The Chemistry of 4-Hydrazino-7-phenylpyrazolo[1,5-*a*]-1,3,5-triazines

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Received August 5, 1974

The reaction of 4-hydrazino-7-phenylpyrazolo[1,5-*a*]-1,3,5-triazine (**4**) with nitrous acid gave 8-phenyltetrazolo[1,5-*e*]pyrazolo[1,5-*a*]-1,3,5-triazine (**5b**), which was determined by pmr and ir spectra to be in equilibrium with 4-azido-7-phenylpyrazolo[1,5-*a*]-1,3,5-triazine (**5a**). The equilibrium between the tetrazolo (**5b**) and azido (**5a**) forms was studied by pmr and an attempt was made to determine if substituents in the pyrazole nucleus could sufficiently stabilize the tricyclic tetrazolo form (**5b**) over the bicyclic azido form (**5a**). Thermal degradation of **5**(a⇌b) in an aprotic solvent gave 4-amino-7-phenylpyrazolo[1,5-*a*]-1,3,5-triazine (**7**), indicating the probability of a nitrene mechanism involved in the decomposition. Heating **5** in aqueous base gave both **7** and the "hydroxy" analog, 7-phenylpyrazolo[1,5-*a*]-1,3,5-triazin-4(3*H*)one (**6**), further substantiating the existence of a nitrene intermediate with a competing nucleophilic displacement of the azido group by a hydroxyl group. Cyclization of **4** with diethoxymethylacetate (DEMA) gave 8-phenyl-*s*-triazolo[4,3-*e*]pyrazolo[1,5-*a*]-1,3,5-triazine (**8**), which underwent thermal rearrangement to 8-phenyl-*s*-triazolo[2,3-*e*]pyrazolo[1,5-*a*]-1,3,5-triazine (**9**). Acid catalyzed ring opening of **9** with formic acid gave 3-*N*-formamido-5-phenyl-2(2-*s*-triazolyl)pyrazole (**10**). The failure of **10** to recyclize to **9** with the resultant loss of water, supported the theory that the rearrangement of **8** to **9** might occur simply as a concerted, thermally induced "anhydrous" rearrangement rather than *via* a covalently hydrated intermediate or a Dimroth type mechanism (in the base catalyzed rearrangement).

The pyrazolo[1,5-*a*]-1,3,5-triazine ring system has been of some interest biologically, because of its isomeric resemblance to the purines (3,4). In the purines, it has been reported that 6-hydrazino derivatives can be cyclized to

Pyrazolo[1,5-*a*]-1,3,5-triazine

s-triazolo[4,3-*i*]purines (5) with diethoxymethylacetate (DEMA), or to tetrazolo[5,4-*i*]purines (6) with nitrous acid. Because of both the biological and physical resemblance of these ring systems (the bridgehead heterocycle has no ionizable proton unlike the purines) it was of interest to us to examine the chemistry of the 4-hydrazinopyrazolo-[1,5-*a*]-1,3,5-triazines.

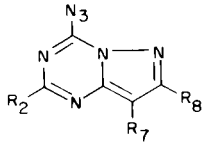
The 4-hydrazino-7-phenylpyrazolo[1,5-*a*]-1,3,5-triazine (**4**) used as a starting material for this study, was prepared by the displacement of the methylthio group of 4-methylthio-7-phenylpyrazolo[1,5-*a*]-1,3,5-triazine (**3**) by hydrazine. The synthesis of **3** was accomplished by alkylating the mercapto group of 4-mercapto-7-phenylpyrazolo[1,5-*a*]-1,3,5-triazine (**2**), which in turn, was synthesized *via* the condensation of 3-amino-5-phenyl-2-thiocarbamolypyrazole (7) with DEMA.

The reaction of the 4-hydrazino compound **4** with nitrous acid was of special interest because of the possible "tetrazolo-azido" equilibrium which might exist between **5a** (4-azido-7-phenylpyrazolo[1,5-*a*]-1,3,5-triazine) and **5b** (10-phenyltetrazolo[1,5-*e*]pyrazolo[1,5-*a*]-1,3,5-triazine). The predominance of the azido isomer **5a** was expected because of the decrease of the electron donating characteristics of the heterocyclic ring (*e.g.*, pyrazolo[1,5-*a*]-1,3,5-triazine) to which the tetrazole ring is attached (8). Thus, it would appear that the electron deficient parent ring system, pyrazolo[1,5-*a*]-1,3,5-triazine, would stabilize the azido conformation **5a** as a result of the electron donating characteristics of the azido group.

