# Synthesis of Nitrogen-Containing Heterocycles. 3. Formation and Structure of New 1,2,4-Triazole Derivatives



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Treatment of *N*(3)-[(2-cyano-2-ethoxycarbonyl)vinyl]amino-*N*(4),*N*(4)-dimethylaminomethylenehydrazones of aromatic carbonyl compounds with hot acetic acid resulted in the formation of symmetrical gem-bis-(3-dimethylamino-1,2,4-triazol-1-yl)methanes, (3-dimethylamino-1,2,4-triazol-1-yl)arylmethyl acetates, and (3-dimethylamino-1,2,4-triazol-1-yl)alkenes of a gem-diaryl type depending upon whether the carbonyl compound was aldehyde or ketone.

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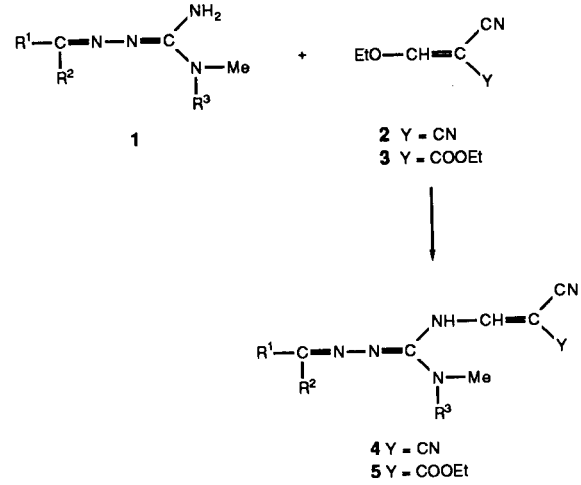
## Introduction.

We have reported that the reaction between diaminomethylenehydrazones of aromatic carbonyl compounds and ethoxymethylenemalononitrile (**2**) proceeds through an initial condensation product *N*(3)-(2,2-dicyanovinyl)-amino-*N*(4)-(substituted-amino)methylenehydrazones **4** which can be cyclized to [1,2,4]triazolopyrimidine derivatives **11** or **13** in neutral to basic media [1]. In our previous report [2], it has been described that *N*(3)-[(2-cyano-2-ethoxycarbonyl)vinyl]amino-*N*(4),*N*(4)-dimethylaminomethylenehydrazones (**5**, $R^3$ = Me) of aromatic carbonyl compounds resist ring-closure under the same conditions as those for the dicyano analog **4**. We have now found that the dicyanovinyl compounds **4** can readily be cyclized in an acidic medium to form either [1,2,4]triazolopyrimidines **11** or **13** or 5-cyano-6-iminodihydropyrimidines **12** depending upon the substitution pattern on *N*(4). The acidic cyclization, however, when applied to the unreactive vinylaminomethylenehydrazones (**5**, $R^3$ = Me), gave no expected products **11** or **13** but led to the formation of some 3-dimethylamino-1,2,4-triazole derivatives **6**, **7**, and **9** with elimination of ethyl cyanoacetate (**10**). The product from the acidic cyclization of **5** was determined by the nature of the carbonyl component of **5**. Thus, if the carbonyl component was an aldehyde, then the major product was a gem-bis(1,2,4-triazol-1-yl)toluene **6**, while if it was ketone, then the product was an *N*-alkenyl-1,2,4-triazole **9** with no formation of any bis-azoles. Because it has been known that an *ortho*-substituent is essential to the formation of an *N*-alkenyl-1,2,4-triazole from similarly structured acetophenone isothiosemicarbazones [3], the behavior of the acetophenone derivatives (**5f**, $R^3$ = Me) having no *ortho*-substituent seems to be a characteristic feature of the diaminomethylenehydrazone series. Furthermore, the bis-azole formation has not yet been observed in the isothiosemicarbazones of aromatic aldehyde [4]. Accordingly, we wish to report new cyclization reactions of diaminomethylenehydrazones of aromatic carbonyl compounds.

