1,2,4-Triazines. Synthesis of Selected Members of the *s*-Triazolo[3,4-*f*]-[1,2,4]triazine and Tetrazolo[1,5-*f*][1,2,4]triazine Ring Systems

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A convenient synthesis of 3-amino-6-hydrazino-5(2*H*)[1,2,4]triazinone **4** has been developed and a study of the reactions of **4** with aliphatic acids, orthoesters and miscellaneous active carbonyl reagents has been undertaken. When **4** was refluxed in either neat acid or orthoester in dimethylformamide, a facile ring closure reaction with the N-1 nitrogen of the 1,2,4-triazine ring occurs affording a novel series of 3-alkyl(aryl)-8(5*H*)-*s*-triazolo[3,4-*f*][1,2,4]triazinones (**6-11**). Ring closure with carbon disulfide and cyanogen bromide is also reported affording 6-amino-3(2*H*)thio-8(5*H*)-*s*-triazolo[3,4-*f*][1,2,4]triazinone **12** and 3,6-diamino-8(5*H*)-*s*-triazolo-[3,4-*f*][1,2,4]triazinone **14**, respectively. In addition **4** has been converted into 3-amino-6-azido-5(2*H*)-1,2,4-triazinone **15** which was employed in a study of azide-tetrazole equilibrium affording 6-amino-8(5*H*)tetrazolo[1,5-*f*][1,2,4]triazinone **16**. Rates for interconversion at various temperatures were measured and an activation energy for the process determined.

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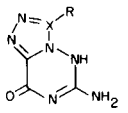
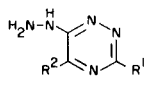
Interest in the synthesis of bridgehead (1) and non-bridgehead (2) fused nitrogen heterocycles prompted an investigation into the preparation of various examples of the *s*-triazolo[3,4-*f*][1,2,4]triazine ring system (I), and tetrazolo[1,5-*f*][1,2,4]triazine (II). Examples of I have been previously reported (3); however, these examples were prepared from suitably substituted *s*-triazoles. Examples of II are novel. It was of considerable interest to examine the nucleophilic character of the N-1 nitrogen atom of an appropriately substituted 1,2,4-triazine ring (III) with respect to ring closure leading to compounds of type I and II. Also, the literature abounds with studies concerning the nucleophilic character of the N-2 and N-4 nitrogen atoms in 1,2,4-triazines (4) but such studies are are lacking with respect to the N-1 position.



I, X=C/R=H, alkyl, aryl

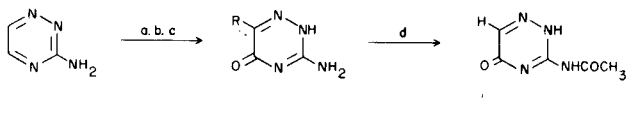
II, X=N



III

A convenient starting point in the synthetic pathway towards compounds of type I, was 3-amino-1,2,4-triazine (**1**) (5). Compound **1** underwent facile oxidation to 3-amino-5(2*H*)-1,2,4-triazinone (**2**) as described by Sasaki and Minamoto (6). The 4*H*-tautomer suggested by the above workers has, however, been shown to be incorrect and the 2*H*-form to be the more likely tautomeric structure (7). Based upon studies employing 3,5(2*H*,4*H*)-1,2,4-triazinedione (6-Azauracil) (8), it was felt that the 6-position of **2** would be vulnerable to electrophilic attack, particularly by bromine. Indeed, when **2** was stirred in bromine water, a new compound, 3-amino-6-bromo-5(2*H*)-1,2,4-triazinone (**3**) was formed. Compound **3** was characterized by means of spectral data, all consistant with bromination at the 6-position. The bromine atom in **3** was reasonably labile, undergoing displacement by hydrazine or methyl hydrazine affording 3-amino-6-hydrazino-5(2*H*)-1,2,4-triazinone (**4**) and 3-amino-6-(1-methylhydrazino)-5(2*H*)-1,2,4-triazinone (**5**), respectively. Again, spectral characteristics and elemental analyses were consistant with the proposed course of the reactions (see Scheme 1).