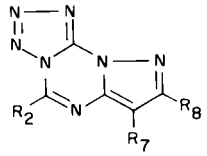
The product **5**, isolated from the reaction of the 4-hydrazino compound **4** with nitrous acid, exhibited a strong azide band at 2150 cm^{-1} as well as a strong band at 1182

TABLE I

Pmr Assignments in the Azido/Tetrazole Equilibrium (a)



"A" (azido)



"T" (tetrazolo)

Structure Type	Compound	Substituents	Pmr Chem. Shifts (a) R_2	R_7	R_8	Temp. °C	Eq. Constant (b) Ka/t
A (azido)	**5a**	R_2=R_7=H	7.70	9.90	---	34	0.5
		R_8=Ph	7.62	9.82	---	70	1.5
T (tetrazole)	**5b**	R_2=R_7=H	7.30	8.48	---	34	0.5
		R_8=Ph	7.23	8.46		70	1.5
A	**14a**	R_2=H; R_7=Br	10.06	---		34	1.3
		R_8=Ph	9.94	---	---	70	3.0
T	**14b**	R_2=H; R_7=Br	8.57	---	---	34	1.3
		R_8=Ph	8.55	---	---	70	3.0
A	(c) **18a**	R_2=SCH_3	---	---	2.82	34	5.0
	(c) **18b**	R_7=R_8=H	---	---	2.57	34	5.0

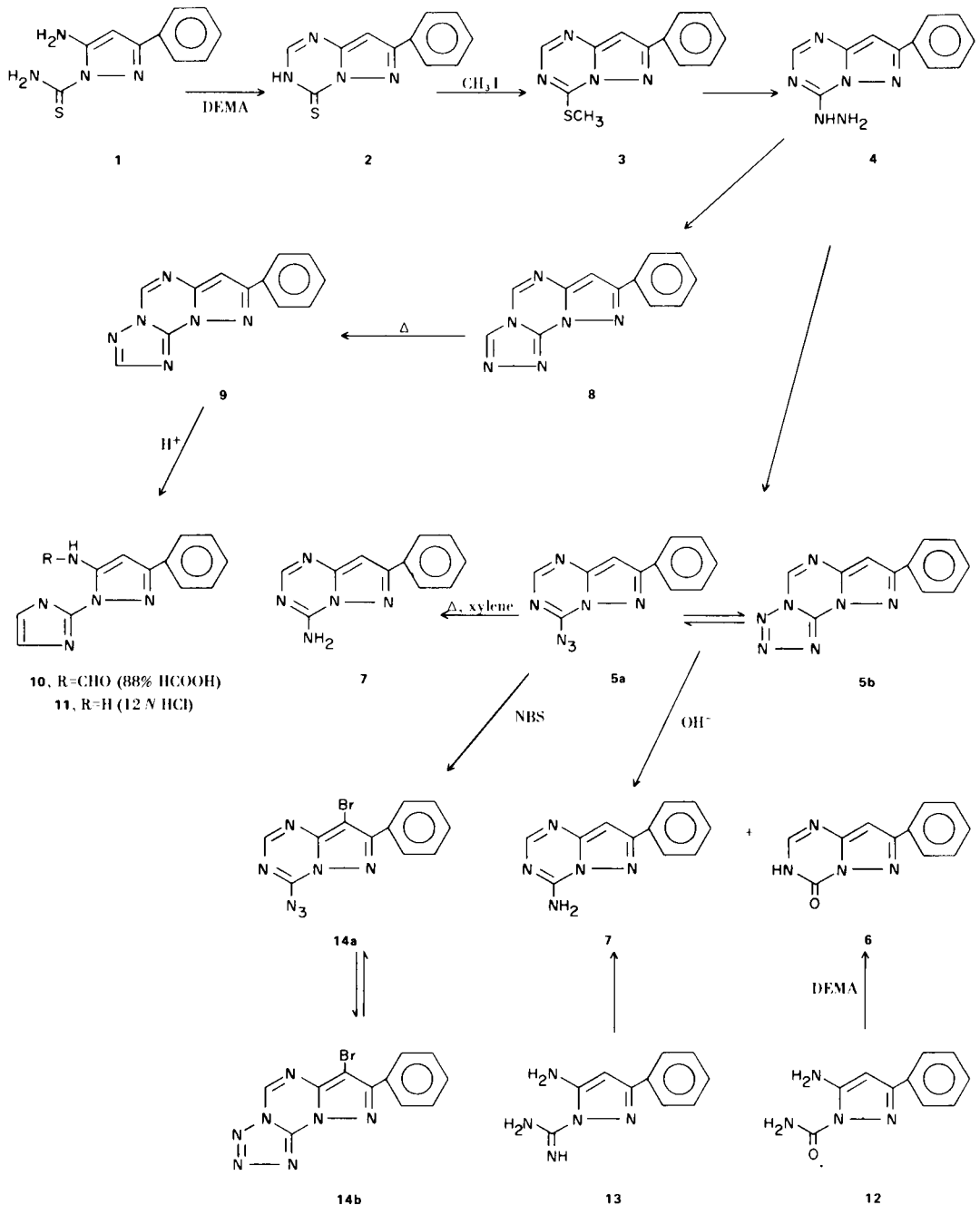
(a) Recorded in DMSO-d_6. (b) Ka/t = ratio of integrated intensities of the proton signals of A to T. (c) Reported in reference 3a.