## Results and Discussion.

*N*(3)-(2,2-Dicyanovinyl)amino-*N*(4)-(substituted-amino)-methylenehydrazones **4** and *N*(3)-[(2-cyano-2-ethoxycarbonyl)vinyl]amino-*N*(4),*N*(4)-dimethylaminomethylenehydrazones **5** were prepared by the reaction between the corresponding diaminomethylenehydrazones **1** and an ethoxymethylene compound **2** or **3** under the conditions as suggested previously [2] (Scheme 1).

Scheme 1

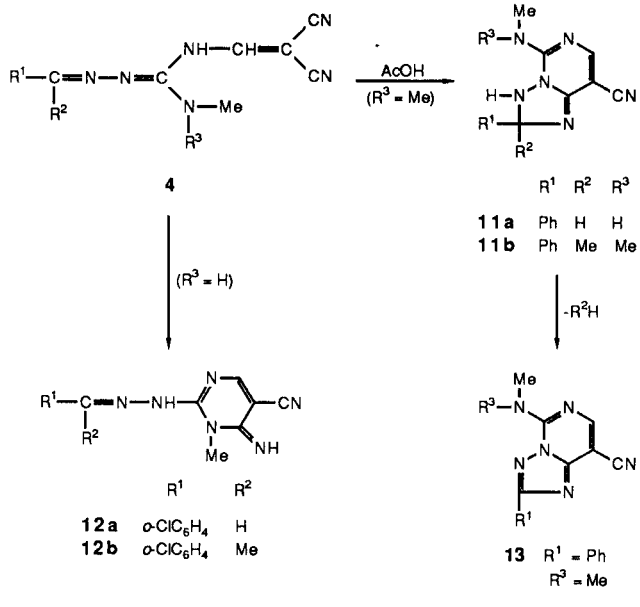



| | $R^1$ | $R^2$ | $R^3$ |
|---|---|---|---|
| a | *o*-$ClC_6H_4$ | H | H |
| b | *o*-$ClC_6H_4$ | Me | H |
| c | Ph | H | Me |
| d | *o*-$ClC_6H_4$ | H | Me |
| e | *o*-$MeOC_6H_4$ | H | Me |
| f | Ph | Me | Me |
| g | *o*-$ClC_6H_4$ | Me | Me |
| h | Ph | Et | Me |
| i | Ph | *n*-Pr | Me |

When *N*(4) of the dicyanovinyl compounds **4** had no hydrogen **4c** and **4f**, brief exposure of **4** to hot acetic acid resulted in the exclusive formation of 2,3-dihydro[1,2,4]-triazolo[1,5-c]pyrimidine derivatives **11a** and **11b** regardless whether the carbonyl component of **4** was

aldehyde or ketone. However, if the carbonyl component was an aldehyde **4c**, partial dehydrogenation of **11a** occurred and the product tended to be somewhat contaminated with **13**, while if it was a ketone **4f**, pure **11b** was obtained quantitatively (Scheme 2). On the other hand, when *N*(4) had a single methyl group ($R^3$ = H), the 2,2-dicyanovinylaminomethylenehydrazones **4a** and **4b** did not produce any triazolopyrimidines but 2-arylmethylenehydrazino-6-imino-1,6-dihydro-1*H*-pyrimidines **12** were the only cyclized product under the same reaction conditions as those for the cyclization of the dimethylamino compounds (Scheme 2). The structural assignment of these products could be made according to the procedure reported previously [1,2].

Scheme 2




When the acidic cyclization was applied to a cyanoacrylate **5c** ($R^3$ = Me) which had been found to resist ring-closure in neutral to basic media, the resulting reaction mixture consisted of **6c** and **8a** in an approximate equimolar proportion (Scheme 3). Chromatographic separation of the mixture gave the bis-azole **6c** in 30% yield. Treatment of **5e** and **5d** under the same acid cyclization conditions as in the compound **5c**, the corresponding **6e** was isolated in 18% yield after chromatography, but no bis-azole was obtained from **5d**. Attempts to improve the yield of **6** were unsuccessful. The presence of an *ortho*-substituent on the phenyl group of **5** is evidently unfavorable sterically to the formation of bis-azole. In the compound **5d**, an additional unfavorable factor arising from the electron-withdrawing *ortho*-chloro group completely inhibits the bis-azole formation and directs the reaction to the formation of a new derivative **7d** (Scheme 3). (3-Dimethylamino-1,2,4-triazol-1-yl) (*o*-methoxyphenyl)methyl acetate (**7e**) was also found as a minor product in the acidic cyclization of **5e** [5].

