Synthesis of Nitrogen-Containing Heterocycles. 5 [1]. A New Route to 5-Amino-[1,2,4]triazolo[1,5-*a*][1,3,5]triazine Derivatives

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Received December 18, 1989

Treatment of certain diaminomethylenehydrazones **1** of aromatic carbonyl compounds with ethyl *N*-cyanoimidate (**2**) in acetonitrile in the presence of a tertiary amine at room temperature gives the corresponding amino(*N*-cyanoiminomethyl)aminomethylenehydrazones **3** in high yields. The intermediate **3** can readily be cyclized to the corresponding 5-amino-2,3-dihydro[1,2,4]triazolo[1,5-*a*][1,3,5]triazines **4** in moderate to good yields by brief heating in acetonitrile. When the reaction of diaminomethylenehydrazones **1** with ethyl *N*-cyanoimidate (**2**) is performed at reflux temperature in the presence of a tertiary amine, 5-amino-2,3-dihydro[1,2,4]triazolo[1,5-*a*][1,3,5]triazines **4** can be directly obtained in moderate yields. The yields of triazolotriazine produced by the one-step synthesis are generally comparable or even higher than the overall yields from the two-step procedure.

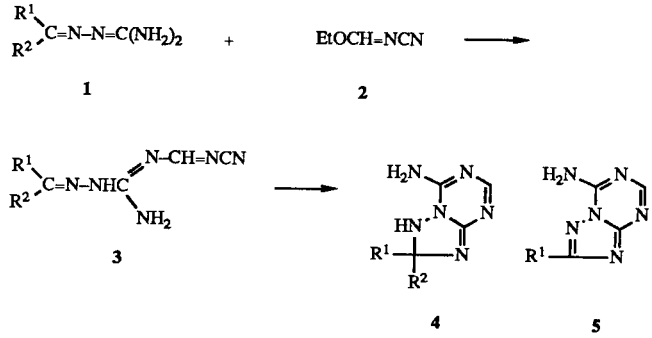
J. Heterocyclic Chem., **27**, 1553 (1990).

We have reported a series of papers dealing with the one-step synthesis of [1,2,4]triazolo[1,5-*c*]pyrimidines through the electrocyclic reaction of intermediate polyazapolyenes starting with isothiosemicarbazones [2] or diaminomethylenehydrazones [3] and active ethoxymethylene compounds. In these reactions, the vinylic carbon which carries two electron-withdrawing groups in the ethoxymethylene compounds becomes the ring carbon at the 8-position upon formation of the product [1,2,4]triazolo[1,5-*c*]pyrimidine. If this vinylic carbon could be replaced by a nitrogen atom, there would be produced a [1,2,4]triazolo[1,5-*a*][1,3,5]triazine ring system by the analogous electrocyclic reaction. Recently, a few reports [4] have been published concerning the syntheses of triazolo[1,5-*a*][1,3,5]triazines which involve multi-step procedures starting with amino-1,3,5-triazines [4a] or amino-1,2,4-triazoles [4b]. To the best of our knowledge, no reports have been published of one-step syntheses of the bicyclic triazines from an open-chain, flexible molecule. Our interest in the possible novel synthetic route to the [1,2,4]triazolo[1,5-*a*][1,3,5]triazine ring system led us to investigate the reaction of ethyl *N*-cyanoimidate with diaminomethylenehydrazones. Thus, the present paper described a one-step synthesis of new [1,2,4]triazolo-[1,5-*a*] [1,3,5]triazines **4** by the reaction of a number of diaminomethylenehydrazones **1** with ethyl *N*-cyanoimidate (**2**) [5] along with data which support the structural assignments of the bicyclic triazine products.

Results and Discussion.

