JOURNAL OF PHYSICAL ORGANIC CHEMISTRY
J. Phys. Org. Chem. 2002; **15:** 324–329
Published online in Wiley InterScience (www.interscience.wiley.com). DOI: 10.1002/poc.491

Gas-phase elimination reactions of 4-arylideneimino-2-cyanoethyl-1,2,4-triazol-3(2*H*)-ones, their thione analogues and 2-glucosyl-1,2,4-triazole-3(2*H*)-thiones: a kinetic and mechanistic study

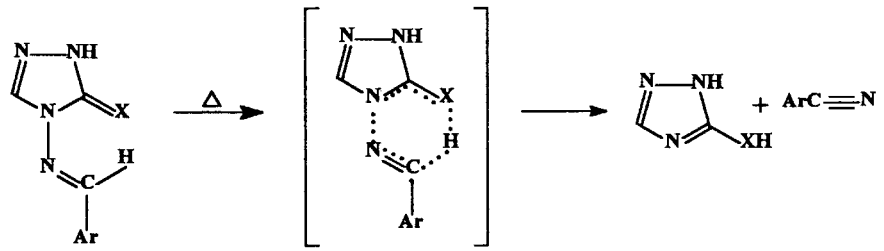
Nouria A. Al-Awadi,* Yehia A. Ibrahim, Hicham Dib and Kamini Kaul

Chemistry Department, Kuwait University, P.O. Box 5969, 13060 Safat, Kuwait

Received 28 September 2001; revised 15 January 2002; accepted 6 February 2002

ABSTRACT: Several 4-arylidenimino-2-cyanoethyl-1,2,4-triazol-3(2*H*)-ones, their 3(2*H*)-thiones and 2-glucosyl-1,2,4-triazol-3(2*H*)-thiones (**1–12**) were synthesized. Selective pyrolytic deprotection of these derivatives was studied in the gas phase and the kinetics of the reactions were measured for each compound. First-order rate constants measured over a 45 °C temperature range were used to calculate the Arrhenius activation parameters. A comparison of the products and the kinetic behavior of the thermal decomposition of these compounds are discussed. Copyright © 2002 John Wiley & Sons, Ltd.

KEYWORDS: 4-arylideneimino-2-cyanoethyl-1,2,4-triazol-3(2*H*)-ones and - thiones; 2-glucosyl-1,2,4-triazole-3(2*H*)-thiones; gas-phase elimination



X = O, S
Ar = C_6H_5, 4-ClC_6H_4, 4-$OMeC_6H_4$ & 4-MeC_6H_4

Scheme 1

INTRODUCTION

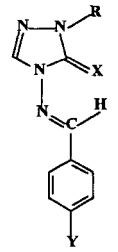
Previously, we have shown that 4-arylideneimino-1,2,4-triazol-3(2*H*)-ones and their thio analogues undergo first-order thermal decomposition in the gas phase. These reactions proceed via aromatization of the transition state which ultimately produces hydroxytriazoles or their thio analogues, which are more stable than the reactant *N*-aminotriazoles[1] (Scheme 1). Electrophilic substitutions of asymmetric heterocyclic urea and thiourea derivatives [represented here by 1,2,4-triazol-3(2*H*)-ones and their thione derivatives] are known to give mixtures of different regioisomeric products.[2] This usually leads to tedious separation and identification. Therefore, we were interested in gaining a detailed understanding of the kinetics and thermal behavior of 2-substituted 1,2,4-triazol-3(4*H*)-ones and their thiones as potential starting material for the protection of N-2 in these triazoles in order to assist in regioselective substitution at other nitrogen sites in the ring.

Here we describe the results of kinetic studies and thermal analysis of the gas-phase pyrolysis of 4-arylidenimino-2-cyanoethyl-1,2,4-triazol-3(2*H*)-ones, their 3(2*H*)-thiones and 2-glucosyl-1,2,4-triazole-3(2*H*)-thiones (**1–12**) (Scheme 2).

RESULTS AND DISCUSSION

The compounds investigated are shown in Scheme 2.