The formation of bis-azoles **6** and triazolylphenylmethyl acetates **7** may involve a common intermediate cation **14** (Scheme 4) reported in the previous paper concerning the cyclization of isothiosemicarbazones [3,4]. The cation **14d** should be destabilized by the *ortho*-chloro group on $R^1$ and therefore its formation might be limited. Furthermore, the *ortho*-substituent should not only prevent the approach of a bulky nucleophile **5d** to the positive center of cation **14d**, but also lower the nucleophilicity of *N*(1) of the attacking species **5d**. Thus the result is the attack by an available, less bulky nucleophile acetate ion at the positive center, thereby leading to the exclusive formation of **7d**. The bis-azole formation is invariably accompanied by an $\alpha$-cyanocinnamate **8**, the by-product being produced

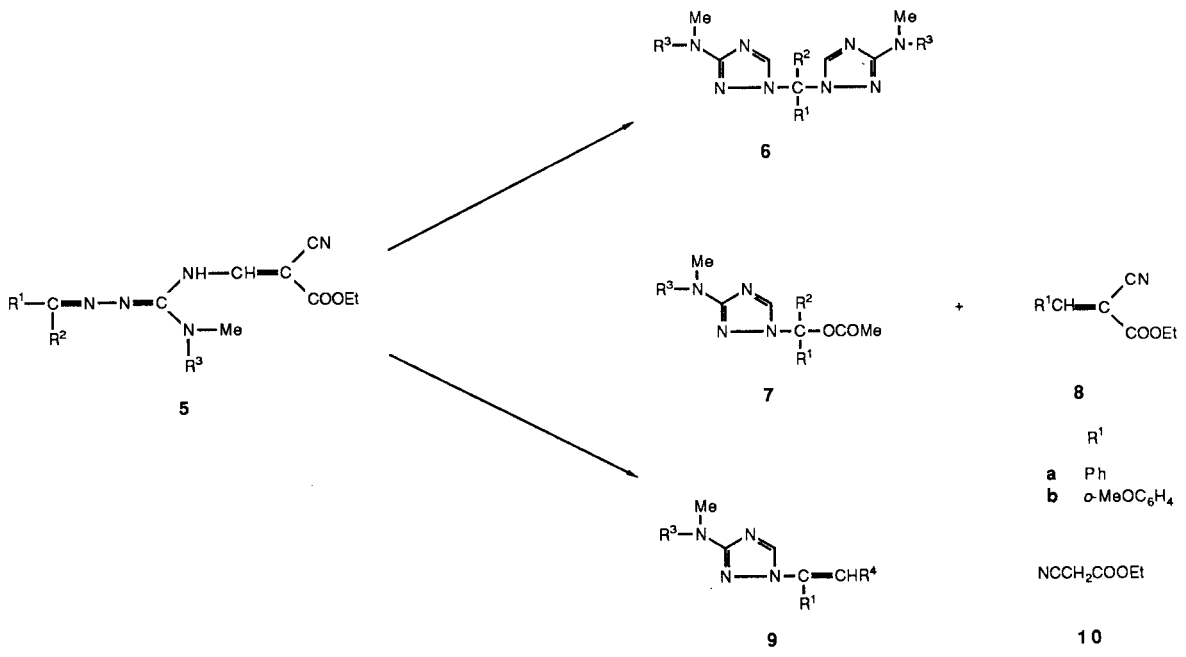
Table 1

*N*(3)-[(2-Cyano-2-ethoxycarbonyl)vinyl]-*N*(4),*N*(4)-dimethylaminomethylenehydrazones