In order to isolate the initial condensation products **3** and to confirm their intermediacy enroute to the final bicyclic triazolotriazines **4**, the reaction between **1** and **2** was performed under relatively moderate conditions. Thus a mixture of **1a** and **2** in a molar ratio of 1a:2 = 1:2 in acetonitrile was allowed to stand at room temperature. Crystallization occurred within a few minutes and analytically pure **3a** was obtained in 51% yield after 30 minutes. When the amount of solvent was appropriately adjusted to facilitate crystallization, a maximum yield of 91% of **3a** could be obtained. In a similar manner, aromatic ketone diaminomethylenehydrazone **1f** gave the corresponding **3f** in 93% yield. Other diaminomethylenehydrazones of both aldehydes and ketones required the presence of a basic catalyst (triethylamine) in order to obtain acceptable results. *o*-Bromobenzaldehyde diaminomethylenehydrazone (**1b**), however, gave a mixture of an open-chain compound **3b** and a cyclized product **4b** when reacted with **2** in the presence of triethylamine. The pure compound **3b** was obtained in the absence of the amine in this case. The compounds **3**, in general, are highly susceptible to cyclization to triazolotriazines **4** upon exposure to heat and therefore cannot be recrystallized in the usual

Scheme



	R^1	R^2
a,	C_6H_5	H
b,	*o*-BrC_6H_4	H
c,	*p*-ClC_6H_4	H
d,	*p*-$MeOC_6H_4$	H
e,	*p*-$O_2NC_6H_4$	H
f,	C_6H_5	CH_3
g,	*p*-ClC_6H_4	CH_3
h,	*p*-$MeOC_6H_4$	CH_3
i,	*p*-$O_2NC_6H_4$	CH_3
j,	C_6H_5	$(CH_3)_2CH$

manner.

Cyclization of the open-chain intermediates **3** to triazolotriazines **4** could be accomplished simply by heating **3** in acetonitrile or methanol depending upon the solubility of the starting material. Thus **4a** was prepared in 70% yield when a suspension of **3a** in acetonitrile was heated at reflux temperature for 30 minutes.

The susceptibility to cyclization of the intermediate products led us to investigate the possibility of a one-step synthesis of the triazolotriazines by carrying out the reaction between **1** and **2** at a higher temperature. The apparent single-step formation of the final cyclized product **4** from the starting material **1** should obviously involve the initial condensation to form the intermediate **3** followed by cyclization. The yields of the final products **4** obtained from the one-step process ranged from 33-61% based on the amount of diaminomethylenehydrazone used. This compares with the overall yields of 26-82% from the stepwise procedure calculated from the amount of diaminomethylenehydrazone which was used initially in the preparation of the intermediate **3**. With the exception of the higher yield (82%) for **4f**, the stepwise procedure gave less satisfactory results and lower yields, especially in the preparation of 2-alkyltriazolotriazines **4g-4i**.

Substituents on the aromatic ring of compounds **3** appeared to have no significant effect on the yield of cyclized products **4**. On the other hand, in the cyclization of compound **3j**, the isopropyl group on the benzylidene carbon was readily eliminated even at ambient temperature, probably after cyclization to the expected product **4j**. Thus, 5-amino-2-phenyl[1,2,4]triazolo[1,5-*a*][1,3,5]triazine (**5**) (R^1 = Ph) was formed rather than the corresponding compound **4j** [6].

Assignment of the 2,3-dihydrotriazolotriazine structure **4** (R^2 = H) was based on analytical and spectral data. The 2,3-dihydro structure was best characterized by the appearance in the ^1H nmr spectrum of an AB-type doublet (δ 5.92-6.23 and 6.55-7.85, J = 10 Hz) arising from spin-spin coupling between the protons at positions 2 and 3.

Exchange with deuterium resulted in disappearance of the downfield resonances (H-3) and collapse to a singlet of the upfield doublet and thus confirmed the peak assignment. Furthermore, the ^{13}C nmr spectra of the two compounds **4a** and **4f** exhibited the C-2 resonances at δ 81.51 and 86.00, respectively, in the sp^3 carbon region, with the former appearing as a doublet ($^1J_{CH}$ = 157 Hz). Further support for the 2,3-dihydro structure was obtained from the characteristic fragmentation observed in the mass spectrum involving C-2 of compound **4**. Prominent fragment ions were produced by elimination of benzonitriles (R^1CN) or two hydrogens (probably H-2 and H-3) from the molecular ions. Compound **4c** gave the ion corresponding to R^1CN (R^1 = *p*-chlorophenyl-) as a base peak. If R^2 was an alkyl group, the base peak had invariably a mass of M^+-R^2. Other appropriate spectral data, such as the amino bands (3,183-3,029 cm^{-1}) in the ir spectra as well as the H-7