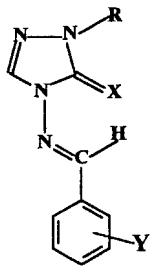
**Correspondence to:* N. A. Al-Awadi, Chemistry Department, Kuwait University, P.O. Box 5969, 13060 Safat, Kuwait.
E-mail: chesc@kuc01.kuniv.edu.kw



Compd. No.	R	X	Y
1	CH_2CH_2CN	O	H
2	CH_2CH_2CN	O	4-NO_2
3	CH_2CH_2CN	O	4-Me
4	CH_2CH_2CN	O	4-OMe
5	CH_2CH_2CN	S	H
6	CH_2CH_2CN	S	4-NO_2
7	CH_2CH_2CN	S	4-Me
8	CH_2CH_2CN	S	4-OMe
9	Glucosyl	S	H
10	Glucosyl	S	4-NO_2
11	Glucosyl	S	4-Me
12	Glucosyl	S	4-OMe

Scheme 2

Table 1. Kinetic data for gas-phase pyrolysis of **1**–**12**

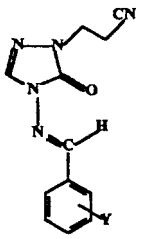
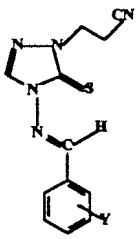
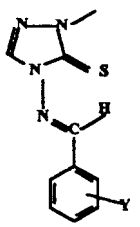


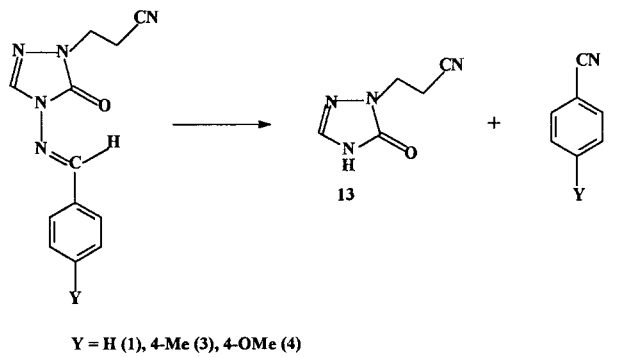
Compound	T (K)	10^4k (s^{-1})	Log[A (s^{-1})]	E_a (kJ mol^{-1})
1	554.65	2.18	11.2 ± 0.34	157.9 ± 3.8
	574.25	6.83		
	584.55	12.75		
	594.45	19.97		
	604.25	36.66		
2	558.55	2.04	10.7 ± 0.10	153.5 ± 1.1
	567.85	3.54		
	579.25	6.62		
	588.65	11.18		
	597.95	17.93		
3	554.65	1.51	13.0 ± 0.27	178.4 ± 3.1
	564.15	3.11		
	574.00	5.94		
	593.80	19.92		
	604.35	28.25		
4	564.00	2.66	13.5 ± 0.12	184.0 ± 1.3
	574.20	5.25		
	584.35	10.33		
	594.10	18.89		
	604.10	36.12		
5	458.85	2.20	13.7 ± 0.6	152.7 ± 5.6
	468.35	4.30		
	478.15	9.52		
	488.35	21.42		
	498.25	52.26		
6	449.55	0.43	12.6 ± 0.2	145.8 ± 1.4
	458.45	1.62		
	478.25	4.37		
	488.15	8.82		
	498.35	19.50		
7	449.55	0.60	15.2 ± 0.2	16.1 ± 1.9
	459.10	1.67		
	468.70	3.82		
	478.85	10.21		
	489.10	22.86		
	498.90	51.26		
8	458.60	2.06	13.4 ± 0.5	150.1 ± 4.7
	468.25	4.35		
	478.40	10.04		
	488.45	19.89		
	498.25	49.15		
9	458.35	1.98	13.9 ± 0.1	154.2 ± 1.1
	467.75	4.60		
	478.15	10.44		
	488.15	23.45		
	498.15	50.92		
10	449.15	0.55	13.2 ± 0.1	150.0 ± 0.7
	458.75	1.30		
	467.95	2.80		
	478.25	6.50		
	487.45	13.32		
11	459.15	1.68	15.2 ± 0.2	166.4 ± 2.1
	468.35	4.13		
	478.55	9.45		
	488.45	23.14		
	498.45	53.02		
12	449.65	0.77	13.5 ± 0.9	151.7 ± 0.8
	468.25	3.78		
	478.05	8.27		
	488.05	18.66		
	497.75	38.67		

