Synthesis of Nitrogen-Containing Heterocycles. 7 Reaction of Aliphatic Diaminomethylenehydrazones with Hindered Ethoxymethylenecyanoacetate

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Aliphatic diaminomethylenehydrazones **1** were reacted with ethyl 2-cyano-3-ethoxy-2-pentenoate **2** to give a number of heterocycles in low to moderate yields, according to the substitution pattern and the size of substituent. When **1** carried a single methyl group on the terminal nitrogen, it gave preferentially 6-oxo-1,6-dihydropyrimidines **4** incorporating *N*(4) into the ring. In contrast, the reaction between **1c** or **1d** and **2** led to 6-imino- and 6-oxo-1,6-dihydropyrimidines **7** and **8** along with **3**. When the alkylidene moiety was bulky, **1e** and **1f**, the similar reaction gave **3** in high yields without any cyclized product. Upon exposure to acid, compound **3** yielded 6-oxo-1,6-dihydropyrimidines **6**, [1,2,4]triazolo[1,5-*c*]pyrimidine-8-carboxylate **5** and *N*-alkenyl-1,2,4-triazoles **9** in addition to **7** and **8** in proportions dictated by the nature of the substituents of **1**. The structural assignment and reaction mechanism are discussed.

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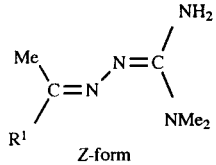
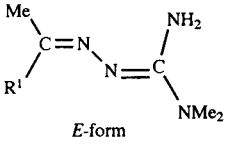
Introduction.

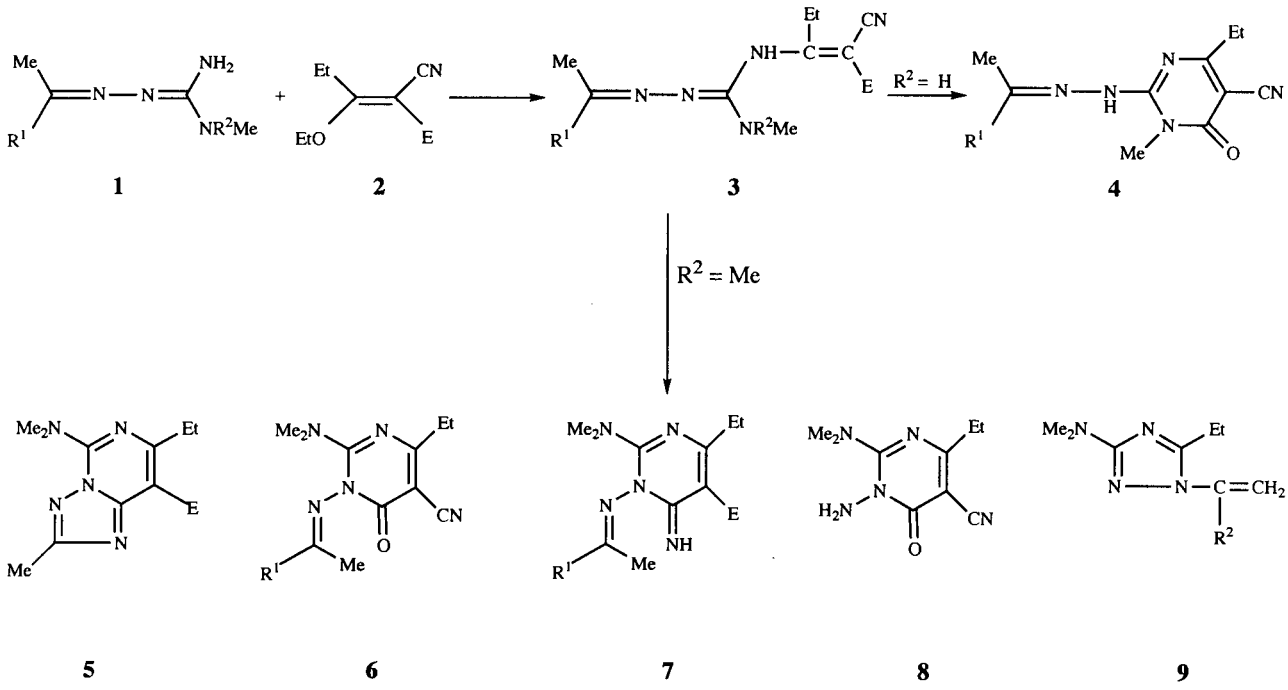
In a previous paper [1], we have reported the direct cyclization of aliphatic *N*(4),*N*(4)-dimethylaminomethylenehydrazones to *gem*-bis(3-dimethylamino-1,2,4-triazol-1-yl)alkanes and *N*-alkenyl-1,2,4-triazoles by the reaction with ethyl ethoxymethylenecyanoacetate which demonstrated much higher nucleophilic character of the alkylideneamino nitrogen than that of aromatic compounds. It was also described in the paper that, when one of the methyl groups on the terminal nitrogen was replaced by a hydrogen atom, the similar reaction gave rise to the unexpected product, 1,2,4-triazolo[1,5-*c*]pyrimidine-8-carboxylate derivative with no formation of the bistriazole. We are now interested in the use of ethyl 2-cyano-3-ethoxy-2-pentenoate in place of ethyl ethoxymethylenecyanoacetate, because, by introduction of an ethyl group into the ethoxymethylene moiety of the latter compound, there might be expected inhibition of nucleophilic attack of *N*(1) on the hindered enamino carbon and/or coplaner arrangement in the intermediate condensation product leading to the formation of triazolopyrimidine derivatives, and thus another mode of cyclization to new compounds.