Scheme I



I

a, H_2O_2 /CH_3COOH

b, Br_2, H_2O

c, $NH(R)NH_2$ (R=H, CH_3), H_2O

d, $(CH_3CO)_2O$

2 R=H

3 R=Br

4 R=$NHNH_2$

5 R=$N(CH_3)NH_2$

15

Ring Closure Reactions with Acids and Anhydrides.

When **4** was treated with hot formic acid, a new material **6** was isolated. The ir spectrum of **6** possessed an intense absorption at 1725 cm^{-1}. This is consistant with the carbonyl absorption reported by H. G. O. Becker, *et. al.* (3), for similar fused triazines leading to the conclusion that ring closure had occured. Supporting

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evidence for this conclusion was found in the pmr spectrum which revealed a highly deshielded proton resonating at δ 9.54. Also, the uv spectrum of **6**, showed the absence of a weak absorption at 302 nm (log Σ = 3.29) possessed by **4** and the appearance of a new absorption at 274 nm (log Σ = 3.07). Thus, compound **6** was assigned the structure 6-amino-8(5*H*)-*s*-triazolo[3,4-*f*][1,2,4]triazinone (Scheme 2).

Treatment of **4** with excess hot acetic anhydride produced compound **7** which precipitated from the reaction mixture upon cooling. The ir spectrum of **7** had intense absorptions at 1740 cm^{-1} and 1700 cm^{-1}. Based upon the analysis of the spectrum of **6**, ring closure had been effected with acetic anhydride (CO, 1740 cm^{-1}). However, the presence of a new carbonyl absorption at 1700 cm^{-1} remained to be explained. This was accomplished as follows: treatment of **4** with one equivalent of acetic anhydride in dry dimethylformamide produced a different material, compound **8**, whose ir spectrum possessed a carbonyl at 1730 cm^{-1} but none at 1700 cm^{-1}. Compound **8** could also be prepared by refluxing **4** in acetic acid. Comparison of the pmr spectra of **7** and **8** showed the presence of a single methyl resonance at δ 2.48 in **8**, while two methyl resonances at δ 2.53 and δ 2.16 were detected in the spectrum of **7**. This suggested that acetylation of the exocyclic 6-amino group had occured in excess anhydride. Further confirmation was obtained when **8** was converted into **7** in refluxing acetic anhydride. Also, when **2** was treated with acetic anhydride at reflux (6), affording 3-acetylamino-5(2*H*)-1,2,4-triazinone (**15**), the pmr spectrum contained a methyl resonance at δ 2.13. This data was consistent with the following structural assignments for **7**, 6-acetyl-amino-3-methyl-8(5*H*)-*s*-triazolo[3,4-*f*][1,2,4]triazinone and **8** as 6-amino-3-methyl-8(5*H*)-*s*-triazolo[3,4-*f*][1,2,4]-triazinone.

When **4** was treated with hot propanoic acid, 6-amino-3-ethyl-8(5*H*)-*s*-triazolo[3,4-*f*][1,2,4]triazinone (**9**) was characterized as described above (see Table I) and all spectral data were consistent with the assigned structure. These reactions are summarized in Scheme 2.

While no evidence for the existence of hydrazides was noted in any of the above reactions, hydrazides were considered prime candidates as intermdiates in the conversion of **4** into the fused ring system. It seemed of interest to prepare such a hydrazide and attempt to effect ring closure. When **4** was treated with benzoyl chloride in aqueous base the product isolated 2-(3-amino-2,5-dihydro-5-oxo-1,2,4-triazin-6-yl)benzhydrazide **10**, had spectral features consistent with hydrazide formation (see Experimental). Compound **10** was placed in ethylene glycol and heated at 200° for 1 hour. A new compound was isolated and an examination of the ir spectrum again revealed a carbonyl absorption at 1735 cm^{-1}. All other spectral data was consistent with the fact that ring closure had taken place affording 6-amino-3-phenyl-8(5*H*)-*s*-triazolo[3,4-*f*][1,2,4]triazine (**11**).