Table I

Amino(*N*-cyanoiminomethyl)aminomethylenehydrazones **3**

Compound	R^1	R^2	Mp, °C	Reaction Solvent	Yield [a] (%)	Formula	Analysis % Calcd./Found C	H	N
3a	C_6H_5	H	169-170	MeCN	91	$C_{10}H_{10}N_6$	56.07 56.07	4.71 4.65	39.23 39.46
3b	*o*-BrC_6H_4	H	142-143	MeCN	68	$C_{10}H_9BrN_6$	40.98 40.82	3.09 3.20	28.67 28.92
3c	*p*-ClC_6H_4	H	223-225	MeCN	73	$C_{10}H_9ClN_6$	48.30 48.14	3.65 3.71	33.80 33.93
3d	*p*-$MeOC_6H_4$	H	174-177	MeCN	94	$C_{11}H_{12}N_6O$	54.09 54.12	4.95 4.89	34.41 34.31
3e	*p*-$O_2NC_6H_4$	H	160-162	MeOH	86	$C_{10}H_9N_7O_2$	46.33 46.38	3.50 3.48	37.82 37.91
3f	C_6H_5	CH_3	200-202	MeCN	93	$C_{11}H_{12}N_6$	57.88 57.63	5.30 5.21	36.82 36.52
3g	*p*-ClC_6H_4	CH_3	224	MeCN	67	$C_{11}H_{11}ClN_6$	50.29 50.03	4.22 4.16	31.99 32.27
3h	*p*-$MeOC_6H_4$	CH_3	220	MeCN	99	$C_{12}H_{14}N_6O$	55.80 55.65	5.46 5.46	32.54 32.49
3i	*p*-$O_2NC_6H_4$	CH_3	233-235	MeCN	66	$C_{11}H_{11}N_7O_2$	48.35 48.27	4.06 4.03	35.88 35.61
3j	C_6H_5	$(CH_3)_2CH$	168-170	MeCN	72	$C_{13}H_{16}N_6$	60.92 60.69	6.29 6.01	32.79 33.03

[a] For the isolated products.

Table II

Spectroscopic Data of Amino(*N*-cyanoiminomethyl)aminomethylenehydrazones **3**

Compound	^{1}H NMR (J in Hz))	IR (KBr) cm^{-1}		MS
		ν NH	ν CN	M$^+$ (%)
3a	7.43 (m, 3H, aromatic), 7.85 (m, 2H, aromatic), 8.10 (br s, 3H, NH_2 and NH), 8.19 (s, 2H, two N=CH)	3428, 3294, 3171	2187	214 (14)
3b	7.25-7.75 (m, 4H, aromatic), 8.25 (br s, 3H, NH_2 and NH), 8.60 (s, 2H, two N=CH)	3387, 3298, 3156	2175	293 (6)
3c	7.51 (d, 2H, 9, aromatic), 7.93 (d, 2H, 9, aromatic), 8.12 (br s, 3H, NH_2 and NH), 8.20 (s, 2H, two N=CH)	3444, 3301, 3169	2188	248 (4)
3d	3.79 (s. 3H, OMe), 6.98 (d, 2H, 9, aromatic), 7.80 (d, 2H, 9, aromatic), 8.10 (br s, 3H, NH_2 and NH), 8.13 (s, 2H, two N=CH)	3433, 3301, 3175	2187	244 (45)
3e	8.02 (br s, 1H, NH), 8.20-8.32 [br s, 8H, (aromatic, two N=CH and NH_2)]	3417, 3153, 3180	2188	259 (10)
3f	2.32 (s, 3H, Me), 7.35 (m, 3H, aromatic), 7.92 [m, 6H, (aromatic, NH_2, NH and N=CH)]	3341, 3051	2208, 2192	228 (19)
3g	2.33 (s, 3H, Me), 7.49 (d, 2H, 9, aromatic), 7.98 [br s, 4H, (NH_2, NH and N=CH)], 8.05 (d, 2H, 9, aromatic)	3342, 3040	2208, 2189	262 (23)
3h	2.30 (s, 3H, Me), 3.77 (s, 3H, OMe), 6.95 (d, 2H, 9, aromatic), 7.95 (d, 2H, 9, aromatic), 7.80-8.35 [br s, 4H, (NH_2, NH and N=CH)]	3341, 3045	2192	258 (60)
3i	2.36 (s, 3H, Me), 7.95 (br s, 3H, NH_2 and NH), 8.22 (s, 5H, aromatic and N=CH)	3341, 3039	2208, 2190	273 (20)
3j	1.06 (d, 6H, 6, $CHMe_2$), 2.87 (q, 1H, 6, $CHMe_2$), 7.45 (m, 5H, aromatc), 7.87 [br s, 4H, (NH_2, NH and N=CH)]	3362, 3035	2193	256 (19)