| Compounds | $R^1$ | $R^2$ | Mp (°C) | Yield [a] (%) | Formula | Analysis % Calcd./Found C | H | N | IR (KBr) cm$^{-1}$ $\nu$ CN | $\nu$ C=O |
|---|---|---|---|---|---|---|---|---|---|---|
| **5d** | *o*-ClC$_6$H$_4$ | H | 156-158 | 54 | $C_{16}H_{18}ClN_5O_2$ | 55.25<br>55.31 | 5.22<br>5.20 | 20.14<br>20.21 | 2200 | 1670 |
| **5e** | *o*-MeOC$_6$H$_4$ | H | 159-160 | 51 | $C_{17}H_{21}N_5O_3$ | 59.46<br>59.62 | 6.16<br>6.16 | 20.39<br>20.48 | 2210 | 1670 |
| **5g** | *o*-ClC$_6$H$_4$ | Me | oil | 48 | $C_{17}H_{20}ClN_5O_2$ | 56.43<br>56.39 | 5.57<br>5.51 | 19.36<br>19.42 | 2200 | 1670 |
| **5h** | Ph | Et | 116-118 | 49 | $C_{18}H_{23}N_5O_2$ | 63.32<br>63.41 | 6.79<br>6.77 | 20.51<br>20.75 | 2220 | 1685 |
| **5i** | Ph | *n*-Pr | 106-107 | 66 | $C_{19}H_{25}N_5O_2$ | 64.21<br>64.37 | 7.09<br>7.01 | 19.71<br>19.87 | 2220 | 1690 |

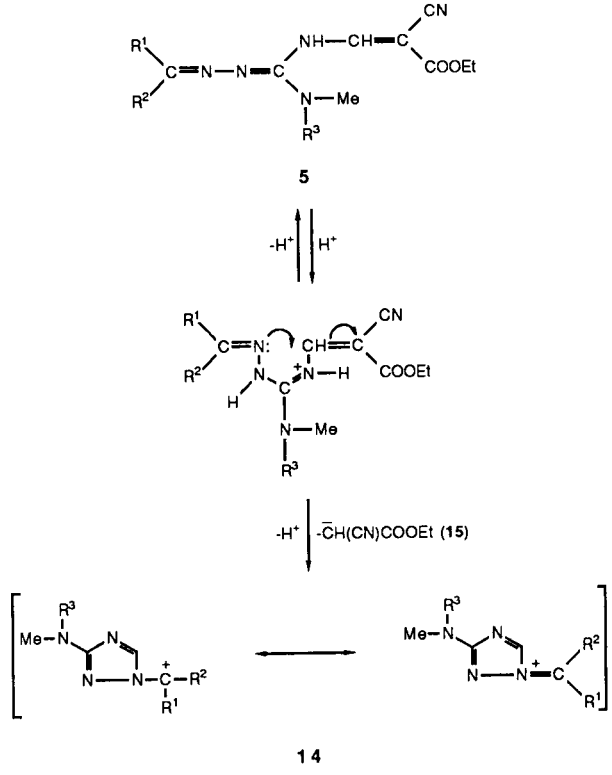
[a] In isolated pure product.

Scheme 3




by combination of a carbanion **15** and the carbonyl component of the corresponding **5** cleaved upon the ring-closure. Cleavage of the carbanion **15** is an essential step to the ring formation of triazole (Scheme 4) and this may be made possible by the stabilizing effect of the electron-withdrawing ethoxycarbonyl group. Because the two cyano groups on the ethylenic carbon of **4** should be insufficient to stabilize the negative charge on the carbanion which would otherwise be generated, the acidic cyclization of **4** can not produce any triazole derivative but the corresponding **11** or **12** depending upon the nature of $R^3$ (Scheme 2).

Scheme 4




When aromatic ketone diaminomethylenehydrazones **5f-5i** were subjected to the acidic cyclization under the same reaction conditions as in the aromatic aldehyde analogs **5c-5e**, neither a bis-azole **6** nor a diarylmethanol acetate **7** were obtained. Instead, *N*-Alkenyl-3-dimethylamino-1,2,4-triazole derivatives **9** was the only heterocyclic product in this case (Scheme 3). This shows that the alkyl group on the benzylidene carbon of **5** that would have appeared as a bridging carbon of **6** causes a marked steric hindrance and completely inhibits bis-azole formation. Thus a new route to the dimethylamino-1,2,4-triazol-1-ylalkenes of a gem-diaryl type was made available by the present reaction and these compounds could be prepared in moderate to good yield.