Table 1

^{1}H and ^{13}C NMR Data for Diaminomethylenehydrazones **1**

		^{1}H NMR ($CDCl_3$, δ ppm)			^{13}C NMR ($CDCl_3$, δ ppm)	
	R^1	$N(CH_3)_2$	NH_2	CH_3	$N(CH_3)_2$	CH_3
 *Z*-form	Me	2.93	4.90	2.02	36.64 (136.3)	17.32 (127.0)
	Et	2.93	4.95	2.00	36.96 (136.3)	15.88 (127.0)
	i-Pr	2.86	5.00	1.93	36.84 (136.3)	13.71 (126.4)
	t-Bu	2.60	4.81	2.16	36.79 (136.3)	12.05 (127.0)
 *E*-form	Me	3.36	7.17	2.28	40.82 (138.5)	20.68 (127.5)
	Et	3.18	6.95	2.12	38.31 (138.5)	17.03 (127.5)
	i-Pr	3.18	6.85	2.10	38.94 (139.6)	15.57 (127.5)
	t-Bu	-	-	-	-	-

Scheme 1



E = COOEt

	R^1	R^2
a	Et	H
b	*t*-Bu	H
c	Me	Me
d	Et	Me
e	*iso*-Pr	Me
f	*t*-Bu	Me

Diaminomethylenehydrazones bearing a single methyl group on the terminal nitrogen (**1a** and **1b**) were allowed to react with **2** in benzene at room temperature. Chromatographic separation or crystallization gave **4** in 31-47% yield; neither the precursor **3** or a triazolopyrimidine derivative could be detected. Little or no formation of triazolopyrim-idine derivatives such as **5** was also observed in the similar reaction of **1c-1f**. As expected, electrocyclic reaction of **3** to form **5,** which requires coplaner arrangement of the nine atoms in the transition state, was found to be substantially inhibited by the ethyl group on the enamino carbon.