Kinetics

Each of the triazoles under investigation gave reproducible kinetic results, first order to 98% reaction. The kinetic results (Table 1) gave excellent Arrhenius plots with no deviant points. This is the most reliable indicator of the absence of surface-catalysed elimination.[3] The rate constants of the reaction at 500 K for each substrate and related compounds are recorded in Table 2. The homogeneous nature of the reaction was confirmed using established procedures.[4]

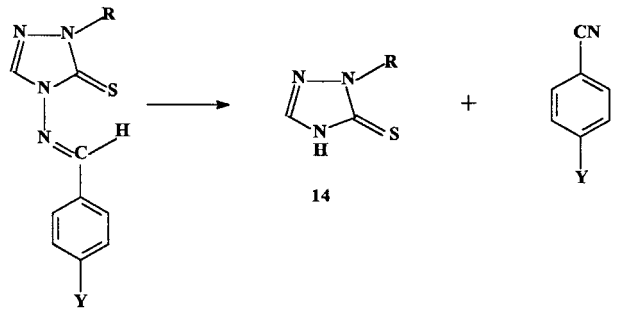
Table 2. Rate constants and relative rates at 500 K for the pyrolysis of 4-arylidenimino-2-cyanoethyl-1,2,4-triazol-3(2*H*)-ones, 4-arylidenimino-2-cyanoethyl and 2-glucosyl-1,2,4-triazole-3(2*H*)-thiones

	10^3k (s^{-1})				
	 (I)	 (II)	 (III)		
Y				k_{rol} (**II**)/(**I**)	k_{rol} (**II**)/(**III**)
H	5.08	5.44	5.77	1.07×10^3	0.94
4-NO_2	4.29	2.14	3.32	0.49×10^3	0.65
4-Cl	1.26	3.33	3.94	2.68×10^3	0.85
4-Me	2.29	5.68	5.94	2.48×10^3	0.96
4-OMe	1.75	5.13	4.52	2.93×10^3	1.14



Y = H (1), 4-Me (3), 4-OMe (4)