Table III

5-Amino-2,3-dihydro[1,2,4]triazolo[1,5-*a*][1,3,5]triazines **4**

Compound	R^1	R^2	Mp, °C	Yield [a]		Formula	Analysis % Calcd./Found		
				A	B		C	H	N
4a	C_6H_5	H	189-191	70	48	$C_{10}H_{10}N_6$	56.07 56.13	4.71 4.67	39.23 38.96
4b	*o*-BrC_6H_4	H	166-167	63	33	$C_{10}H_9BrN_6$	40.98 41.12	3.09 3.30	28.67 28.71
4c	*p*-ClC_6H_4	H	273-274	60	-	$C_{10}H_9ClN_6$	48.30 48.39	3.65 3.61	33.80 33.63
4d	*p*-$MeOC_6H_4$	H	188-190	84	-	$C_{11}H_{12}N_6O$	54.09 53.90	4.95 4.90	34.41 34.53
4e	*p*-$O_2NC_6H_4$	H	182	40	48	$C_{10}H_9N_7O_2$	46.33 46.62	3.50 3.57	37.82 37.56
4f	C_6H_5	CH_3	210-211	88	56	$C_{11}H_{12}N_6$	57.88 57.63	5.30 5.32	36.82 36.71
4g	*p*-ClC_6H_4	CH_3	239	40	51	$C_{11}H_{11}ClN_6$	50.29 50.15	4.22 4.25	31.99 31.79
4h	*p*-$MeOC_6H_4$	CH_3	209-210	50	-	$C_{12}H_{14}N_6O$	55.80 55.90	5.46 5.41	32.54 32.49
4i	*p*-$O_2NC_6H_4$	CH_3	246-247	79	59	$C_{11}H_{11}N_7O_2$	48.35 48.52	4.06 4.03	35.99 35.78

[a] For the isolated products.

resonances (δ 7.35-7.60) in the ^{1}H nmr spectra are in line with the assigned structures.

Compound **5** (R^1 = Phenyl) was a high-melting substance with solubility too low to afford a reasonable ^{13}C nmr analysis. In contrast to the corresponding dihydro compound **4a**, the resonance of the *ortho*-protons of the 2-phenyl group in **5** was greatly deshielded (δ 8.23) relative to that of the *meta*- and *para*-protons (δ 7.55). This can be ascribed to the anisotropic deshielding influence of the heteroaromatic ring [7] to which the phenyl group attaches. This supports the presence of a rigid aromatic structure in compound **5** as presented in the Scheme.

Table IV

Spectroscopic Data of 5-Amino-2, 3-dihydro[1,2,4]triazolo[1,5-*a*][1,3,5]triazines **4**