cm^{-1}. The latter band was not present in the infrared spectra of other 7-phenylpyrazolo[1,5-*a*]-1,3,5-triazines and it was thought to be indicative of the existence of the tetrazolo isomer (**5b**), as suggested by the work of both Montgomery (3) and Avramenko (10). The pmr spectra of **5** in dimethyl-sulfoxide (d_6-DMSO), conducted at 34° and at 70° indicated that both the azido (**5a**) and tetrazolo (**5b**) forms were present. All four of the possible heteroaromatic protons of **5a** and **5b** were detected in d_6-DMSO solution disclosing the presence of the suspected equilibrium. The furthest downfield proton at a value of δ 9.90 was thought to be representative of the tetrazolo form (**5b**) since the deshielding factor of an annelated tetrazole ring was more likely to cause this effect than the azide group (9,10). The equilibrium constant Ka/t = [azido]/[tetrazolo] was found to increase with elevated temperature. Thus, at 34°, Ka/t = 0.5 and at 70°, Ka/t = 1.5 (Table I), indicating a shift to the azido form (**5**) at higher temperatures.

Presumably, an electronegative group introduced into the pyrazole portion of this ring system would destabilize the tricyclic structure (the tetrazolo form) and favor the azido form. Therefore, bromination of **5a** ⇌ **5b** with *N*-bromosuccinimide gave 4-azido-8-bromo-7-phenylpyrazolo-[1,5-*a*]-1,3,5-triazine (**14**), which existed primarily in the azido form, as evidenced by Ka/t = 1.3 at 34° and Ka/t = 3.0 at 70°. The introduction of a methylthio group into the triazine ring also had a destabilizing effect. Thus, 4-azido-2-methylthiopyrazolo[1,5-*a*]-1,3,5-triazine (3a) appeared to exist in only 20% of the tetrazolo form, as shown by the pmr spectrum of this compound in d_6-DMSO at 34° (Table I).

When 8-phenyltetrazolo[1,5-*e*]pyrazolo[1,5-*a*]-1,3,5-triazine (**5b**) was refluxed in xylene for 98 hours, 4-amino-7-phenylpyrazolo[1,5-*a*]-1,3,5-triazine (**7**) was obtained as the product. The structure of **7** was confirmed by condensing 2-acetimidoyl-3-amino-5-phenylpyrazole (**13**) (7) with DEMA. The formation of **7** can be explained on the basis of the thermal decomposition of the azido-tetrazolo (**5a** ⇌ **5b**) compound to yield an intermediate nitrene which then abstracted hydrogen from the solvent to yield the amine (**7**). This mechanism has been substantiated by other investigators, for example in the thermal decomposition of tetrazolo[1,5-*a*]pyrimidines (11) in cyclohexane or acetic acid.