Scheme 3



Compound 5, 7, 8, 9, 10, 11 and 12

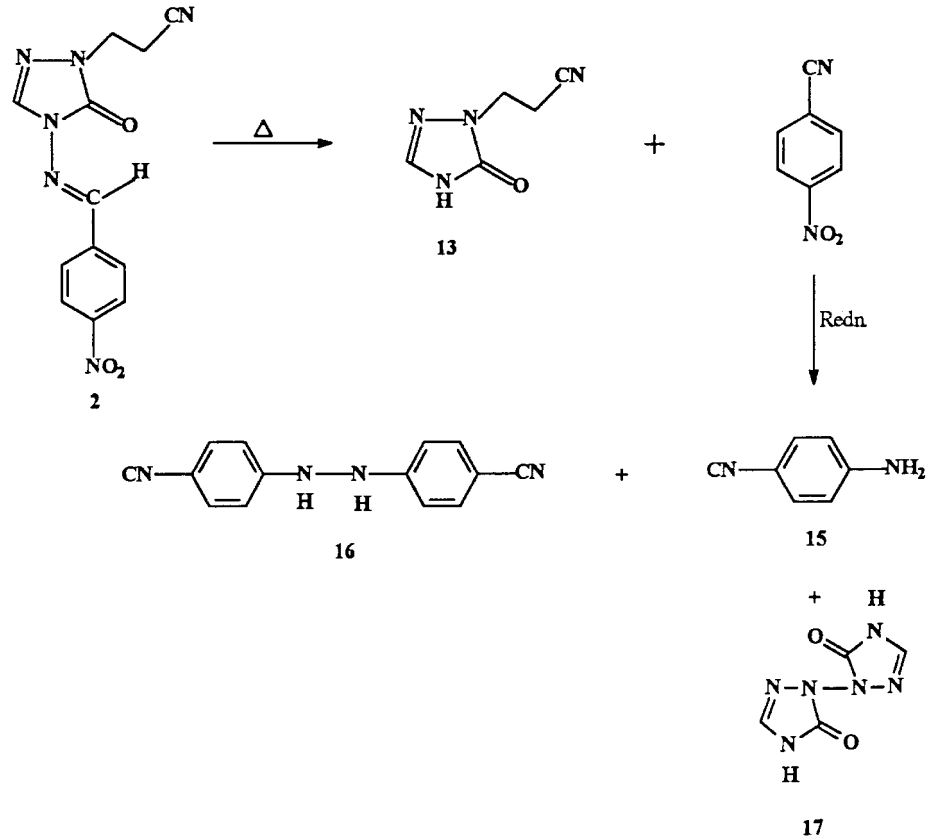
Scheme 4

Product analysis

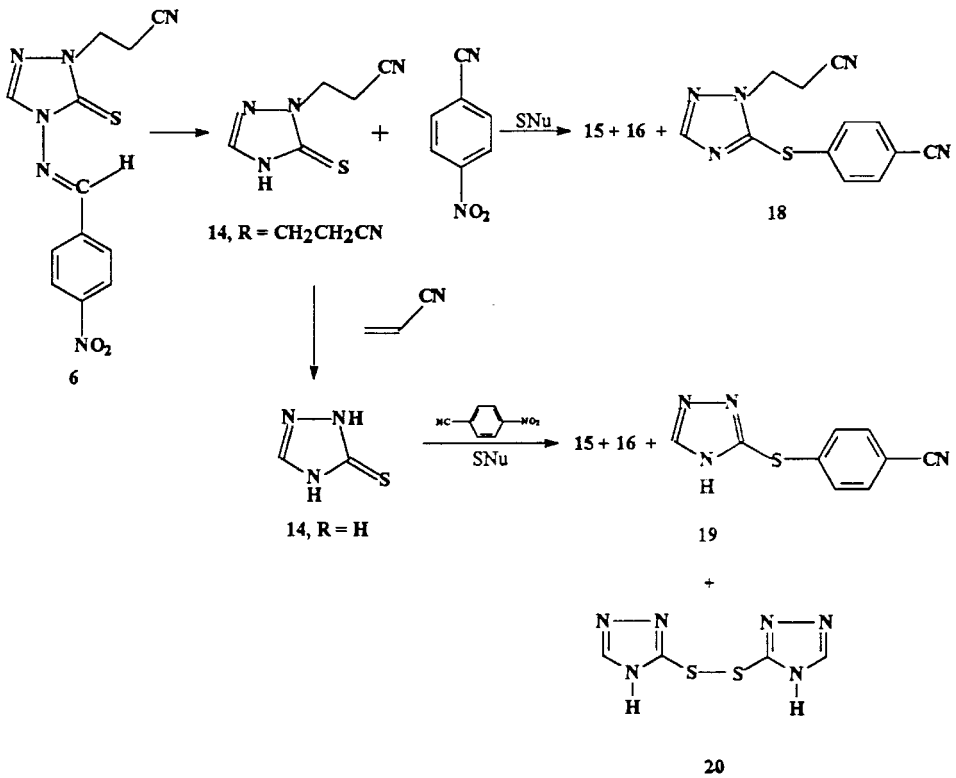
Products of pyrolysis were analysed by ^{1}H and ^{13}C NMR spectroscopy and LC–MS. We investigated the selective removal of the group at N-4. Pyrolysis of **1**, **3** and **4** gave almost quantitative yields of arylnitriles and 2-cyanoethyl-1,2,4-triazol-3(2*H*)-one (13) (Scheme 3). Similarly, pyrolysis of **5**, **7** and **8** gave arylnitriles and 2-cyanoethyl-1,2,4-triazole-3(2*H*)-thione (**14**, R = CH_2CH_2CN). Pyrolysis of **9**–**12** also gave arylnitriles and 2-glucosyl-1,2,4-triazole-3(2*H*)-thione (**14**, R = glucosyl) (Scheme 4). On the other hand, pyrolysis of the 4-nitro derivative **2** gave the expected **13**, but no 4-nitrobenzonitrile was detected, 4-aminobenzonitrile (**15**) and *N*,*N*′-bis(4-cyanophenyl)hydrazine (**16**) being detected instead, which most probably resulted from reduction of 4-nitrobenzonitrile (Scheme 5), in addition to the oxidation products 4*H*, 4′*H*−[1,1′]bi{[1,2,4]triazolyl} − 5,5′-dione (**17**). Compound **6** is no exception, pyrolysis produced 4-nitrobenzonitrile and **14** (R = CH_2CH_2CN), The latter undergo further elimination reaction of cyanoethylene to produce **14** (R = H), the 4-nitrobenzonitrile produced reacts with both the primary elimination product **14** (R = CH_2CH_2CN) to give **18** and with the secondary elimination product (**14**, R = H) to give **19** (Scheme 6) and reduction products **15** and **16**. The proposed pathway for the formation of **18** was substantiated by reacting each of **14** (R = H, CH_2CH_2CN) with 4-nitrobenzonitrile under the same pyrolytic conditions. Analysis of the product mixture in both cases revealed the formation of **18** (from **14**, R = CH_2CH_2CN) and **19** (from **14**, R = H) in addition to **15** and **16**. We were also able to identify the oxidation product in this case as the (1,2,4-triazol-3-yl)disulfide **20**.