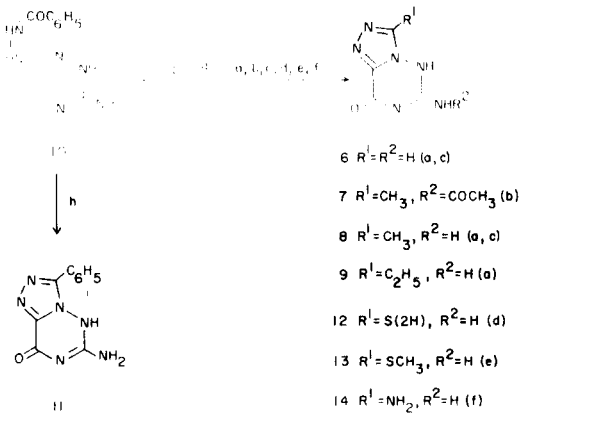
Reaction with Orthoesters.

When **4** was treated under reflux with orthoesters such as triethylorthoformate or triethylorthoacetate, only starting material was recovered. When the reaction was attempted in nitrobenzene as solvent (9), similar results were obtained. However, when the solvent was changed to dimethylformamide facile ring closure occurred, resulting in the alternate synthesis of compounds **6** and **8**. For synthetic purposes the reaction with orthoesters offered no significant advantage over reaction with aliphatic acids. These results are summarized in Scheme 2.

Reaction with Aliphatic Acids in Dimethylformamide.

When **4** was treated with two equivalents of acetic acid in excess dimethylformamide under reflux, the reaction

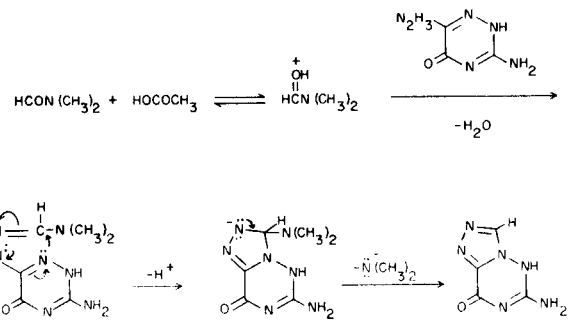
Scheme 2



a, R^1COOH. b, $(CH_3CO)_2O$. c, $R^1C(OC_2H_5)_3$, DMF. d, CS_2, C_5H_5N/H_2O.

e, CH_3I, OH^-. f, CNBr, H_2O. g, C_6H_5COCl, OH^-. h, $CH_2(OH)CH_2OH$, 200°.

Scheme 3



6

followed a different course than observed with neat acid. In this case no **7** or **8** was isolated, but rather compound **6** formed in high yield. No evidence for the formation of **7** or **8** was detected in this reaction and no attempt was made to extend this reaction to other *N,N*-disubstituted alkylamides. These results are not without precedent in the literature (10). A probable mechanism for the conversion is outlined in Scheme 3 and protonation on oxygen by acid in the first step has been previously established (11).

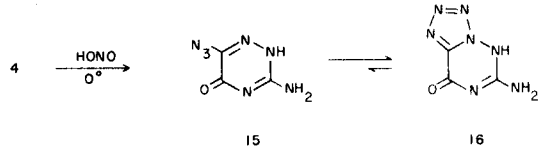
Reaction with Miscellaneous Reagents.

Treatment of compound **4** with carbon disulfide (12) in pyridine-water (1:1) under reflux produced a pale yellow solid, compound **12**. Again, the ir spectrum of **12** revealed the amide carbonyl (1730 cm^{-1}) characteristic of ring closure. Also an intense absorption at 1350 cm^{-1} was assigned to the C=S thioamide stretching frequency (13). Compound **12** was dissolved in concentrated aqueous ammonia and methyl iodide was added to the solution. This produced a new material, compound **13**, whose pmr spectrum possessed a singlet integrating for 3 protons at δ 2.62. The ir spectrum contained the amide carbonyl at 1745 cm^{-1} and no absorption at 1350 cm^{-1}. This data indicated alkylation had occured on sulfur as expected. Thus, ring closure with carbon disulfide occurs smoothly and the resultant thione can be cleanly alkylated on the sulfur atom (Scheme 2).