Alkaline hydrolysis of **5a** ⇌ **5b** gave both the amine (**7**) and the analogous "hydroxy" compound, 7-phenylpyrazolo[1,5-*a*]-1,3,5-triazin-4(3*H*)one (**6**). The isolation of both these products would indicate that nucleophilic substitution of the azido group by hydroxyl ion was in competition with nitrene formation (with abstraction of hydrogen from the water present) in aqueous media. The structure of **6** was confirmed by condensation of the known (7) 3-amino-2-carbamoyl-5-phenylpyrazole (**12**) with DEMA. The cyclization of the 4-hydrazino group of **4** to give a fused *s*-triazole, in analogy with the purines mentioned earlier (5), took place with ease. Thus, 4-hydrazino-7-phenylpyrazolo[1,5-*a*]-1,3,5-triazine (**4**) was condensed with DEMA at room temperature to afford 8-phenyl-*s*-triazolo[4,3-*e*]pyrazolo[1,5-*a*]-1,3,5-triazine (**8**). Because

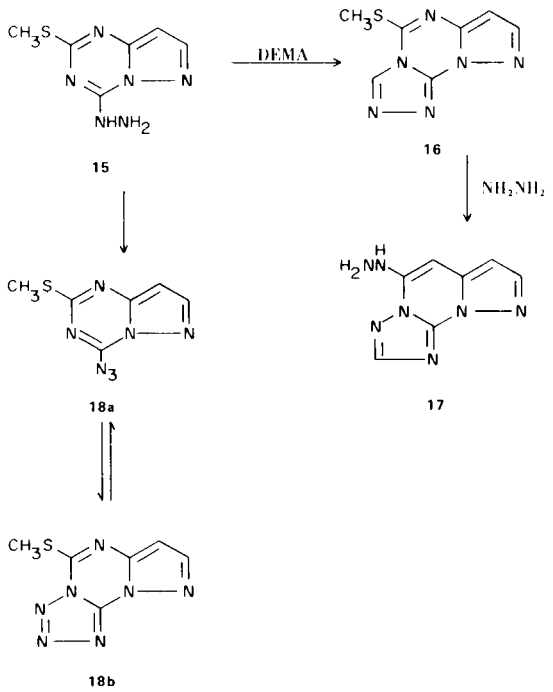


SCHEME I

of the low electron density at the nitrogen bridgehead, it was expected that isomerization of the tricyclic ring system would take place under acid or base catalysis or thermal scission (12-16). It was anticipated that the rearrangement would take place on the basis of literature reports (17) that other fused triazole ring systems have undergone similar rearrangements to isomeric fused triazole ring systems.

Thus, when **8** was heated to its melting point and maintained at that temperature for 5 minutes, the rearrangement did take place, yielding the isomeric 8-phenyl-*s*-triazolo-[2,3-*c*]pyrazolo[1,5-*a*]-1,3,5-triazine (**9**). The infrared spectrum of **9** differed greatly from that of **8**, and the former did not exhibit any vibrations in the N-H region, indicating that the new ring system was still intact. The pmr spectrum of **9** (in DMSO-d_6) was consistent with the proposed structural assignment. The lone triazolo (C_3) proton of **9** was shifted upfield to δ 8.57 (in ppm) in comparison to the triazolo (C_2) proton of **8** which appeared at δ 9.17.

Acid catalyzed hydrolysis opened the tricyclic ring sys-



SCHEME 2

tem to afford pyrazolotriazoles as products. Thus, when **9** was treated with 88% formic acid, the product obtained was established as 3-*N*-formamido-5-phenyl-2-*s*-triazolylpyrazole (**10**) on the basis of ir (formamido carbonyl absorption) and pmr (5) spectra. Hydrolysis with concentrated hydrochloric acid directly converted **9** to 3-amino-5-phenyl-2(2-*s*-triazolyl)pyrazole (**11**). Alternatively, **10** was degraded to **11** with hydrochloric acid.