Kinetic data together with the products of pyrolytic elimination reaction of the substrates **1**–**12** allow the following conclusions and comparison to be made:

(i) The six-membered TS, mechanism (Scheme 1) adopted in order to account for the kinetic results and reaction products involves thermal extrusion of 4-arylbenzoni-



Scheme 5



Scheme 6

trile from the substrates; it is noteworthy that the values obtained for Arrhenius parameters are typical of polar homogeneous pyrolytic gas-phase reactions.[5]

(ii) 4-Arylidenimino-2-cyanoethyl-1,2,4-triazol-3(2*H*)-thiones **5**–**8** are 490–2930 times more reactive than their oxygen analogues **1**–**4** (Table 2). This large difference in molecular reactivity is due to the greater protophilicity and lability together with the relative thermodynamic stability and the π-bond energy difference of the thio and carbonyl bonds. This contribution from the π-bond to the molecular reactivity of these substrates together with the almost negligible electronic effect of the substituent on the aryl ring indicates that breaking of the π-bond is the rate-controlling step of the reaction.

(iii) 4-Nitroarylidenimino-2-cyanoethyl-1,2,4-triazol-3(2*H*)-one **2** and its thio analogue **6** were exceptional in term of the pyrolysis products; the primary thermal elimination products underwent further reactions. Thus, *p*-nitrobenzonitrile produced from **2** is reduced to the corresponding aniline and hydrazine derivatives **15** and **16**. On the other hand, *p*-nitrobenzonitrile reacted with the other pyrolysis products of **6** through aromatic nucleophilic substitution of the nitro group to give the corresponding 3-*p*-cyanophenylthio-1,2,4-triazole derivatives **18** and **19**.

EXPERIMENTAL

Kinetic measurements

Procedures for the kinetic measurements have been detailed in an earlier paper.[6]

Product analysis

About 100 mg of the neat substrate was taken in a custom-made pyrolysis tube and sealed under vacuum (0.28 mbar). It was placed inside a Eurotherm 093 pyrolysis unit at a temperature and time comparable to those used in the kinetic investigations. The pyrolysis tube was jacketed by an insulating aluminium block, fitted with a platinum resistance thermometer and a thermocouple connected to a Comark microprocessor thermometer. After pyrolysis, the tube was allowed to cool to room temperature and the pyrolysate obtained was analysed using NMR, IR and LC–MS techniques.

Synthesis

Preparation of 4-Arylidenimino-2-β-cyanoethyl-1,2,4-triazol-3(2*H*)-ones. A solution of 4-arylidenimino-1,2,4-triazol-3(2*H*)-one (5 mmol) in aqueous pyridine (50%, 10 ml) and acrylonitrile (0.4 ml, 5.7 mmol) was heated under reflux for 18 h. After cooling, the mixture was poured over crushed ice and acidified with concentrated HCl (5 ml). The precipitate was collected, dried and recrystallized from ethanol. The following compounds were thus prepared.