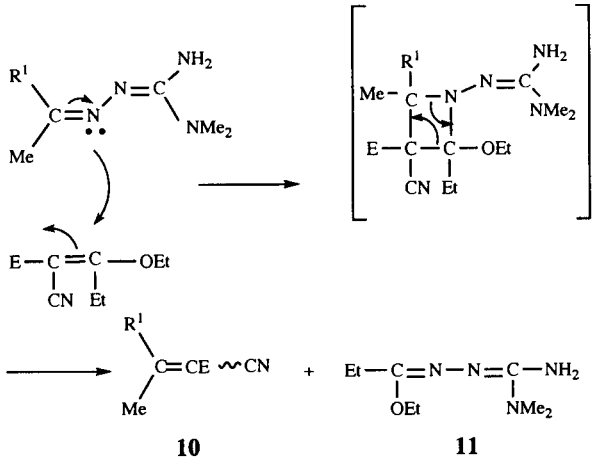
Diaminomethylenehydrazones **1c-1f** occurred as isomeric pairs consisting of a form reactive towards the addition-elimination reaction with **2** and a non-reactive form. The ^1H and ^{13}C nmr spectroscopy easily established the presence of two isomers in each pair (Table 1). The reactivity of diaminomethylenehydrazone on **2** to produce **3** may depend upon the proximity of the unsubstituted amino group to the bulky alkylideneamino group. Thus, the reactive species in each pair of isomers should have a (*Z*) configuration about the *N*(2)=C double bond. This was confirmed by observing the carbon-13 nmr data on the dimethylamino carbon. The reactive form showed resonances at higher magnetic fields (δ 36.64-36.96 ppm) than those for the unreactive species (δ 38.31-40.82 ppm). The upfield resonance of the dimethylamino carbon for the reactive species may be interpreted as the steric compression effect [2] caused by the proximity between the dimethylamino group and the alkylideneamino grouping.

The reactive isomers (*Z*-form) [3] of **1c-1f** were obtained in the stereochemically pure form except for **1d** by performing the reaction between a methyl ketone and 1-amino-3,3-dimethylguanidine in methanol at the autogenetic *p*H under reflux. Compound **1d,** however, was obtained as a mixture consisting of *E* and *Z* forms in a

molar ratio *E*:*Z* = 1:4 and employed directly without further purification. On the other hand, the unreactive isomer (*E*-form) could be obtained when the reaction of a ketone with the guanidine was carried out in an acidic medium. Compound **1f** occurred as the *Z*-form under either neutral or acidic conditions.

The reactive diaminomethylenehydrazones thus obtained were reacted with **2** under the same conditions as described in the reaction for **1a** and **1b.** Compounds **1c** and **1d** gave directly cyclized products **7c** (19%) and **8d** (23%), respectively, along with the intermediate **3** in 10% for **1c** and 20% for **1d.** With increase in the bulkiness of R^1, the intermediate **3** tends to resist ring closure. This was true for **1e** and **1f** which gave the corresponding **3** in high yield (~85%) without any cyclized product. The poor yields of either cyclized product or **3** in the reaction of **1c** and **1d** can be ascribed, in part, to the predominant formation of 2-cyano-2-alkenoate **10** in 35% for **1c** and 42% for **1d.** Compound **10** may possibly be formed through a four-membered cyclic intermediate and considered to be a retro-cycloaddition product (Scheme 2). Compounds **1e** and **1f** which had bulky R^1 groups did not produce a 2-cyano-2-alkenoate. The imidoester **11** which could concomitantly have been produced, was not isolated.