The formamido compound **10** could not be recyclized to the tricyclic system **8** by gradually heating the former (**10**) to its melting point. Therefore, one would not suspect the acid hydrolysis of **9** to **10** to occur *via* a covalent hydrate (13-16) intermediate. An alternative attempt was made, *via* pmr, to determine whether or not such covalent hydrate species were involved. When the pmr spectra of **8** in trifluoroacetic acid was studied both with and without the addition of deuterium oxide, no discernible differences were observed. Only the structure **10** could be conclusively identified in the spectra.

One might conclude that the rearrangement of the triazolo[4,3-*e*] system (**8**) to the triazolo[2,3-*e*] system (**9**) in these tricyclic compounds occurs *via* a thermally induced "anhydrous" mechanism, even in the presence of a solvent. Such a mechanism has been proposed by both Shirakawa (12) and by Rose (13). When 4-hydrazino-2-methylthiopyrazolo[1,5-*a*]-1,3,5-triazine (**15**) was condensed with DEMA, 5-methylthio-*s*-triazolo[4,3-*e*]pyrazolo[1,5-*a*]-1,3,5-triazine (**16**) was obtained. Treatment of **16** with hydrazine hydrate in methanol at reflux led to 5-hydrazino-*s*-triazolo[2,3-*e*]pyrazolo[1,5-*a*]-1,3,5-triazine (**17**), demonstrating that the rearrangement of the tricyclic system could take place even in the presence of a solvent. This type of thermally induced "anhydrous" mechanism of the rearrangement of a fused triazole system has also been suggested to some extent by the work of Shirikawa (12) and also by Rose (13).

In a Dimroth type rearrangement (15,16,17), it could be suggested that the action of a strong base favors the ring closure over the degradation of an intermediate of type **10**. Although this type of rearrangement cannot be excluded as a mechanism for the transformation of **8** to **9** (which in this case would be *via* the covalent hydration of **8** under basic conditions to yield **10**, which would then eliminate water to cyclize to **9**), it seems more likely, with the evidence at hand, that a thermally induced, concerted mechanism accounts for this type of rearrangement from the triazolo[4,3-*e*] to the triazolo[2,3-*e*] system in either the presence or absence of solvent.

EXPERIMENTAL

Melting points were recorded with the standard Thomas-Hoover apparatus, and are reported here uncorrected. All pmr spectra were recorded on a Hitachi Perkin-Elmer R20A instrument at 60 MHz. Chemical shifts are reported in δ (parts per million) relative to TMS as a standard. All ir spectra were recorded in potassium bromide discs on a Perkin-Elmer 257 instrument. Analyses were performed for C, H and N by the Heterocyclic Chemical Corporation. The pmr spectra not reported in this section are reported in Table I.

7-Phenylpyrazolo[1,5-*a*]-1,3,5-triazin-4(3*H*)one (**2**).

A mixture of 2.18 g. (10 mmoles) of 3-amino-5-phenyl-2-*N*-thiocarbomoylpyrazole (**1**) (7) and 5.00 g. (excess) of diethoxymethyl acetate was refluxed for 5 minutes. The mixture was cooled and the precipitate was filtered and washed with ethyl acetate. Recrystallization of this material from ethyl acetate-hexane gave 1.2 g. (55%) of yellowish cubettes, m.p. 231-233°.

Anal. Calcd. for $C_{11}H_8N_4S$: C, 57.9; H, 3.53; N, 24.3. Found: C, 58.1; H, 3.79; N, 24.7.

4-Methylthio-7-phenylpyrazolo[1,5-*a*]-1,3,5-triazine (**3**).

A solution of sodium hydroxide (100 mg.) in 15 ml. of 33% aqueous ethanol was added to 550 mg. (2.5 mmoles) of 7-phenylpyrazolo[1,5-*a*]-1,3,5-triazin-4(3*H*)one (**2**). Then 600 mg. of methyl iodide was added dropwise to the resultant solution, with stirring. The mixture was stirred 30 minutes at room temperature and then the product, which had precipitated, was filtered. The material was recrystallized from ethyl acetate-hexane to yield 500 mg. (75%) of white crystals, m.p. 140-142°.

Anal. Calcd. for $C_{12}H_{10}N_4S$: C, 59.5; H, 4.16; N, 23.1. Found: C, 59.9; H, 4.47; N, 23.4.