4-Benzylidenimino-2-β-cyanoethyl-1,2,4-triazol-3(2H)-one (1). White crystals, yield 70%, m.p. 132–133 °C. MS: *m/z* 241 (M^+). IR: 3130, 2251, 1706, 761, 727, 693 cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.89 (t, 2H, $J = 6.9$ Hz, CH_2CN), 4.17 (t, 2H, $J = 6.9$ Hz, CH_2N), 7.50 (m, 3H, ArH), 7.80 (m, 2H, ArH), 7.82 (s, 1H, CH═N triazole), 9.75 (s, 1H, ArCH═N). ^{13}C NMR ($CDCl_3$): δ 17.3, 41.1, 116.7, 128.1, 128.9, 131.8, 133.1, 136.6, 149.4, 155.6. Anal. Calcd for $C_{12}H_{11}N_5O$ (241): C, 59.75; H, 4.56; N, 29.05. Found: C, 59.62; H, 4.56, N, 29.10%.

*4-*p*-Nitrobenzylidenimino-2-β-cyanoethyl-1,2,4-triazol-3(2H)-one (2).* Yellow powder, yield 55%, m.p. 166–168 °C. MS: *m/z* 287 (M^+). ^1H NMR (DMSO-d_6): δ 2.98 (t, 2H, $J = 6.9$ Hz, CH_2CN), 4.04 (t, 2H, $J = 6.9$ Hz, CH_2N), 8.08 (m, 2H, ArH), 8.36 (m, 2H, ArH), 8.68 (s, 1H, CH═N triazole), 9.55 (s, 1H, ArCH═N). Anal. Calcd for $C_{12}H_{10}N_6O_3$ (286): C, 50.34; H, 3.49; N, 29.47. Found: C, 50.27; H, 3.53, N, 28.75%.

*4-*p*-Methylbenzylidenimino-2-β-cyanoethyl-1,2,4-triazol-3(2H)-one (3).* White crystals, yield 68%, m.p. 136–137 °C. MS: *m/z* 255 (M^+). IR: 3126, 2249, 1706, 813, 756 cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.43 (s, 3H, CH_3), 2.88 (t, 2H, $J = 6.9$ Hz, CH_2CN), 4.16 (t, 2H, $J = 6.9$ Hz, CH_2N), 7.27 (m, 2H, ArH), 7.69 (m, 2H, ArH), 7.81 (s, 1H, CH═N triazole), 9.70 (s, 1H, ArCH═N). ^{13}C NMR ($CDCl_3$): δ 17.3, 21.6, 41.1, 116.7, 128.1, 129.7, 130.4, 136.5, 142.4, 149.5, 155.7. Anal. Calcd for $C_{13}H_{13}N_5O$ (255): C, 61.18; H, 5.10; N, 27.45. Found: C, 61.39; H, 5.08, N, 27.12%.

*4-*p*-Methoxybenzylidenimino-2-β-cyanoethyl-1,2,4-triazol-3(2H)-one (4).* White plates, yield 65%, m.p. 129–130 °C. MS: *m/z* 271 (M^+). IR: 3149, 2251, 1703, 832, 723 cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.89 (t, 2H, $J = 6.9$ Hz, CH_2CN), 3.89 (s, 3H, OCH_3), 4.17 (t, 2H, $J = 6.9$ Hz, CH_2N), 6.99 (m, 2H, ArH), 7.78 (m, 2H, ArH), 7.80 (s, 1H, CH═N triazole), 9.66 (s, 1H, ArCH═N). ^{13}C NMR ($CDCl_3$): δ 17.7, 41.4, 55.8, 114.7, 116.8, 125.7, 129.8, 136.5, 149.5, 155.3, 162.5. Anal. Calcd for $C_{13}H_{13}N_5O_2$ (271): C, 57.56; H, 4.79; N, 25.83. Found: C, 57.10; H, 4.84, N, 25.51%.

Preparation of 4-Arylidenimino-2-β-cyanoethyl-1,2,4-triazole-3(2*H*)-thiones. A solution of 4-arylidenimino-1,2,4-triazole-3(2H)-thione (5 mmol) in aqueous pyridine (50%, 10 ml) and acrylonitrile (0.4 ml, 5.7 mmol) was heated under reflux for 18 h. After cooling, the mixture was poured over crushed ice and acidified with concentrated HCl (5 ml). The precipitate was collected, dried and recrystallized from ethanol. The following compounds were thus synthesized.