Scheme 2



10 **11**

An additional factor for lowering the yield of cyclized product from **1c** may be the facile removal of the elements of acetone from the isopropylideneamino moiety, probably through hydrolytic cleavage. Once the alkylidene group ("protective group") has been removed before ring closure, attack of the exposed, highly nucleophilic hydrazino group of the guanidine thus formed on **2** could prevail over the desired reaction of **2.** The concomitant formation of 6-imino-1,6-dihydropyrimidines **7**, which contradicts the report by Whitehead and coworker [4], and 6-oxo-1,6-dihydropyrimidine **8** suggests that this reaction might proceed by the addition-elimination reaction process involving a structure possible to rotate the enamine double bond. The linear intermediates **3e** and **3f** could be cyclized to three types of heterocycles **5**, **6** and **9** under the influence of acetic acid. Compound **3e** gave substantially a single product **9e** while **3f** produced all of the three compounds, with 6-oxo-1,6-dihydropyrimidine-8-carbonitrile **6** being the major product. Ethyl 7-ethyl-5-dimethylamino-2-methyl[1,2,4]triazolo[1,5-*c*]pyrimidine-8-carboxylate **5** is obviously the result of loss of the R^1 group from the corresponding 2,2-disubstituted 1,2-dihydro[1,2,4]triazolo[1,5-*c*]pyrimidines [5].

The structures of products **3-10** have been established by analytical and spectral data which appear in the Experimental.

EXPERIMENTAL

Melting points were determined in open capillary tubes and are uncorrected. The ir spectra were recorded in potassium bromide pellets on a Perkin-Elmer 983 spectrophotometer. The ^1H and ^{13}C nmr spectra were obtained with a JNM EX-400 (400 MHz) Spectrometer in deuteriochloroform using TMS as the internal standard (δ in ppm, J in Hz). The mass spectra (75 eV) were recorded on a JEOL JMS-D100 mass spectrometer. Microanalysis were performed with a Perkin-Elmer 240D elemental analyser at Microanalytical Laboratory of Kitasato University.

The diaminomethylenehydrazones used were prepared according to literature methods [1].

5-Cyano-4-ethyl-2-(1-methylpropylidene)hydrazino-1-methyl-6-oxo-1,6-dihydropyrimidine (**4a**).

A solution of **1a** (0.14 g, 1 mmole) and **2** (0.2 g, 1 mmole) in benzene (1 ml) was allowed to stand at room temperature. After 5 hours, the reaction mixture was evaporated to give the crude product as an oil. The oil, after being dissolved in chloroform, was subjected to preparative hplc on silica gel with chloroform as an eluent giving **4a** (0.077 g, 31%) as colorless needles, mp 126-127°; ir: ν 2230, 1680 cm^{-1} ; ^1H nmr: δ 1.10 (t, 3H, J = 7, CH_3), 1.30 (t, 3H, J = 7, CH_3), 2.10 (s, 3H, =C-CH_3), 2.48 and 2.72 (each q, 4H, J = 7, 2 x CH_2), 3.29 (s, 3H, NCH_3), 8.25 (bs, 1H, NH); ^{13}C nmr: δ 10.7 (q), 11.2 (q), 17.0 (q), 26.6 (t), 27.6 (q), 31.9 (t), 84.7 (s), 114.3 (s), 147.9 (s), 159.2 (s), 163.1 (s), 168.8 (s); ms: m/z 247 (M^+, 35%), 218 (M^+-29, 100%).

Anal. Calcd. for $C_{12}H_{17}N_5O$: C, 58.28; H, 6.93; N, 28.32. Found: C, 58.22; H, 6.89; N, 28.22.

5-Cyano-4-ethyl-2-(1,2,2-trimethylpropylidene)hydrazino-1-methyl-6-oxo-1,6-dihydropyrimidine (**4b**).

In a similar manner as described for **4a,** treatment of **1b** (0.17 g, 1 mmole) with **2** (0.2 g, 1 mmole) in benzene (1 ml) afforded **4b** as colorless needles, yield 0.13 g (47%), mp 176-177°; ir: ν 2200, 1660 cm^{-1}; ^1H nmr: δ 1.21 [s, 9H, $C(CH_3)_3$], 1.31 (t, 3H, J = 7, CH_3), 2.11 (s, 3H, CH_3), 2.75 (q, 2H, J = 7, CH_2), 3.31 (s, 3H, NCH_3), 8.00 (bs, 1H, NH); ^{13}C nmr: δ 10.7 (q), 13.5 (q), 26.5 (t), 27.5 (q), 27.7 (q), 38.8 (s), 84.8 (s), 114.4 (s), 149.1 (s), 159.4 (s), 163.3 (s), 172.2 (s), ms: m/z 275 (M^+, 42%), 218 (M^+-57, 100%).