The idea of the intervention of the cation **14** in the formation of **6** and **7** from the cyanoacrylates **5c-5e** may also be applicable to the formation of *N*-alkenyltriazole **9** from **5f-5i**. Abstraction of an *alpha*-hydrogen from the iminium cations **14f-14i** should occur in preference to nucleophilic attack of the corresponding cyanoacrylate **5** or an acetate ion due to the presence of a bulky alkyl group ($R^2$) in place of a hydrogen atom.

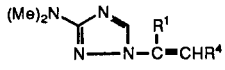
Table 2

*N*-Alkenyl-3-dimethylamino-1,2,4-triazoles **9**

| Compounds | $R^1$ | $R^4$ | Mp (°C) | Yield [a] (%) | Formula | Analysis % Calcd./Found C | H | N |
|---|---|---|---|---|---|---|---|---|
| **9a** | Ph | H | oil | 82 | $C_{12}H_{14}N_4 \cdot \frac{1}{2}H_2O$ | 64.56 | 6.76 | 25.09 |
| | | | | | | 64.60 | 6.35 | 25.27 |
| **9b** | Ph | Me | oil | 56 | $C_{13}H_{16}N_4$ | 68.39 | 7.06 | 24.54 |
| | | | | | | 68.78 | 7.00 | 24.23 |
| **9c** | Ph | Et | oil | 53 | $C_{14}H_{18}N_4$ | 69.39 | 7.49 | 23.12 |
| | | | | | | 69.01 | 7.32 | 23.49 |
| **9d** | *o*-$ClC_6H_4$ | H | 81-83 | 62 | $C_{12}H_{13}ClN_4$ | 57.95 | 5.27 | 22.53 |
| | | | | | | 58.04 | 5.22 | 22.80 |

[a] In isolated pure product.

Table 3



| Compounds | $R^1$ | $R^4$ | $^1$H NMR (J in Hz) (Deuteriochloroform, TMS) $NMe_2$ | $=CHR^4$ | $R^4$ | H-5 | $^{13}$C NMR ($^1J_{CH}$ in Hz) (Deuteriochloroform, TMS) $NMe_2$ | $=CHR^4$ | $=CAr$ | C-5 | C-3 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **9a** | Ph | H | 3.04 | 5.05 | 5.63 | 7.69 | 38.41 q (136) | 104.18 t (163) | 142.43 | 142.43 d (209) | 167.03 |
| **9b** | Ph | Me | 3.08 | 6.38 q (8) | 1.71 d (8) | 7.37 | 38.45 q (136) | 114.30 d (163) | 135.62 | 141.43 d (209) | 166.76 |
| **9c** | Ph | Et | 3.08 | 6.30 t (8) | 2.08 t (8) | 7.35 | 38.45 q (136) | 120.98 d (163) | 134.60 | 141.58 d (209) | 166.86 |
| **9d** | *o*-$ClC_6H_4$ | H | 3.05 | 4.88 | 5.91 | 7.35 | 38.36 q (136) | 104.19 t (163) | 141.67 | 141.67 d (209) | 166.62 |

The structures of the new heterocycles **6**, **7**, and **9** were determined by the appropriate spectral data and the elemental analyses.

The symmetrical structure of bis-azole **6** was supported by the $^{13}$C and $^1$H nmr spectra. The ring carbon signals (C-3) and C-5) from two 1,2,4-triazole rings appeared at $\delta$ 167 and $\delta$ 143, respectively, and each set of the signals from the respective carbon completely overlapped with each other. Therefore the bis-azoles **6c** and **6e** showed two resonances of the ring carbons arising from the two triazole rings with appropriate multiplicities. In the $^1$H nmr spectra of **6**, two dimethylamino groups on the triazole rings (four *N*-methyl groups) resonated in a single signal of twelve-proton intensities at $\delta$ 3.00. The ring protons (H-5) of **6c** and **6e** resonated at $\delta$ 7.85 and 7.71, respectively, and appeared as a sharp singlet of two-proton intensities. These observations should demonstrate the equivalency of the two triazole rings for each compound and thus their symmetric structure. In the mass spectra of **6**, predominant fragmentation occurred between the bridging carbon and the ring nitrogen *N*(1) and produced an abundant fragment ion ($M^+$ -111) as a base peak. All the spectroscopic behavior is well consistent with the proposed structure.