4-Hydrazino-7-phenylpyrazolo[1,5-*a*]-1,3,5-triazine (**4**).

A mixture of 750 mg. (3.1 mmoles) of 4-methylthio-7-phenylpyrazolo[1,5-*a*]-1,3,5-triazine (**3**) in 30 ml. of methanol and 0.2 ml. of 85% hydrazine hydrate, was stirred overnight at room temperature, and then heated to reflux, with stirring, for 30 minutes. The mixture was allowed to cool to room temperature and the product was filtered and washed with methanol to afford 550 mg. (78%) of

the title compound as yellowish-white needles, m.p. 201-203°.

Anal. Calcd. for $C_{11}H_{10}N_6$: C, 58.4; H, 4.46; N, 37.1. Found: C, 55.4; H, 4.47; N, 37.21.

8-Phenyltetrazolo[1,5-*e*]-pyrazolo[1,5-*a*]-1,3,5-triazine (**5b**) in Equilibrium with 4-Azido-7-phenylpyrazolo[1,5-*a*]-1,3,5-triazine (**5a**).

A solution of 4-hydrazino-7-phenylpyrazolo[1,5-*a*]-1,3,5-triazine (**4**) in 5 ml. of 2*N* hydrochloric acid was cooled to 10° and a solution of sodium nitrite (120 mg.) in water (10 ml.) was added dropwise, with stirring. The mixture was stirred an additional 2 hours at room temperature and then the product was filtered off and washed with water. The title compound was recrystallized from methanol to afford 250 mg. (85%) of the product as white needles, m.p. 188-190°; ir (potassium bromide): 2150 cm^{-1} (azido), 1182 cm^{-1} (tetrazolo).

Anal. Calcd. for $C_{11}H_7N_7$: C, 55.7; H, 2.97; N, 41.3. Found: C, 55.4; H, 3.02; N, 41.5.

7-Phenylpyrazolo[1,5-*a*]-1,3,5-triazin-4(3*H*)one (**6**).

A mixture of 370 mg. (2 mmoles) of 3-amino-2-carbamoyl-5-phenylpyrazole (**12**) (7) and 1.25 ml. (excess) of diethoxymethyl acetate was refluxed for 10 minutes. The product separated from the solution upon cooling to room temperature and the crystals were filtered. The material was recrystallized from ethanol-water to afford 300 mg. (78%) of the title compound, m.p. 258-260°.

Anal. Calcd. for $C_{11}H_8N_4O$: C, 62.2; H, 3.80; N, 26.4. Found: C, 62.2; H, 3.77; N, 26.4.

4-Amino-7-phenylpyrazolo[1,5-*a*]-1,3,5-triazine (**7**).

A mixture of 750 mg. (3.7 mmoles) of 2-*N*-acetimidoyl-3-amino-5-phenylpyrazole (**13**) (7) in 3.5 ml. of diethoxy acetate, was refluxed for 5 minutes. The solution obtained was then evaporated (50°/10 mm) to yield a residue. The residue was recrystallized from ethanol-water to give 750 mg. (80%) of the title compound as white needles, m.p. 283-286°.

Anal. Calcd. for $C_{11}H_9N_5$: C, 62.54; H, 4.29; N, 33.15. Found: C, 62.70; H, 4.30; N, 33.02.

Thermal Decomposition of **5a**⇌**5b** in Xylene.

A solution of 100 mg. of 8-phenyltetrazolo[1,5-*e*]pyrazolo-[1,5-*a*]-1,3,5-triazine (**5b**), which may also exist as 4-azido-7-phenylpyrazolo[1,5-*a*]-1,3,5-triazine (**5a**), was refluxed in 5 ml. of xylene for 98 hours. The solution was cooled and a white precipitate, identified as 4-amino-7-phenylpyrazolo[1,5-*a*]-1,3,5-triazine (**7**) was obtained. Recrystallization of the product from ethanol-water gave 45 mg. (60%) of **7**, m.p. 283-286°.

The product was identical in all respects (ir, pmr, uv, and mixed melting point) to an authentic sample of **7**, prepared *via* the reaction described above.

Alkaline Saponification of **5a**⇌**5b**.