Anal. Calcd. for $C_{14}H_{21}N_5O$: C, 61.07; H, 7.69; N, 25.43. Found: C, 61.02; H, 7.68; N, 25.21.

3-Methyl-2-butanone *N*(3)-[(2-Cyano-2-ethoxycarbonyl-1-ethyl)vinyl]amino-*N*(4),*N*(4)-dimethylaminomethylenehydrazone (**3e**).

A solution of **1e** (0.17 g, 1 mmole) and **2** (0.2 g, 1 mmole) in benzene (1 ml) was allowed to stand at room temperature. After 20 hours, the reaction mixture was evaporated to give the crude product as an oil. The oil, after being dissolved in chloroform, was subjected to preparative hplc on silica gel with chloroform as an eluent to give the pure **3e** as colorless oil (0.27 g, 85%); ir: ν 2230, 1680 cm^{-1}; ^1H nmr δ 1.03 [d, 6H, J = 6.8, $CH(CH_3)_2$], 1.14 (t, 3H, J = 7.6, CH_3), 1.31 (t, 3H, J = 7, ester CH_3), 1.93 (s, 3H, CH_3), 2.45 [quin, 1H, J = 6.8, $CH(CH_3)_2$], 2.53 (q, 2H, J = 7.6, CH_2), 2.93 (s, 6H, $N(CH_3)_2$], 4.21 (q, 2H, J = 7, OCH_2), 10.61 (bs, 1H, NH); ^{13}C nmr: δ 12.1 (q), 12.4 (q), 13.8 (q), 19.9 (q), 25.9 (t), 37.2 (d), 40.0 (q), 61.0 (t), 75.3 (s), 117.7 (s), 149.7 (s), 166.9 (s), 170.1 (s), 175.1 (s).

Anal. Calcd. for $C_{16}H_{27}N_5O_2$: C, 59.79; H, 8.47; N, 21.79. Found: C, 59.59; H, 8.46; N, 21.53.

3,3-Dimethyl-2-butanone *N*(3)-[(2-Cyano-2-ethoxycarbonyl-1-ethyl)vinyl]amino-*N*(4),*N*(4)-dimethylaminomethylenehydrazone (**3f**).

In a similar manner as described for **3e**, treatment of **1f** (0.18 g, 1 mmole) with **2** (0.2 g, 1 mmole) in benzene (1 ml) afforded **3f**, yield 0.23 g (68%), mp 67-69°; ir: ν 2200, 1660 cm^{-1}; ^1H nmr: δ 1.08 [s, 9H, $C(CH_3)_3$], 1.14 (t, 3H, J = 7.6, ethyl CH_3), 1.31 (t, 3H, J = 7, ester CH_3), 1.95 (s, 3H, CH_3), 2.54 (q, 2H, ethyl CH_2), 2.96 [s, 6H, $N(CH_3)_2$], 4.22 (q, 2H, J = 7, ester CH_2), 10.66 (bs, 1H, NH); ^{13}C nmr: δ 12.3 (q), 12.7 (q), 14.3 (q), 26.5 (t), 27.89 (q), 38.1 (q), 38.6 (s), 60.8 (t), 75.3 (s), 117.7 (s), 149.9 (s), 168.2 (s), 170.3 (s), 175.3 (s).

Anal. Calcd. for $C_{17}H_{29}N_5O_2$: C, 60.87; H, 8.71; N, 20.88. Found: C, 60.83; H, 8.71; N, 20.60.

Reaction of Diaminomethylenehydrazone **1c** with **2**.