(3-Dimethylamino-1,2,4-triazol-1-yl) (phenyl or substituted-phenyl)methyl acetates **7d** and **7e** showed a strong carbonyl band at 1730 $cm^{-1}$ in the ir spectra. The proton on the diarylmethane carbon that well characterized the structure of the compound **7** resonated at $\delta$ 7.85 in the $^1$H nmr spectra. The $^{13}$C nmr spectra of **7d** showed the diarylmethane carbon resonance at $\delta$ 77.45 as a doublet ($^1J_{CH}$ 162 Hz). These spectroscopic observations as well as the other appropriate spectral data from the two aromatic rings gave confirmation of the structure of **7**. Further support for the structure of diarylmethyl acetate comes from hydrolytic examination of **7d**. The compound **7d** was susceptible to hydrolysis and gave the corresponding three products 3-dimethylamino-1*H*-1,2,4-triazole, an *o*-chlorobenzaldehyde, and acetic acid after brief exposure to 1% sodium hydroxide in ethanol at room temperature.

The direct support for the terminal methylene structure of *N*-alkenyltriazoles **9a** and **9d** was obtained from the $^{13}$C

nmr spectra of these compounds that exhibited a triplet in the ethylenic region (δ 104.2, $^1J_{CH}$ 163 Hz) (Table 3). Similarly, the methine carbon signal from the compounds **9b** and **9c** ($R^4$ = alkyl) appeared at δ 114-121 as a doublet ($^1J_{CH}$ 163 Hz). The compounds **9b** and **9c** probably have the *E* configuration in view of the chemical shift values (δ 6.30) of the ethylenic proton [3,4]. In the ir spectra of **9**, the stretching band of the ethylenic linkage appeared at near 1660-1640 $cm^{-1}$ in a carbon tetrachloride solution.

## EXPERIMENTAL

Melting points were determined in open capillary tubes and are uncorrected. The infrared spectra were obtained in potassium bromide pellets or in carbon tetrachloride solution with 0.2-mm KRS-5 cells on a Hitachi 260-30 spectrophotometer. The $^1H$ and $^{13}C$ nmr spectra were determined in deuteriochloroform solution on a JNM-FX90Q spectrometer operating at 89.55 and 22.50 MHz, respectively. The chemical shift values are reported in parts per million on the δ scale with tetramethylsilane as the internal reference. The mass spectra (75 eV) were recorded on a JEOL JMS D100 mass spectrometer. Microanalyses were performed with a Perkin-Elmer 240D elemental analyser at the Microanalytical Laboratory of Kitasato University. Preparative high-performance liquid chromatography (hplc) was carried out on a Kusano Kagaku KHLC-201 instrument with a 300 x 22 or a 300 x 15 mm glass column packed with silica gel.

The preparation of dicyanovinyl compounds **4a-c** and **4f** and cyanoacrylates **5c** and **5f** were described in references [1] and [2], respectively.

*N*(3)-[(2-Cyano-2-ethoxycarbonyl)vinyl]amino-*N*(4),*N*(4)-dimethylaminomethylenehydrazones **5d**, **5e**, and **5g-i**.

These compounds were prepared by the literature method [2] and are listed in Table 1.

2-*o*-Chlorobenzylideneamino-5-cyano-1,6-dihydro-6-imino-1-methyl-1*H*-pyrimidine (**12a**).

A solution of **4a** (0.29 g, 1 mmole) in acetic acid (1 ml) was heated at 80-85° for 5 minutes and then allowed to cool to room temperature. The separated crystals were collected on a filter and washed with acetonitrile, yield 0.10 g (34%). Recrystallization from acetonitrile gave the desired product as yellow needles, mp 232-233°; ir (potassium bromide): 3297, 3075 br (NH), 2213 (CN) $cm^{-1}$; $^1H$ nmr (DMSO-$d_6$, TMS): δ 3.45 (s, 3H, 1-$CH_3$), 7.43 and 8.25 (br s, each 1H, together NH), 7.44 (s, 4H, *o*-chlorophenyl), 8.05 (s, 1H, H-4), 8.59 (s, 1H, CH=N); ms: m/e 286 ($M^+$, 100%), 175 ($M^+$ -111, 75%).