Compound **4** was refluxed with cyanogen bromide in water, affording compound **14**. The sturcture of **14** was determined by spectral means and elemental analysis (see Experimental). In particular, the increased complexity of the NH stretching region of the ir spectrum was consistent with the presence of an additional amino group (Scheme 2).

3-amino-6-azido-5(2*H*)-1,2,4-triazinone (**15**) was most conveniently prepared by treating **4** with nitrous acid at 0° and rapidly isolating the resulting precipitate. Evidence for the existence of the azide function was obtained from the ir spectrum (potassium bromide) which exhibited an intense absorption at 2140 cm^{-1}. Compound **15** was stable in the solid state for periods of two months after which surface decomposition was noted. However, when compound **15** was stirred for a few minutes in polar solvents such as acetone, water or ethanol and the ir spectrum of the precipitate (**16**) reexamined, the azide band had disappeared completely and new absorptions at 1290, 1080, and 1015 cm^{-1} were noted. These absorptions have been assigned to the presence of a tetrazole ring (14,15). Other spectral evidence was consistent with the structure proposed for compound **16**, 6-amino-8(5*H*)tetrazolo[1,4-*f*][1,2,4]triazinone. These reactions are illustrated in Scheme 4. Compound **16** was also prepared in low yield from **3** and sodium azide in water-ethanol.

Scheme 4



Attempts to study the thermal behavior and reactivity of the azide group in **15** can be summarized as follows. When **15** was refluxed in toluene for extended periods of time, the only product isolated was **16**, forming in quantitative yield. When **15** was stirred with an excess of dimethyl acetylenedicarboxylate (DMAD) at room temperature for extended periods, only **16** was isolated, forming in high yield. If the reaction was attempted with one equivalent of DMAD in refluxing chloroform, identical results were obtained. The absence of any **15** in **16** in the solid state was confirmed by ir spectroscopy since the 2140 cm^{-1} band and an intense absorption at 760 cm^{-1} were undetectable in the spectrum of **16**. The

Table 1

Compound	M.p (a)	Habit (b)	Yield (%)	Molecular Formula	Analysis Calcd. C, H, N	Analysis Found	Spectral Data Ir (d) (ν, cm^{-1})	^{1}H Nmr (e) (δ)	Mass Spectrum m/e (R.A.)	Uv (f) Nm (log ϵ)
1	175	yellow needles (c)	61	$C_3H_3N_4$			3290, 1640	8.62 (d, 1, J = 2 Hz), 8.28 (d, 1, J = 2 Hz), 7.22 (s, 2)	96 (84)	321 (2.50), 226 (3.22)
2	<300	needles	85	$C_3H_4N_4O$	32.14, 3.60, 49.99	32.28, 3.62, 50.21	3275, 1660	7.30 (s, 1), 6.93 (s, 2)	112 (59)	252 (3.15), 204 (3.82)
3	270	needles	94	$C_3H_3BrON_4$	18.86, 1.58, 29.34	18.94, 1.64, 29.10	3340, 1640	7.05 (s, 1)	192 (7.7), 190 (10)	259 (3.36), 205 (4.08)
4	<300	orange plates	58	$C_3H_4N_4O$	25.35, 4.26, 59.13	25.78, 4.22, 59.39	3440, 3310, 1665		142 (23)	302 (3.29), 231 (3.63), 204 (3.81)
5	235	yellow plates	30	$C_6H_8N_8O$•1/8 H_2O	30.33, 5.09, 53.06	30.54, 5.25, 52.63	3440, 3330, 1680	6.4 (s, 5), 2.9 (s, 3)		
6	<300	plates	80	$C_4H_4N_4O$	31.58, 2.65, 55.25	31.51, 2.64, 55.36	3420, 3280, 1725	9.54 (s, 1), 6.76 (s, 2)		274 (3.07), 213 (4.17)
7	<300	needles	82	$C_4H_6N_4O$•1/4 H_2O	39.58, 3.79, 39.52	39.39, 3.73, 39.37	3180, 1740, 1700	2.53 (s, 3), 2.16 (s, 3)	208 (80)	254 (3.45), 224 (4.00)
8	<300	plates	84	$C_4H_6N_4O$	36.14, 3.64, 50.58	36.08, 3.69, 50.16	3350, 3190, 1730	6.43 (s, 2), 2.48 (s, 3)	166 (100)	276 (2.99), 217 (4.02)
9	<300	plates	82	$C_6H_8N_8O$	40.00, 4.48, 46.65	39.93, 4.66, 46.49	3400, 3200, 1745	6.42 (s, 2), 2.82 (q, 2, J = 4 Hz), 1.32 (t, 3, J = 4 Hz)		269 (3.28), 242 (3.48), 217 (4.32)
10	<250	irregular prisms	70	$C_{10}H_{10}N_8O_2$•H_2O	45.45, 4.58, 31.80	45.56, 4.51, 31.90	3400, 3190, 1665	7.45 (m, 5), 6.42 (s, 2)		270 (3.91), 224 (4.48)
11	<300	plates	86	$C_{10}H_{10}N_4O$	52.63, 3.53, 36.83	52.34, 3.64, 36.37	3440, 3100, 1735	8.03 (m, 5), 6.15 (s, 2)		247 (4.38)