4-Benzylidenimino-2-β-cyanoethyl-1,2,4-triazole-3(2H)-thione (5). Pale buff crystals, yield 89%, m.p. 112–114 °C. MS: *m/z* 257 (M^+). IR: 3098, 2251, 751, 690 cm^{-1}. ^1H NMR ($CDCl_3$): δ 3.02 (t, 2H, *J* = 6.9 Hz, CH_2CN), 4.54 (t, 2H, *J* = 6.9 Hz, CH_2N), 7.53 (m, 3H, ArH), 7.86 (m, 2H, ArH), 8.11 (s, 1H, CH=N triazole), 10.40 (s, 1H, ArCH=N). ^{13}C NMR ($CDCl_3$): δ 16.8, 44.8, 117.0, 129.2, 129.5, 132.5, 133.1, 140.0, 161.0, 161.9. Anal. Calcd for $C_{12}H_{11}N_5S$ (257): C, 56.03; H, 4.28; N, 27.23; S, 12.45. Found: C, 56.11; H, 4.28, N, 26.93; S, 12.89%.

*4-*p*-Nitrobenzylidenimino-2-β-cyanoethyl-1,2,4-triazole-3(2H)-thione (6).* Pale yellow crystals, yield 85%, m.p. 183–186 °C. MS: *m/z* 302 (M^+). IR: 3125, 2250, 1594, 850, 771, 749 cm^{-1}. ^1H NMR ($CDCl_3$): δ 3.02 (t, 2H, *J* = 6.9 Hz, CH_2CN), 4.55 (t, 2H, *J* = 6.9 Hz, CH_2N), 8.04 (m, 2H, ArH), 8.06 (s, 1H, CH=N triazole), 8.35 (m, 2H, ArH), 10.92 (s, 1H, ArCH=N). ^{13}C NMR ($CDCl_3$): δ 16.3, 44.2, 116.5, 124.2, 129.3, 138.2, 140.0, 149.9, 155.9, 161.4. Anal. Calcd for $C_{12}H_{10}N_6O_2S$ (302): C, 47.68; H, 3.31; N, 27.81; S, 10.59. Found: C, 48.05; H, 3.40, N, 27.41; S, 10.37%.

*4-*p*-Methylbenzylidenimino-2-β-cyanoethyl-1,2,4-triazole-3(2H)-thione (7).* Colorless crystals, yield 88%, m.p. 150–151 °C. MS: *m/z* 271 (M^+). IR: 3083, 2251, 817, 753 cm^{-1}. ^1H NMR ($CDCl_3$) δ 2.46 (s, 3H, CH_3), 3.00 (t, 2H, *J* = 6.9 Hz, CH_2CN), 4.54 (t, 2H, *J* = 6.9 Hz, CH_2N), 7.35 (m, 2H, ArH), 7.79 (m, 2H, ArH), 8.09 (s, 1H, CH=N triazole), 10.28 (s, 1H, ArCH=N). ^{13}C NMR ($CDCl_3$): δ 16.5, 21.8, 44.4, 116.6, 128.8, 129.7, 129.9, 139.4, 143.5, 161.0, 161.5. Anal. Calcd for $C_{13}H_{13}N_5S$ (271): C, 57.56; H, 4.79; N, 25.83; S, 11.81. Found: C, 58.02; H, 4.89, N, 25.93; S, 12.08%.

*4-*p*-Methoxybenzylidenimino-2-β-cyanoethyl-1,2,4-triazole-3(2H)-thione (8).* White crystals, yield 82%, m.p. 125–127 °C. MS: *m/z* 287 (M^+). IR: 3097, 3038, 2252, 819, 758 cm^{-1}. ^1H NMR ($CDCl_3$): δ 3.00 (t, 2H, *J* = 6.9 Hz, CH_2CN), 3.89 (s, 3H, OCH_3), 4.53 (t, 2H, *J* = 6.9 Hz, CH_2N), 6.98 (m, 2H, ArH), 7.81 (m, 2H, ArH), 8.06 (s, 1H, CH=N triazole), 10.11 (s, 1H, ArCH=N). ^{13}C NMR ($CDCl_3$): δ 16.4, 44.4, 55.5, 114.5, 116.6, 124.5, 130.7, 139.2, 160.9, 163.3. Anal. Calcd for $C_{13}H_{13}N_5OS$ (287): C, 54.36; H, 4.53; N, 24.39; S, 11.14. Found: C, 54.17; H, 4.50, N, 24.21; S, 11.20%.