*Anal.* Calcd. for $C_{13}H_{11}ClN_6$: C, 54.46; H, 3.87; N, 29.31. Found: C, 54.40; H, 3.79; N, 29.30.

2-(α-Methyl-*o*-chlorobenzylidene)hydrazino-5-cyano-1,6-dihydro-6-imino-1-methyl-1*H*-pyrimidine (**12b**).

Similar acidic cyclization of **4b** (0.10 g, 0.3 mmole) gave the corresponding **12b** (0.04 g, 40%) as yellow needles (from acetonitrile), mp 236-237°; ir (potassium bromide): 3302, 3129 br (NH), 2207 (CN) $cm^{-1}$; $^1H$ nmr (DMSO-$d_6$, TMS): δ 2.22 (s, 3H, α-$CH_3$), 3.43 (s, 3H, 1-$CH_3$), 7.40 (s, 4H, *o*-chlorophenyl), 7.33 and 8.18 (br s, each 1H, together NH), 7.91 (s, 1H, H-4); ms: m/e 300 ($M^+$, 77%), 265 ($M^+$ -35, 100%).

*Anal.* Calcd. for $C_{14}H_{13}ClN_6$: C, 55.91; H, 4.36; N, 27.94. Found: C, 55.87; H, 4.37; N, 27.90.

8-Cyano-5-dimethylamino-2,3-dihydro-2-phenyl[1,2,4]triazolo[1,5-*c*]pyrimidine (**11a**) and 8-Cyano-5-dimethylamino-2,3-dihydro-2-methyl-2-phenyl[1,2,4]triazolo[1,5-*c*]pyrimidine (**11b**).

A solution of **4c** or **4f** (1 mmole) in acetic acid (1 ml) was heated at 80-85° for 5 minutes and then allowed to cool to room temperature. The separated crystals were filtered off and washed with acetonitrile to give the corresponding triazolopyrimidines in 80-95% yield. The product from **4c** was consisted of **11a** and **13** in a molar proportion 2:1 and easily separated into the component by recrystallization from acetonitrile. These compounds are consistent with the compounds reported in the previous paper [1].

α,α-Bis(3-dimethylamino-1,2,4-triazol-1-yl)toluene (**6c**).

A solution of **5c** (0.31 g, 1 mmole) in acetic acid (2 ml) was heated at 80° for 5 minutes 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 pale yellow oil, after being dissolved in chloroform, was subjected to preparative hplc on silica gel, with the same solvent as eluent to give three fractions, I (0.04 g), II (0.08 g), and III (0.09 g) in the eluting order. Fractions I and II yielded ethyl α-cyanocinnamate (**8a**) and ethyl cyanoacetate, respectively. Fraction III gave spectroscopically pure **6c** (30%) as colorless prisms, mp 122-123°; ir (carbon tetrachloride): 1585 $cm^{-1}$ (vs); $^1H$ nmr (deuteriochloroform, TMS): δ 3.00 [s, 12H, $N(CH_3)_2$], 7.40 (s, 1H, PhC*H*), 7.42 (m, 5H, phenyl), 7.85 (s, 2H, H-5 of two triazoles); $^{13}C$ nmr (deuteriochloroform, TMS): δ 38.41 [q, $^1J_{CH}$ = 136.3 Hz, $N(CH_3)_2$], 73.45 (d, $^1J_{CH}$ = 145.1 Hz, Ph*C*H), 143.29 (d, $^1J_{CH}$ = 208.8 Hz, C-5 of two triazoles), 167.05 (s, C-3 of two triazoles); ms: m/e 312 ($M^+$, 28%), 201 ($M^+$ -111, 100%).

*Anal.* Calcd. for $C_{15}H_{20}N_8$: C, 57.67; H, 6.45; N, 35.88. Found: C, 57.41; H, 6.40; N, 35.64.

α,α-Bis(3-dimethylamino-1,2,4-triazol-1-yl)-*o*-methoxytoluene (**6e**).