A mixture of 500 mg. of 8-phenyltetrazolo[1,5-*e*]pyrazolo-[1,5-*a*]-1,3,5-triazine (**5a**⇌**5b**) and 5 ml. of 1*N* sodium hydroxide solution was stirred at room temperature for 24 hours. The mixture was filtered and the insoluble precipitate (100 mg.) was identified as 4-amino-7-phenylpyrazolo[1,5-*a*]-1,3,5-triazine (**7**) upon recrystallization from water, m.p. 283-286°. The identity of this material was substantiated by mixed melting point with **7** prepared by the alternate procedure (as well as by spectral comparison). The aqueous filtrate was carefully acidified with 1*N* hydrochloric acid to *p*H 5 and a precipitate formed. The precipitate was filtered, washed with water and recrystallized from ethanol-water to yield 100 mg. of product identified as 7-phenylpyrazolo[1,5-*a*]-1,3,5-triazin-4(3*H*)one (**6**) by spectral and mixed melting point (231-233°) with an authentic sample of **6**.

8-Phenyl-*s*-triazolo[4,3-*e*]pyrazolo[1,5-*a*]-1,3,5-triazine (**8**).

A suspension of 1.0 g. (4.4 mmoles) of 4-hydrazino-7-phenylpyrazolo[1,5-*a*]-1,3,5-triazine (**4**) in 5.0 ml. of diethoxymethyl acetate was stirred at room temperature for one hour. The product which precipitated was filtered and recrystallized from dimethylformamide-toluene to yield 1.0 g. (90%) of the title compound, m.p. 263-265°; pmr (DMSO-d_6): δ 9.17 (s, 1, H_3); δ 9.30 (s, 1, H_4); δ 7.48 (s, 1, H_6); δ 7.55 and 8.1 (m, 5, phenyl); (deuteriotrifluoroacetic acid with deuterium oxide): δ 8.73 (s, 1, CHO of formamido); δ 8.85 (s, 1, triazolyl); δ 7.96 (s, 1, pyrazole).

Anal. Calcd. for $C_{12}H_8N_6$: C, 61.0; H, 3.41; N, 35.6. Found: C, 60.9; H, 3.18; N, 35.3.

8-Phenyl-*s*-triazolo[2,3-*e*]pyrazolo[1,5-*a*]-1,3,5-triazine (**9**).

A sample of 250 mg. of 8-phenyl-*s*-triazolo[4,3-*e*]pyrazolo-[1,5-*a*]-1,3,5-triazine (**8**) was heated at its melting point (263-265°) for 5 minutes. The melt was allowed to cool gradually to room temperature and then the solid was recrystallized from ethyl acetate to yield 200 mg. (80%) of the title compound, m.p. 213-215°; pmr (DMSO-d_6): δ 8.57 (s, 1, H_2); δ 9.43 (s, 1, H_4); δ 7.50 (s, 1, H_6); δ 7.55 and 8.1 (m, 5, phenyl).

Anal. Calcd. for $C_{12}H_8N_6$: C, 61.0; H, 3.41; N, 35.6. Found: C, 61.0; H, 3.37; N, 35.5.

3-*N*-Formamido-5-phenyl-2(2-*s*-triazolyl)pyrazole (**10**).

To 6 ml. of 88% formic acid was added 500 mg. of 8-phenyl-*s*-triazolo[4,3-*e*]pyrazolo[1,5-*a*]-1,3,5-triazine (**8**) at room temperature. The solid initially dissolved in the formic acid but upon stirring the solution for 2 hours, a white solid separated. The solid was filtered and recrystallized from ethanol to give 450 mg. (85%) of the title compound, m.p. 203-205°; pmr (DMSO-d_6): δ 8.75 (s, 1, formyl); δ 8.50 (s, 1-*s*-triazolyl); δ 7.18 (s, 1, pyrazole); δ 7.45 and 7.90 (m, 5, phenyl); ir (potassium bromide): 1710 cm^{-1} (formamide carbonyl).

Anal. Calcd. for $C_{12}H_{10}N_6O$: C, 56.68; H, 3.96; N, 33.06. Found: C, 56.61; H, 4.14; N, 33.21.

3-Amino-5-phenyl-2(2-*s*-triazolyl)pyrazole (**11**).

