.37; H, 4.65; N, 21.52; S, 12.32. Found: C, 55.76; H, 4.66; N, 21.52; S, 12.52%.

*4-p-Methoxylbenzylidenamino-3-methylthio-1,2,4-triazin-5(4H)-one (**2e**).* White crystals, yield 65%, m.p. 168 °C. MS: *m/z* 276 (M^+). IR: 3440, 3056, 3011, 2932, 1683 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 2.57 (s, 3H, SCH_3), 3.84 (s, 3H, OCH_3), 6.95 (d, 2H, J = 8.8 Hz, ArH), 7.78 (d, 2H, J = 8.8 Hz, ArH), 8.30 (s, 1H, triazine H), 9.12 (s, 1H, CH═N). ^{13}C NMR: δ 14.8, 55.5, 114.5 124.4, 131.3, 147.1, 149.6, 160.8, 163.8, 165.7. Anal. Calcd. for $C_{12}H_{12}N_4O_2S$ (276.31): C, 52.16; H, 4.38; N, 20.28; S, 11.60. Found: C, 52.35; H, 4.33; N, 20.41; S, 12.09%.

Acknowledgements

The support of the University of Kuwait received through research grant (SC03/00) and the facilities of Analab/SAF (GS01/01, GS02/01, GS03/01) is gratefully acknowledged.

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