This compound was similarly obtained as colorless needles (18%), mp 169-170° (from acetonitrile); ir (potassium bromide): 1570 $cm^{-1}$ (vs); $^1H$ nmr (deuteriochloroform, TMS): δ 3.00 [s, 12H, $N(CH_3)_2$], 3.80 (s, 3H, $OCH_3$), 7.25 (s, 1H, bridging CH), 7.71 (s, 2H, H-5 of two triazoles), 7.40 (m, 4H, aromatic); $^{13}C$ nmr (deuteriochloroform, TMS): δ 38.43 [q, $^1J_{CH}$ = 136.3 Hz, $N(CH_3)_2$], 55.63 (q, $^1J_{CH}$ = 144.5 Hz, $OCH_3$), 68.81 (d, $^1J_{CH}$ = 154.4 Hz, bridging carbon), 142.97 (d, $^1J_{CH}$ = 208.9 Hz, C-5 of two triazoles), 167.23 (s, C-3 of two triazoles); ms: m/e 342 ($M^+$, 4%), 231 ($M^+$ -111, 100%).

*Anal.* Calcd. for $C_{16}H_{22}N_8O$: C, 56.13; H, 6.48; N, 32.72. Found: C, 56.09; H, 6.42; N, 32.71.

A trace of *o*-methoxyphenyl(3-dimethylamino-1,2,4-triazol-1-yl)methyl acetate (**7e**) was separated from a fraction preceding to that of compound **6e** [5]. Ethyl α-cyano-*o*-methoxycinnamate (**8e**) was also obtained from the first fraction of preparative hplc for **6e** and identified spectroscopically [6].

*o*-Chlorophenyl(3-dimethylamino-1,2,4-triazol-1-yl)methyl Acetate (**7d**).

When **5d** was treated by the same procedure as described for the preparation of **6c**, the title compound **7d** was obtained as colorless needles (50%), mp 80-83° (from acetonitrile); ir (potassium bromide): 1730 (CO) $cm^{-1}$; $^1H$ nmr (deuteriochloroform, TMS): δ 2.16 (s, 3H, $CH_3CO$), 2.94 [s, 6H, $N(CH_3)_2$], 7.32 (m, 4H, aromatic), 7.83 (s, 1H, H-5), 7.85 (s, 1H, AcOC*H*); $^{13}C$ nmr (deuteriochloroform, TMS): δ 20.74 (q, $^1J_{CH}$ = 129.7 Hz, *C*$H_3$CO), 38.36 [q, $^1J_{CH}$ = 136.3 Hz, $N(CH_3)_2$], 77.45 (d, $^1J_{CH}$ = 161.6 Hz, AcO*C*H), 143.92 (d, $^1J_{CH}$ = 212.2 Hz, C-5), 167.25 (s, C-3); ms: m/e 294 ($M^+$, 27%), 112 ($M^+$ -182, 100%).

*Anal.* Calcd. for $C_{13}H_{15}ClN_4O_2$: C, 52.98; H, 5.13; N, 19.01. Found: C, 52.89; H, 5.04; N, 19.19.

A solution of **5f** (0.32 g, 1 mmole) in acetic acid (2 ml) was heated at 80° for 5 minutes and evaporated under reduced pressure. The residue was dissolved in chloroform, washed with 10% aqueous sodium carbonate solution and water, and then dried. After removal of the solvent, the residue was subjected to preparative hplc on silica gel with chloroform as eluent to give **9a** as colorless oil (0.16 g, 75%). Its spectral and analytical data were given in Tables 2 and 3.

According to the procedure described for the preparation of **9a**, triazolylalkenes **9b-9d** were prepared and listed in Tables 2 and 3.

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[5] Compound **7e** could only be deduced spectroscopically; $^1$H nmr (deuteriochloroform, TMS): $\delta$ 2.17 (s, 3H, $COCH_3$), 2.99 [s, 6H, $N(CH_3)_2$], 3.77 (s, 3H, $OCH_3$), 6.80-7.40 (m, 4H, aromatic), 7.77 (s, 1H, H-5 of triazole), and 7.85 (s, 1H, C*H*OAc); ir (carbon tetrachloride): 1730 (C=O) $cm^{-1}$.

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