A mixture of 500 mg. of 8-phenyl-*s*-triazolo[4,3-*e*]pyrazolo-[1,5-*a*]-1,3,5-triazine (**8**) and 5 ml. of concentrated hydrochloric acid was heated for 2 hours on the steam bath. To this solution was added 50 ml. of water. Then the cooled (25°) solution was neutralized with sodium bicarbonate and the precipitated product was filtered. Recrystallization of this solid from ethanol afforded 200 mg. (42%) of white crystals, m.p. 183-185°; pmr (DMSO-d_6): δ 8.52 (s, 1, -*s*-triazolyl); δ 7.2 (s, 1, pyrazole); δ 7.45 and 7.90 (m, 5, phenyl); ir (potassium bromide): 3305 and 3315 cm^{-1} (amino).

Anal. Calcd. for $C_{11}H_{10}N_6$: C, 58.40; H, 4.42; N, 37.16. Found: C, 58.5; H, 4.4; N, 37.3.

4-Azido-8-bromo-7-phenylpyrazolo[1,5-*a*]-1,3,5-triazine (**14**).

A solution of 660 mg. (3 mmoles) of 4-azido-7-phenylpyrazolo-[1,5-*a*]-1,3,5-triazine (**5a**⇌**5b**) in 30 ml. of chloroform was treated with 500 mg. of *N*-bromosuccinimide. The initial red color was discharged after refluxing the solution for 10 minutes. The solution was washed twice with sodium bicarbonate solution and the dried (sodium sulfate) chloroform solution was evaporated (rotovac) to yield a solid. Recrystallization of this material from ethyl acetate-hexane afforded 780 mg. (87%) of the title compound, m.p. 153-155°.

Anal. Calcd. for $C_{11}H_6N_7Br$: C, 41.79; H, 1.91; N, 31.01. Found: C, 41.62; H, 1.69; N, 31.31.

5-Methylthio-*s*-triazolo[4,3-*e*]pyrazolo[1,5-*a*]-1,3,5-triazine (**16**).

A suspension of 1.5 g. (7.6 mmoles) 4-hydrazino-2-methylthiopyrazolo[1,5-*a*]-1,3,5-triazine (**15**) (3) in 15 ml. of dimethoxyethyl acetate was heated at 80° for 10 minutes. The voluminous white precipitate that formed was filtered and washed with ethyl acetate. The product was recrystallized from dimethylformamide-toluene to yield 1.2 g. (78%) of the product as white needles, m.p. 260-261°; pmr (DMSO-d_6): δ 9.18 (s, 1, H_3); δ 2.83 (s, 3, SCH_3); δ 6.68 (d, 1, H_6); δ 8.13 (d, 1, H_7); $J_{2,3}$ = 2.1 H_z.

Anal. Calcd. for $C_7H_6N_6S$: C, 40.78; H, 2.93; N, 40.77. Found: C, 40.59; H, 3.15; N, 40.53.

4-Hydrazino-*s*-triazolo[2,3-*e*]pyrazolo[1,5-*a*]-1,3,5-triazine (**17**).

A suspension of 510 mg. (2.5 mmoles) of 5-methyl-*s*-triazolo[4,3-*e*]pyrazolo[1,5-*a*]-1,3,5-triazine (**16**) and 0.15 ml. of 85% hydrazine hydrate in 25 ml. of methanol was refluxed for 16 hours. The mixture was filtered and washed with methanol to yield 300 mg. (63%) of analytically pure product, m.p. 278-280°; pmr (DMSO-d_6): δ 8.30 (s, 1, H_2); δ 6.22 (d, 1, H_6); δ 7.98 (d, 1, H_7); $J_{2,3}$ = 2.1 H_z.

Anal. Calcd. for $C_6H_6N_8$: C, 37.89; H, 3.18; N, 58.93. Found: C, 37.95; H, 3.46; N, 58.89.

5-Methylthio-8-phenyltetrazolo[1,5-*e*]pyrazolo[1,5-*a*]-1,3,5-triazine (**18b**) in Equilibrium with 4-Azido-7-phenylpyrazolo[1,5-*a*]-1,3,5-triazine (**18a**).

The synthesis and identification of both the title compounds have been reported previously (3a). The pmr spectral assignments for these isomers are reported in Table I.

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