A solution of **1c** (0.28 g, 2 mmoles) and **2** (0.4 g, 2 mmoles) in benzene (2 ml) was allowed to stand at room temperature. After 20 hours, the reaction mixture was evaporated to give the crude product as an oil. The oil was purified by hplc on silica gel (chloroform) to give products **3c** (10%), **7c** (19%) and **10c** (35%).

Acetone *N*(3)-[(2-Cyano-2-ethoxycarbonyl-1-ethyl)vinyl]amino-*N*(4),*N*(4)-dimethylaminomethylenehydrazone (**3c**).

This compound had mp 67-69°; ^1H nmr: δ 1.18 (t, 3H, J = 7.6, ethyl CH_3), 1.45 (t, 3H, J = 7.0, ester CH_3), 1.97 (s, 3H, CH_3), 2.00 (s, 3H, CH_3), 2.56 (2H, J = 7.6, ethyl CH_3), 2.97 [s, 6H, $N(CH_3)_2$], 4.25 (q, 2H, J = 7, ester CH_2), 10.58 (bs, 1H, NH).

Anal. Calcd. for $C_{14}H_{23}N_5O_2$: C, 57.32; H, 7.90; N, 23.87. Found: C, 57.53; H, 7.82; N, 24.00.

Ethyl 4-Ethyl-6-imino-1-isopropylideneamino-2-dimethylamino-1,6-dihydropyrimidine-5-carboxylate (**7c**).

This compound has mp 84-89°; ir: ν 3360, 1670, 1660, 1580, 1560, 1190 cm^{-1}; ^1H nmr: δ 1.24 (t, 3H, J = 7.0, ethyl CH_3), 1.25 (t, 3H, J = 6.8, ester CH_3), 2.15 (s, 6H, CH_3 x 2), 2.53 (q, 2H, ethyl CH_2), 3.00 [s, 6H, $N(CH_3)_2$], 4.12 (q, 2H, J = 7, ester CH_2), 5.45 (s, 1H, NH); ^{13}C nmr: δ 12.0 (q, 14.5 (2 x q), 22.1 (t), 41.7 (q), 59.3 (t), 77.1 (s), 151.7 (s), 159.7 (s), 163.5 (s x 2), 170.3 (s).

Anal. Calcd. for $C_{14}H_{23}N_5O_2$: C, 57.32; H, 7.90; N, 23.87. Found: C, 57.62; H, 7.91; N, 23.99.

Ethyl 2-Cyano-3-methyl-2-butenoate (**10c**).

This compound was obtained as an oil: ^1H nmr: δ 1.37 (t, 3H, J = 7, CH_3), 2.36 (s, 3H, CH_3), 2.46 (s, 3H, CH_3), 4.28 (q, 2H, J = 7, CH_2).

Anal. Calcd. for $C_8H_{11}NO_2$: C, 62.73; H, 7.24; N, 9.15. Found: C, 62.88; H, 7.38; N, 9.05.

Reaction of Diaminomethylenehydrazone **1d** with **2**.

A solution of **1d** (0.16g, 1 mmole) and **2** (0.2 g, 1 mmole) in benzene (1 ml) was allowed to stand at room temperature. After 20 hours, the reaction mixture was evaporated to give the crude product as an oil. The oil was purified by hplc on silica gel (chloroform) to give products **3d** (20%), **7d** (33%), **8** (23%) and **10d** (42%).

Butanone *N*(3)-[(2-Cyano-2-ethoxycarbonyl-1-ethyl)vinyl]-amino-*N*(4),*N*(4)-dimethylaminomethylenehydrazone (**3d**).

This compound was obtained as an oil; ^1H nmr: δ 1.12 (t, 3H, J = 7.6, ethyl CH_3), 1.27 (t, 3H, J = 7.6, ethyl CH_3), 1.95 (s, 3H, CH_3), 2.50 (m, 4H, CH_2 x 2), 2.98 [s, 6H, $N(CH_3)_2$], 4.25 (q, 2H, J = 7, ester CH_2), 10.56 (bs, 1H, NH).