Compound	^{1}H NMR (J in Hz)				IR	MS
	H-2	H-3	H-7	Others	υ NH	m/e (%)
4a	5.95 d (10)	6.51 d (10)	7.54	7.31 (s, 5H, phenyl), 7.60 (br s, 2H, NH_2)	3294, 3139	214 (M^+, 14) 111 (100)
4b	6.35 d (10)	6.83 d (10)	7.60	7.47 (m, 4H, aromatic), 7.62 (br s. 2H, NH_2)	3280, 3068	293 (M^+, 4) 83 (100)
4c	6.03 d (10)	6.66 d (10)	7.62	7.43 (s, 4H, aromatic), 7.71 (br s, 2H, NH_2)	3285, 3128	248 (M^+, 11) 137(100)
4d	5.90 d (10)	6.40 d (10)	7.58	3.75 (s, 3H, OMe), 6.83 (d, 2H, 9, aromatic), 7.50 (d, 2H, 9, aromatic) 7.60 (br s, 2H, NH_2)	3289, 3129	244 (M^+, 14) 111(100)
4e	6.16 d (10)	6.86 d (10)	7.61	7.67 (2H, d, 9, aromatic), 7.76 (br s, 2H, NH_2), 8.27 (d, 2H, 9, aromatic)	3439, 3137	259 (M^+, 6) 43 (100)
4f	1.59	6.24	7.51	7.20-7.91 (m, 7H, phenyl and NH_2)	3433, 3183	228 (M^+, 16) 213 (100)
4g	1.56	6.30	7.51	7.25-7.40 (m, 4H, aromatic), 7.64 (br s, 2H, NH_2)	3390, 3157	262 (M^+, 13) 247 (100)
4i	1.64	6.51	7.54	7.83 (d, 2H, 9, aromatic), 7.85 (br s, NH_2), 8.21 (d, 2H, 9, aromatic)	3397, 3157	273 (M^+, 17) 258 (100)

Table V

^{13}C NMR Chemical Shift Data of Compounds **4** [a]

Compound	C-2	C-5	C-7	C-9	Others
4a	81.51 d (157)	153.74 d (12)	164.13 d (197)	153.74 d (12)	126.36, 127.58, 128.07, 142.12 (aromatic)
4b	80.92 d (159)	153.64 d (13)	164.28 d (197)	154.23 d (12)	121.77, 127.72, 128.46, 129.68, 132.41, 140.76 (aromatic)
4d	81.26 d (157)	158.81 m	164.08 d (196)	153.74 m	55.00 (q, 144, OMe), 113.43 (d, 159, aromatic), 127.63 (d, 154, aromatic), 134.21 (m)
4f	86.00	153.64 d (13)	163.93 d (197)	152.76 d (13)	29.19 (q, 128, Me), 125.19, 126.90, 127.77, 146.03 (aromatic)

[a] The spectra of compounds **4c, 4e, 4g** and **4i** could not be obtained because of poor solubility.

EXPERIMENTAL

Microanalyses were performed with a Perkin-Elmer 240D elemental analyser at the Microanalytical Laboratory of Kitasato University. Infrared and mass spectra were recorded on Perkin-Elmer 983 and JMS-D-100 instruments, respectively. Proton and carbon-13 magnetic resonance spectra were obtained with a JNM-FX90Q spectrometer operating at 89.55 and 22.50 MHz, respectively. Unless otherwise stated, the ir spectra were recorded as potassium bromide pellets and the nmr spectra were recorded as solutions in hexadeuteriodimethyl sulfoxide.

(*E*)-Diaminomethylenehydrazones.

The diaminomethylenehydrazones used, except for compounds **1b** and **1j**, are all known compounds and were prepared according to the literature methods [3,8]. Compounds **1b** and **1j** were similarly synthesized to give **1b** (55%) as light yellow needles, mp 164-166°; ^{1}H nmr (DMSO-d_6): δ 5.65 and 5.97 (br s, each 2H, NH_2 x 2), 7.15-8.22 (m, 4H, aromatic), 8.27 (s, 1H, CH = N).

Anal. Calcd. for $C_8H_9BrN_4$: C, 39.86; H, 3.76; N, 23.24. Found: C, 39.77; H, 3.89; N, 23.39.

Compound **1j** was obtained as prisms, (31%), mp 194-195° (from water); ^{1}H nmr (DMSO-d_6): δ 1.05 (d, 6H, J = 6 Hz, CH*Me*$_2$), 2.78 (quin, 1H, J = 6 Hz, C*H*Me$_2$), 5.83 (br s, 4H, NH_2 x 2) and 7.26 (5H, s, aromatic).