(a) Uncorrected. (b) Colorless unless otherwise noted; recrystallized from water unless otherwise noted. (c) Recrystallized from isopropanol. (d) Potassium bromide disk. (e) DMSO-d_6/tetramethylsilane as internal standard. (f) In water.

Table II

T (°K)	Solvent	Slope (a)	Km (b) (min^{-1})	Ln Km	ΔE_a (c)
293	3*N* hydrochloric acid	1.5699 (γ = 100)	4.5101×10^{-3}	-5.4014	
	2nd run	1.8874 (γ = 150)	4.2346×10^{-3}	-5.4645	
295.5	3*N* hydrochloric acid	1.7853 (γ = 90)	6.4398×10^{-3}	-5.0452	
298	3*N* hydrochloric acid	2.5477 (γ = 110)	8.5017×10^{-3}	-4.7675	
	2nd run	2.5697 (γ = 110)	8.5799×10^{-3}	-4.7583	
300.5	3*N* hydrochloric acid	1.8308 (γ = 60)	1.0079×10^{-2}	-4.5973	
303	3*N* hydrochloric acid	2.0451 (γ = 50)	1.4308×10^{-2}	-4.2496	
	2nd run	1.9841 (γ = 50)	1.3703×10^{-2}	-4.2901	
					20.5757 cal/mole

(a) Calculated by regression analysis; γ = time-interval. (b) Calculated by means of equation 1 (see Experimental). (c) Slope calculated by regression analysis.

solution spectrum (DMSO) of **16**, isolated in the above reactions also confirmed the absence of the azide group. This data strongly suggests that the azide form undergoes rapid and complete isomerization to the fused tetrazole in polar and non-polar solvents. This result is not unexpected since the electron-releasing 6-amino group stabilizes the electron withdrawing tetrazole ring and destabilizes the electron releasing azide group (16).

While the isomerization was too rapid at room temperature (> 1 minute by uv spectroscopy) in water and > 5 minutes in absolute ethanol for convenient kinetic investigation it was possible to slow down the conversion when 3*N* hydrochloric acid was employed as the solvent. Undoubtedly, this was caused by protonation of the exocyclic 6-amino group, converting it into an electron-withdrawing group. The obtention of the kinetic data for the interconversion is described in the experimental section and the results summarized in Table II. Construction of an Arrhenius plot afforded an estimation of the energy of activation for the interconversion in 3*N* hydrochloric acid. The value of E_a was 20.58 kcal/mole (see Experimental), while application of the Bunnett equation (17) afforded a value of 20.54 kcal/mole. This activation energy seems to exhibit a reasonable agreement with activation energies observed in other systems (18).

Summary.