Preparation of 2-*N*-glucosylbenzylideneamino-1,2,4-triazoles. To a solution of the substituted benzylidene aminotriazoles (5 mmol) in dimethylformamide (5 ml) was added dry triethylamine (1 ml) and the solution was stirred for 5 min. Acetobromoglucose (6 mmol) was added and the solution was heated at 100° for 2 min and stirred overnight. The precipitate formed upon dilution with water was filtered and crystallized from ethanol to afford crystals of the following compounds.

*4-Benzylideneimino-2-N-tetra-O-acetyl-β-*D*-glucosyl-1,2,4-triazole-3(2H)-thione (9).* Yield 50%, m.p. 192–193 °C (lit.[7] m.p. 193 °C). MS: *m/z* 535 ($M^+ + 1$). IR: 3474, 3151, 2976, 1751, 1611, 1547, 1427, 1365, 1235 cm^{-1}.

*4-*p*-Nitrobenzylideneimino-2-N-tetra-O-acetyl-β-*D*-glucosyl-1,2,4-triazole-3(2H)-thione (10).* Yield 55%, m.p. 196–197 °C. MS: *m/z* 580 ($M^+ + 1$). IR: 3400, 1751, 1593, 1525, 1425, 1365, 1349, 1233 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.97, 2.06, 2.09, 2.10 (4s, 12H, CH_3), 4.02 (dd, 1H, CH-5′), 4.18, 4.25 (2 dd, 2H, CH_2-6′), 5.28 (t, 1H, CH-4′), 5.47 (t, 1H, CH-3′), 5.80 (t, 1H, CH-2′), 6.23 (d, 1H, CH-1′), 8.04 (d, 2H, ArH), 8.11 (s, 1H, CH=N triazole), 8.35 (d, 2H, ArH), 10.92 (s, 1H, CH=N). Anal. Calcd for $C_{23}H_{25}N_5O_{11}S$ (579): C, 47.67; H, 4.32; N, 12.09; S, 5.53. Found: C, 47.62; H, 4.16; N, 12.06; S, 5.35.

*4-*p*-Methylbenzylideneimino-2-N-tetra-O-acetyl-β-*D*-glucosyl-1,2,4-triazole-3(2H)-thione (11).* Yield 50%, m.p. 217–218 °C. MS: *m/z* 549 ($M^+ + 1$). IR: 1751, 1606, 1235 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.96, 2.06, 2.08, 2.10 (4s, 12H, CH_3), 2.45 (s, 3H, $ArCH_3$), 4.00 (m, 1H, CH-5′), 4.20, 4.30 (2dd, 2H, CH_2-6′), 5.27 (t, 1H, CH-4′), 5.44 (t, 1H, CH-3′), 5.80 (t, 1H, CH-2′), 6.25 (d, 1H, H-1′), 7.30 (d, 2H, ArH), 7.75 (d, 2H, ArH), 8.07 (s, 1H, CH=N triazole), 10.25 (s, 1H, CH=N). ^{13}C NMR($CDCl_3$): δ 21.0, 21.2, 22.2, 62.0, 68.1, 69.4, 74.0, 75.0, 82.0, 129.2, 129.7, 130.2, 140.3, 144.0, 161.6, 164.5, 169.4, 169.8, 170.6, 171.1. Anal. Calcd for $C_{24}H_{28}N_4O_9S$ (548): C, 52.55; H, 5.11 N; 10.22; S, 5.84. Found: C, 52.75; H, 4.97; N, 10.31; S, 5.55.

*4-*p*-Methoxybenzylideneimino-2-N-tetra-O-acetyl-β-*D*-glucosyl-1,2,4-triazole-3(2H)-thione (12).* Yield 50%, m.p. 194–195 °C (lit.[6] m.p. 188 °C). MS: *m/z* 564 (M^+). IR: 3455, 3136, 2964, 2937, 2838, 1750, 1605, 1572, 1547, 1515, 1425, 1256, 1223 cm^{-1}.

Acknowledgement

The support of the University of Kuwait received through research grant (SC 03/00) and the facilities of ANALAB and SAF are gratefully acknowledged.

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