Ethyl 4-Ethyl-6-imino-2-dimethylamino-1-methylpropylideneamino-1,6-dihydropyrimidine-5-carboxylate (**7d**).

This compound was obtained as an oil; ^1H nmr: δ 1.14 (t, 3H, J = 7.6, ethyl CH_3), 1.20 (t, 3H, J = 7.6, CH_3), 1.27 (t, 3H, J = 7, ester CH_3), 2.09 (s, 3H, CH_3), 2.47 (q, 2H, J = 7.6, CH_2), 2.63 (q, 2H, J = 7.6, CH_2), 3.02 [s, 6H, $N(CH_3)_2$], 4.15 (q, 2H, J = 7, ester CH_2), 5.50 (s, 1H, NH); ^{13}C nmr: δ 11.9 (q), 14.5 (q x 3), 22.1 (t), 59.3 (t), 77.6 (s), 151.7 (s), 156.9 (s), 159.7 (s), 163.4 (s), 164.2 (s), 170.3 (s).

1-Amino-4-ethyl-2-dimethylamino-6-oxo-1,6-dihydropyimidine-5-carbonitrile (**8**).

This compound was obtained as an oil; ir: ν 2200, 1650 cm^{-1}; ^1H nmr: δ 1.14 (t, 3H, J = 7.6, CH_3), 2.15 (t, 2H, J = 7.6, CH_2), 2.96 [s, 6H, $N(CH_3)_2$], 9.30 (bs, 2H, NH); ^{13}C nmr: δ 12.3 (q), 21.1 (t), 38.8 (q), 88.2 (s), 115.7 (s), 155.2 (s), 157.3 (s), 188.6 (s).

Ethyl 2-Cyano-3-methyl-2-pentenoate (**10d**).

This compound was obtained as an oil: ^1H nmr: δ 1.19 (t, 3H, J = 7.6, CH_3), 1.30 (t, 3H, J = 7, CH_3), 2.30 (s, 3H, CH_3), 2.60 (q, 2H, J = 7.6, CH_2), 4.25 (q, 2H, J = 7, CH_2).

Anal. Calcd. for $C_9H_{13}NO_2$: C, 64.65; H, 7.84; N, 8.38. Found: C, 64.16; H, 7.92; N, 8.23.

Treatment of 3-Methyl-2-butanone *N*(3)-[2-Cyano-2-ethoxycarbonyl-1-ethyl)vinyl]amino-*N*(4),*N*(4)-dimethylaminomethylene-hydrazone (**3e**) with Acetic Acid.

A solution of **3e** (0.12 g, 0.3 mmole) in acetic acid (3 ml) was heated at 85-90° for 1 hour and then evaporated under reduced pressure. The residue was partitioned between 10% aqueous sodium carbonate and chloroform. The organic phase was washed with water, dried over sodium sulphate, and then evaporated. The residual brown oil was purified by hplc on silica gel

(chloroform) to give products **5** (trace), **6e** (trace) and **9e** (26%).

Ethyl 7-Ethyl-5-dimethylamino-2-methyl[1,2,4]triazolo[1,5-*c*]pyrimidine-8-carboxylate (**5**).

This compound had mp 72-74°; ^{1}H nmr: δ 1.26 (t, 3H, J = 7.2, ethyl CH_3), 1.39 (t, 3H, J = 6.8, ester CH_3), 2.53 (s, 3H, CH_3), 2.94 (q, 2H, J = 7.2, ethyl CH_2), 3.52 [s, 6H, $N(CH_3)_2$], 4.44 (q, 2H, J = 6.8, ester CH_2); ^{13}C nmr: δ 13.3 (q), 14.4 (q), 14.7 (q), 29.7 (t), 40.5 (q), 61.2 (t), 103.3 (s), 147.1 (s), 155.1 (s), 163.2 (s), 163.6 (s), 165.1 (s).