It has been determined that 3-amino-6-hydrazino-5-(2*H*)-1,2,4-triazinone (**4**) undergoes a facile and clean ring closure reaction with organic acids, orthoesters and active carbonyl compounds at the N-1 nitrogen of the triazine ring affording a series of 3-alkyl/aryl and miscellaneously substituted *s*-triazolo[3,4-*f*][1,2,4]triazines previously obtained by a circuitous route from *s*-triazoles. In addition 3-amino-6-azido-5(2*H*)-1,2,4-triazinone **15**, was prepared from **4** and rate of conversion into 6-amino-8(5*H*)tetrazolo[1,5-*f*][1,2,4]triazinone (16) was investigated.

EXPERIMENTAL

All melting points are uncorrected. Ir spectra were obtained on a Beckman Acculab 2. Nmr spectra were obtained on a Perkin-Elmer R-12. Uv spectra were obtained on a Perkin-Elmer 200. Elemental Analyses were performed by Instranal Labs, Inc., East Greenbush, New York. Mass spectra were obtained on a Perkin-Elmer RMU-6. Identity of compounds prepared by different reagents was established by superimposable spectra. The physical properties and spectral data for compounds 1-11 are contained in Table 1.

3-Amino-1,2,4-triazine (**1**).

This compound was prepared as described by Erickson (5).

3-Amino-5(2*H*)-1,2,4-triazinone (**2**).

This compound was prepared as described by Sasaki and Minamoto (6).

3-Amino-6-bromo-5(2*H*)-1,2,4-triazinone (**3**).

Compound **2** (1.5 g., 1.3×10^{-2} mole) was added to a stirred solution of bromine (2.14 g., 1.3×10^{-2} mole) in water (200 ml.) at 25°. Stirring was continued for 3 hours, then additional bromine (1 g.) was added to insure an excess and the mixture was stirred overnight. The precipitate that resulted was collected and washed with copious quantities of water.

3-Amino-6-hydrazino-5(2*H*)-1,2,4-triazinone (**4**).

Compound **3** (1.9 g., 1×10^{-2} mole) was suspended in water (50 ml.) and hydrazine (95%, 0.65 g., 2×10^{-2} mole) was added. The pale orange solution was heated under reflux for 3 hours. The precipitate that formed during the course of the reaction was collected, 0.84 g. (58%).

3-Amino-6-(1-methylhydrazino)-5(2*H*)-1,2,4-triazinone (**5**).

Compound **3** (1.0 g., 5.2×10^{-3} mole) was suspended in water and methyl hydrazine (0.46 g., 1×10^{-2} mole) was added. The solution was heated under reflux for 2 hours. Cooling produced a crop of yellow plates (0.23 g., 30%).

General Preparation of 3-Alkyl-8(5*H*)-*s*-triazolo[3,4-*f*][1,2,4]-triazinones from **4** and Aliphatic Acids.

Compound **4** (0.5 g., 3.5×10^{-3} mole) was suspended in an excess of the acid then refluxed for 12 hours. Removal of excess acid at reduced pressure followed by recrystallization afforded the appropriate 3-substituted derivatives, compounds **6**, **8** and **9**.

General Preparation of 3-Alkyl-8(5*H*)-*s*-triazolo[3,4-*f*][1,2,4]triazinones from Orthoesters in Dimethylformamide.

Compound **4** (0.5 g., 3.3 x 10^{-1} mole) and the orthoester (7 x 10^{-1} mole) were suspended in 30 ml. of *N,N*-dimethylformamide, refluxed with a Dean-Stark trap for 12 hours. Cooling at 0° afforded the product. Compound **4** and triethylorthoformate afforded **6**, identical in every respect with compound **6** isolated from the reaction with formic acid. Compound **4** and triethylorthoacetate afforded **8**, identical in every respect with compound **8** isolated from the reaction with acetic acid.

6-Acetylamino-3-methyl-8(5*H*)-*s*-triazolo[3,4-*f*][1,2,4]triazinone (**7**).

Compound **4** (0.5 g., 3.5 x 10^{-3} mole) and acetic anhydride (20 ml.) were gently refluxed for 20 hours. At the end of this time, the solution was cooled to room temperature and the precipitate collected.