Anal. Calcd. for $C_{11}H_{16}N_4$: C, 64.68; H, 7.89; N, 27.43. Found: C, 64.62; H, 7.77; N, 27.58.

Anisaldehyde Amino(*N*-cyanoiminomethyl)aminomethylenehydrazone (**3d**).

General Procedure for Preparation of Amino(*N*-cyanoiminomethyl)aminomethylenehydrazones **3**.

To a solution of anisaldehyde diaminomethylenehydrazone (**1d**) (0.19 g, 1 mmole) in acetonitrile (3 ml) was added triethyl amine (0.3 ml), followed by addition of ethyl *N*-cyanoimidate (0.20 g, 2 mmoles). The resulting mixture was allowed to stand at room temperature for 1 hour with occasional agitation. The separated crystals were collected by filtration, washed with acetonitrile, and dried to give the title compound **3d** as a light yellow crystalline

powder (0.23 g, 94%), mp 174-177°; ^{1}H nmr (DMSO-d_6): δ 3.79 (s, 3H, OMe), 6.98 (d, 2H, J = 9 Hz, aromatic), 7.80 (d, 2H, J = 9 Hz, aromatic), 8.10 (br s, 3H, NH_2 and NH), 8.13 (s, 2H, two N = CH); ir (potassium bromide): 3433, 3301 and 3175 (NH_2 and NH), 2187 (CN) cm^{-1}; ms m/e 244 (M^+, 44%).

Anal. Calcd. for $C_{11}H_{12}N_6O$: C, 54.09; H, 4.95; N, 34.41. Found: C, 54.12; H, 4.89; N, 34.31.

When the reaction was performed in the absence of the tertiary amine, the yield of the product **3d** decreased to 82%. Other new amino(*N*-cyanoiminomethyl)aminomethylenehydrazones were made similarly, with appropriate modifications, and are listed in Table I. Their spectroscopic data are shown in Table II.

5-Amino-2-(*p*-methoxyphenyl)-2,3-dihydro[1,2,4]triazolo[1,5,-*a*]-[1,3,5]triazine (**4d**). A Typical Example for the Cyclization of Amino[3-*N*-cyanoiminomethyl]aminomethylenehydrazones **3**. Procedure A.

A solution of anisaldehyde amino[3-*N*-cyanoiminomethyl]-aminomethylenehydrazone (**3d**) (0.1 g, 0.41 mmoles) in acetonitrile (2 ml) was heated under reflux for 1 hour and then allowed to cool to ambient temperature. The separated crystals were collected, washed with acetonitrile, and then dried to give analytically pure compound **4d** as small plates (84 mg, 84%), mp 188-190°; ^{1}H nmr (DMSO-d_6): δ 3.75 (s, 3H, OMe), 5.90 (d, 1H, J = 10 Hz, H-2), 6.40 (d, 1H, J = 10 Hz, H-3), 6.83 (d, 2H, J = 9 Hz, *p*-methoxyphenyl), 7.50 (d, 2H, J = 9 Hz, *p*-methoxyphenyl), 7.58 (s, 1H, H-7), 7.60 (br s, NH_2); ^{13}C nmr (DMSO-d_6): δ 55.00 (q, $^1J_{CH}$ 144 Hz, OMe), 81.26 (d, $^1J_{CH}$ = 157 Hz, C-2), 113.43 (d, $^1J_{CH}$ = 159 Hz, *p*-methoxyphenyl), 127.63 (d, $^1J_{CH}$ = 154 Hz, *p*-methoxyphenyl), 134.21 (m, *p*-methoxyphenyl), 153.74 (m, C-9), 153.81 (m, *p*-methoxyphenyl), 158.81 (m, C-5), 164.08 (d, $^1J_{CH}$ = 196 Hz, C-7); ir (potassium bromide): 3289 and 3129 (NH and NH_2) cm^{-1}; ms m/e 244 (M^+ 14%), 111 (M^+-133, 100%).

Anal. Calcd. for $C_{11}H_{12}N_6O$: C, 54.09; H, 4.95; N, 34.41. Found: C, 53.90; H, 4.90; N, 34.53.