Anal. Calcd. for $C_{13}H_{19}N_5O_2$: C, 56.30; H, 6.91; N, 25.25. Found: C, 56.60; H, 6.90; N, 25.50.

5-Ethyl-3-dimethylamino-1-(3-methyl-1-buten-2-yl)-1*H*-1,2,4-triazole (**9e**).

This compound was obtained as an oil; ^{1}H nmr: δ 1.08 [t, 6H, J = 6.8, $CH(CH_3)_2$], 1.30 (t, 3H, J = 6.8, CH_3), 2.68 (q, 2H, J = 6.8, CH_2), 2.90 [hept, 1H, J = 6.8, $CH(CH_3)_2$], 2.98 [s, 6H, $N(CH_3)_2$], 4.98 (s, 1H, =CH), 5.16 (s, 1H, =CH); ^{13}C nmr: δ 12.8 (q), 19.8 (t), 20.2 (q), 32.3 (d), 38.7 (q), 108.0 (t), 150.6 (s), 156.5 (s), 165.5 (s).

Anal. Calcd. for $C_{11}H_{20}N_4$: C, 63.43; H, 9.68; N, 26.90. Found: C, 63.56; H, 9.58; N, 26.80.

Treatment of *N*(4)-(Substituted amino)methylenehydrazone (**3f**) with Acetic Acid.

A solution of **3f** (0.4 g, 1.2 mmoles) in acetic acid (3 ml) was heated at 85-90° for 1 hour and then evaporated under reduced pressure. The residue was partitioned between 10% aqueous sodium carbonate and chloroform. The organic phase was washed with water, dried over sodium sulphate, and then evaporated. The residual brown oil was purified by hplc on silica gel (chloroform) to give the products **5** (8%), **6f** (33%) and **9f** (25%).

4-Ethyl-2-dimethylamino-1-(1,2,2-trimethylpropylidene)amino-6-oxo-1,6-dihydropyrimidine-5-carbonitrile (**6f**).

This compound had mp 86-89°; ^{1}H nmr: δ 1.25 (t, 3H, J = 7.2, ethyl CH_3), 1.30 [s, 9H, $(CH_3)_3$], 1.89 (s, 3H, CH_3), 2.68 (q, 2H, J = 7.6, CH_2), 3.09 [s, 6H, $N(CH_3)_2$]; ^{13}C nmr: δ 11.8 (q), 16.5 (q), 27.8 (q), 30.0 (t), 40.2 (s), 41.4 (q), 88.2 (s), 115.7 (s), 157.3 (s), 173.7 (s), 188.6 (s).

Anal. Calcd. for $C_{15}H_{23}N_5O_2$: C, 62.26; H, 8.01; N, 24.20 Found: C, 62.17; H, 8.03; N, 24.11.

5-Ethyl-3-dimethylamino-1-(3,3-dimethyl-1-buten-2-yl)-1*H*-1,2,4-triazole (**9f**).

This compound was obtained as an oil; ^{1}H nmr: δ 1.17 [s, 9H, $(CH_3)_3$], 1.26 (t, 3H, J = 6.8, CH_3), 2.59 (q, 2H, J = 6.8, CH_2), 2.97 [s, 6H, $N(CH_3)_2$], 5.00 (s, 1H, =CH), 5.42 (s, 1H, =CH); ^{13}C nmr: δ 12.8 (q), 19.9 (t), 27.2 (q), 38.7 (q), 38.8 (s), 107.8 (t), 150.0 (s), 156.1 (s), 165.2 (s).

Anal. Calcd. for $C_{12}H_{22}N_4$: C, 64.83; H, 9.97; N, 25.20. Found: C, 64.77; H, 9.89; N, 24.90.

REFERENCES AND NOTES

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[3] Throughout the discussion, the designation *E* or *Z* refers to the configuration about the N(2)=C double bond.

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