From Compound **8**.

Compound **8** (2.0 g. x 10^{-3} mole) in acetic anhydride (15 ml.) was refluxed for 12 hours. Cooling at room temperature followed by recrystallization from water afforded 50 mg. of a material identical in every respect with compound **7**.

Preparation of Compound **6** from Acetic Acid and *N,N*-Dimethylformamide.

Compound **4** (0.5 g., 3.5 x 10^{-3} mole) acetic acid (7 x 10^{-3} mole) and *N,N*-dimethylformamide (50 ml.) were refluxed for 12 hours. After cooling to room temperature, crystals were induced to form by adding ether. These were collected and were identical in every respect to compound **6** (0.4 g., 75%). This reaction was repeated under identical conditions employing propanoic acid and compound **6** was isolated (0.32 g., 60%).

2(3-Amino-2,5-dihydro-5-oxo-1,2,4-triazin-6-yl)benzhydrazide (**10**).

Compound **4** (0.5 g., 3.5 x 10^{-3} mole) was dissolved in aqueous potassium hydroxide (1*N*, 20 ml.) and benzoyl chloride (1.0 g., 7 x 10^{-3} mole) was added. The two-phase system was rapidly stirred for 30 minutes. The *p*H was then adjusted to **7** with dilute hydrochloric acid and the resultant precipitate collected.

6-Amino-3-phenyl-8(5*H*)-*s*-triazolo[3,4-*f*][1,2,4]triazinone (**11**).

Compound **10** (0.25 g., 1 x 10^{-3} mole) was suspended in ethylene glycol (25 ml.) and then heated to 200° for 1 hour. After cooling at room temperature, the solution was poured into 50 ml. of water and the resultant precipitate was collected.

6-Amino-3(2*H*)thio-8(5*H*)-*s*-triazolo[3,4-*f*][1,2,4]triazinone (**12**).

Compound **4** (0.5 g., 3.5 x 10^{-3} mole) in pyridine/water (1:1, 50 ml.) had carbon disulfide (0.3 g., 4 x 10^{-3} mole) added. The mixture was then heated under reflux until hydrogen sulfide ceased to be evolved (12 hours). Concentration of the yellow mother liquid under reduced pressure afforded a crude yellow solid which recrystallized from water (charcoal) as pale yellow prisms (0.23 g., 36%), m.p. < 300°; ir (potassium bromide): 3400, 3300, 1730, 1350; uv (water): 313, log ϵ = 4.09, 256, log ϵ = 5.14, 212, log ϵ = 5.10. Compound **12** (0.2 g., 1 x 10^{-3} mole) was dissolved in aqueous ammonia (25 ml.) and excess methyl iodide was added then stirred at room temperature for 30 minutes. Addition of 6*N* hydrochloric acid produced a crop of crude crystals which were recrystallized from water affording 6-amino-3-methylthio-8(5*H*)-*s*-triazolo[3,4-*f*][1,2,4]triazinone (**13**) as colorless needles, (0.1 g., 50%), m.p. 300°; ir (potassium bromide) 3370, 3160, 1745; uv (water): 275 (shoulder), log ϵ = 3.38, 238 (shoulder), log ϵ = 4.04, 226, log ϵ = 4.10, 207, log ϵ = 4.14; nmr (DMSO-d_6): 6.4 (broad s, 2, NH_2), 2.65 (s, 3, SCH_3).

Anal. Calcd. for $C_5H_6N_6OS$: C, 30.30; H, 3.05; N, 42.40. Found: C, 30.08; H, 2.90; N, 42.36.

3,6-Diamino-8(5*H*)-*s*-triazolo[3,4-*f*][1,2,4]triazinone (**14**).

Compound **4** (0.5 g., 3.5 x 10^{-3} mole) was suspended in an aqueous solution of cyanogen bromide (0.74 g., 7 x 10^{-3} mole) and heated under reflux with stirring for 24 hours. The precipitate was collected by means of suction filtration. Recrystallization from water produced cream prisms, (0.37 g., 63%) m.p. < 300°; ir (potassium bromide): 3400, 3220, 3100, 1730, 1650, 1550, 1365, 1295, 865, 750, 680.