5-Amino-2-(*p*-methoxyphenyl)-2-methyl-2*H*-[1,2,4]triazolo[1,5-*a*]-[1,3,5]triazine (**4h**). A Typical Example of One-step Cyclization of Diaminomethylenehydrazones **1**. Procedure B.

A mixture of *p*-methoxyacetophenone diaminomethylenehydrazone (**1h**) (0.21 g, 1 mmole), ethyl *N*-cyanoimidate (**2**) (0.20 g, 2 mmoles), triethylamine (0.9 ml), and acetonitrile (9 ml) was heated under reflux for 10 minutes during which time the starting materials went into a clear solution and then the desired compound rapidly separated. The crystals were filtered off, washed with acetonitrile, and dried to give analytically pure **4h** as light yellow fine crystals, mp 209-210°; ^{1}H nmr (DMSO-d_6): δ 1.54 (s, 3H, 2-Me), 3.72 (s, 3H, OMe), 6.13 (s, 1H, H-3), 6.86 (d, 2H, J = 9 Hz, *p*-methoxyphenyl), 7.43 (d, 2H, J = 9 Hz, *p*-methoxyphenyl), 7.51 (s, 1H, H-7), 7.80 (br s, NH_2); ^{13}C nmr (DMSO-d_6): δ 29.14 (q, $^1J_{CH}$ = 126 Hz, 2-Me), 55.00 (q, $^1J_{CH}$ = 144 Hz, OMe), 85.70 (s, C-2), 113.18 (d, $^1J_{CH}$ = 159 Hz, *p*-methoxyphenyl), 126.46 (d, $^1J_{CH}$ = 160 Hz, *p*-methoxyphenyl), 138.17 (m, *p*-methoxyphenyl), 152.71 (d, $^3J_{CH}$ = 13 Hz, C-9), 153.69 (d, $^3J_{CH}$ = 12 Hz, C-5), 158.27 (m, *p*-methoxyphenyl), 163.89 (d, $^1J_{CH}$ = 197 Hz, C-7); ir (potassium bromide): 3390, 3167 (NH_2 and NH) cm^{-1}; ms m/e 258 (M^+, 30%), 243 (M^+-15, 100%).

Anal. Calcd. for $C_{12}H_{14}N_6O$: C, 55.80; H, 5.46; N, 32.54. Found: C, 55.90; H, 5.41; N, 32.49.

Other triazines **4** were similarly prepared and are listed in Tables III, IV and V.

Cyclization of Isobutyrophenone Diaminomethylenehydrazone (**1j**) with Ethyl *N*-Cyanoimidate. Formation of 5-Amino-2-phenyl-[1,2,4]triazolo[1,5-*a*][1,3,5]triazine (**5**).

A mixture of isobutyrophenone diaminomethylenehydrazone (**1j**) (0.2 g, 1 mmole), ethyl *N*-cyanoimidate (**2**) (0.2 g, 2 mmoles), triethylamine (0.1 ml) in methanol (1 ml) was allowed to stand at room temperature with occasional stirring for 3 hours and then evaporated. The residual oil was triturated with acetonitrile (0.5 ml) to give the triazolotriazine **5** as a crystalline powder (68 mg, 32%). It was recrystallized by dissolving in a hot mixture of dimethyl sulphoxide and pyridine (1:1, v/v) followed by diluting with water to precipitate the product **5** as fine plates, mp 298-300°; ^{1}H nmr (DMSO-d_6): δ 7.55 (m, 3H, phenyl), 8.23 (m, 2H, phenyl), 8.35 (s, 1H, H-7), 8.85 (br s, 2H, NH_2); ir (potassium bromide): 3035 (s, NH_2) cm^{-1}; ms m/e 212 (M^+, 100%).

Anal. Calcd. for $C_{10}H_8N_6$: C, 56.60; H, 3.80; N, 39.60. Found: C, 56.69; H, 3.71; N, 39.79.

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[6] Preferential elimination of a highly branched alkyl group was observed in the similar cyclization of pinacolone *S*-methylisothiosemicarbazone with ethoxymethylenemalononitrile. The product was 8-cyano-2-methyl-5-methylthio[1,2,4]triazolo[1,5-*c*]pyrimidine (unpublished data).

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