Anal. Calcd. for $C_4H_5N_7O$: C, 28.36; H, 2.98; N, 57.89. Found: C, 28.70; H, 3.06; N, 57.74.

6-Amino-8(5*H*)tetrazolo[1,5-*f*][1,2,4]triazinone (**16**).

Compound **4** (2.0 g., 1.41 x 10^{-2} mole) was dissolved in 10 ml. of 6*M* hydrochloric acid. This solution was cooled to -5° and was accompanied by formation of a precipitate. To the stirred suspension, sodium nitrite (1.1 equivalents) in 10 ml. of water was added dropwise while maintaining the temperature at 0°. After addition was complete, stirring was continued for an additional 10 minutes and the precipitate collected and dried over solid potassium hydroxide at reduced pressure for 24 hours. This produced 1.92 g. (98%) of 3-amino-6-azido-5(2*H*)-1,2,4-triazinone (**15**); ir (potassium bromide): 3320, 3120, 2140, 1630. Compound **15** (0.5 g., 3.3 x 10^{-3} mole) was suspended in 50 ml. of water and was stirred at room temperature overnight. Collection of the precipitate followed by recrystallization from water produced 0.48 g. (100%) of compound **16**, m.p. 220 dec.; ir (potassium bromide): 3400, 3220, 2800 (broad), 1750, 1290, 1080, 1015; uv (water): 245, log ϵ = 3.80, 206, log ϵ = 4.34; (in 3*N* hydrochloric acid): 278 (shoulder) log ϵ = 3.45, 246, log ϵ = 3.64, 211, log ϵ = 4.19; ms: (m/e, RA) 153 (68).

Anal. Calcd. for $C_3H_8N_7O$: C, 23.53; H, 1.98; N, 64.04. Found: C, 23.41; H, 2.00; N, 64.27.

Reaction of Compound **15** in Refluxing Toluene.

Compound **15** (0.25 g., 1.6 x 10^{-3} mole) was suspended in toluene (25 ml.) and heated under reflux for 24 hours. The suspension was cooled to room temperature and the precipitate was recrystallized from water (0.23 g., 100%) and was identical in every respect with compound **6**.

Reaction of Compound **5** with Dimethyl Acetylenedicarboxylate.

Compound **15** (0.2 g., 1.3 x 10^{-3} mole) was suspended in 25 ml. of chloroform to which dimethyl acetylenedicarboxylate (0.18 g., 1.3 x 10^{-3} mole) had been added. The suspension was refluxed for 24 hours. The precipitate was collected and recrystallized from water affording 0.14 g. (70%) of a material identical in every respect with compound **6**.

Kinetics.

An examination of the uv spectrum of compound **15** in 3*N* hydrochloric acid showed an absorption at 295 nm (log ϵ = 3.77), attributed to the N_3 functional group (19), that collapsed with respect to time. However, the collapse was not to zero absorbance since the fused tetrazole possessed a sholder at 278 nm (log ϵ = 3.45) in the above solvent. A convenient graphical method for

analysis of rate data of the type described above is the time-lag method (20) and the best fit straight line was obtained by regression analysis. The slope of this line was related to the macroscopic rate constant at the particular temperature by means of Equation 1:

$$(1)\quad \text{Slope} = e^{m\gamma}$$

γ being the time-interval employed in the time-lag plot. Macroscopic rate constants were obtained in this fashion for the following temperatures 20, 22.5, 25, 27.5 and 30°. An Arrhenius plot was constructed in the usual fashion and the best straight-line fit obtained by means of regression analysis. The macroscopic rate constants and activation energy are summarized in Table II. Finally the rate constant was evaluated by means of Equation 2

$$(2)\quad \log\left[\frac{K_2}{K_1}\right] = \frac{E_2}{4.576}\left[1/T_2 - 1/T_1\right]$$

(17): for the average macroscopic rate constant determined at 30 and 20°. This afforded a value for E_a of 20.54 kcal/mole in good agreement with the value obtained graphically.

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