0.048 mmol) was added and the reaction warmed to rt with continued stirring for 36 h. Water (2 mL) was added, and the aqueous layer was washed with CH_2Cl_2 (5 × 1 mL), then lyophilized to a yellow residue. The crude product was chromatographed (10:2:1 CH_3CN/H_2O/HOAc) to afford diene **3** (4.1 mg 80%) as an oil: R_f 0.48; $[\alpha]_D$ -194° (c = 0.18, H_2O); ^1H NMR (D_2O) 6.44 (br s, 1 H), 6.20 (dt, 1 H, J = 10.0, 2.0 Hz), 5.83 (dd, 1 H, J = 10.0, 2.7 Hz), 4.90-4.76 (m, 3 H), 4.59 (dt, 1 H, J = 11.4, 2.6 Hz), 3.43 (d, 3 H, J = 11.0 Hz); ^{13}C NMR (D_2O, acetone external standard) 173.1, 154.0 (d, J = 211.8 Hz), 133.8, 129.3, 128.4, 123.5, 96.8 (d, J = 22.2 Hz), 78.7 (d, J = 9.8 Hz), 69.4, 51.7 (d, J = 5.3 Hz); IR (KBr) 3400, 1425, 1240, 1085, 1050 cm^{-1}; FABMS m/z 297 (monosodium salt, M - 1, 5).

Deesterification of 24 to 25. A precooled solution of TMSBr (69 μL, 0.52 mmol) and pyridine (85 μL, 1.04 mmol) in CH_2Cl_2 (0.3 mL) was added to a stirred suspension of monomethyl phosphonate **24** (24.9 mg, 0.052 mmol) in CH_2Cl_2 (0.22 mL) at 5 °C under argon in a flame-dried flask. The mixture was stirred for 3 h, then poured into basic H_2O (5.0 mL, to pH 10 with NaOH). Solvents were removed in vacuo, and the aqueous residue was lyophilized. The resulting solid was triturated with anhydrous CH_3OH (4 × 1 mL), and the combined CH_3OH layers were evaporated then triturated again with absolute ethanol (4 × 1 mL). The insoluble portion from trituration was dissolved in H_2O and lyophilized to afford the desired phosphonate **25** as its sodium salt (pale yellow solid, 22.8 mg, 90%): R_f 0.45 (10:2:1, CH_3CN/H_2O/HOAc); $[\alpha]_D$ -7.7° (c = 1.14, H_2O); ^1H NMR (D_2O) 7.57-7.59 (m, 2 H), 7.23-7.29 (m, 3 H), 6.28 (br s, 1 H), 4.58 (d, 1 H, J = 33.3 Hz), 4.57 (br s, 1 H), 4.40 (d, 1 H, J = 29.7 Hz), 3.68 (dd, 1 H, J = 11.7, 7.8 Hz), 3.43 (dt, 1 H, J = 11.7, 5.8 Hz), 2.63 (dd, 1 H, J = 17.7, 5.8 Hz), 2.34 (ddm, 1 H, J = 17.7, 11.2 Hz); ^{13}C NMR (D_2O, acetone as external standard) 174.4, 162.8 (d, J = 141.7 Hz), 136.9, 135.6, 129.1, 128.7, 126.3, 91.8 (d, J = 20.5 Hz), 78.0 (d, J = 5.5 Hz), 72.2, 42.5; IR (KBr) 3400, 1585, 1400, 1340, 1225, 1100, 990 cm^{-1}; FABMS m/z 441 (M - 1, 100).

Synthesis of Phosphonochorismate 4. A solution of 30% H_2O_2 (5.5 μL, 0.047 mmol) was added to triacid **25** (20 mg, 0.043 mmol) in anhydrous CH_3OH (0.4 mL) at 5 °C under argon. The mixture was stirred for 1 h, then 3,5-dimethoxyaniline (20 mg, 0.129 mmol) was added; the reaction mixture warmed to rt and stirred an additional 36 h. Water (1 mL) was added; the aqueous layer was washed with CH_2Cl_2 (5 × 2 mL) then lyophilized. The residue was chromatographed (10:2:1 CH_3CN/H_2O/HOAc) to afford **4** as a pale yellow solid (mono-Na salt, 9.2 mg, 75%); R_f 0.26 (10:2:1 CH_3CN/H_2O/HOAc), $[\alpha]_D$ -147° (c = 0.34, H_2O); ^1H NMR (D_2O) 6.81 (br s, 1 H), 6.24 (br d, 1 H, J = 10.1 Hz), 5.91 (dd, 1 H, J = 10.0, 2.6 Hz), 4.94 (br d, 1 H, J = 11.6 Hz), 4.88 (dd, 1 H, J = 12.2, 3.2 Hz), 4.70 (dm, 1 H, J, = 11.6 Hz), 4.60 (dd, 1 H, J = 31.3, 3.2 Hz); ^{13}C NMR (D_2O, acetone as external standard) 179.1, 163.1 (d, J = 209.8 Hz), 139.6, 135.6, 135.2, 129.6, 100.3 (d, J = 21.7 Hz), 84.9 (d, J = 9.5 Hz), 75.9; IR (KBr) 3400, 1420, 1085, 980 cm^{-1}; FABMS m/z 265 (monosodium salt, M - 18, 15).

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Supplementary Material Available: NMR spectra (^1H and/or ^{13}C) for compounds **11**, **12**, **14-20**, **21-25**, **3**, and **4** (16 pages). Ordering information is given on any current masthead page.

The Reaction of Benzoyl-Substituted Heterocyclic Ketene Aminals with Aryl Azides

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The reaction between heterocyclic ketene aminals, 2-(benzoylmethylene)imidazolidines **3**, -hexahydropyrimidines **4**, and phenyl azides **5** was investigated. Both the reaction rate and products were strongly dependent on the substituents on **3** or **4** and **5**. The reaction rate decreased with the decrease of the electron-withdrawing ability of the Y on the aryl azide **5** with the order NO_2 > Cl > H > CH_3O, as well as with the decrease of the electron-donating ability of the X on the **3** or **4** following the order CH_3O > CH_3 > H > Cl. Substituents X and Y affected the course of the reaction. Thus, **3** or **4** reacted with *p*-nitrophenyl azide **5a** to give exclusively highly substituted 1,2,3-triazole derivatives **6aa-da** and **7aa-da**. The reaction between **3** or **4** and other aryl azides **5b-d** afforded respectively fused triazoles **8a-d** or **9a-d** (6-31%) in addition to triazoles **6ab-bd** or **7ab-bd** (8-76%). It is concluded that **3** and **4** behave mostly as nucleophiles rather than 1,3-dipolarophiles in reaction with aryl azides **5**. Only in the case of unfavorable electronic factors may **3** and **4** act as 1,3-dipolarophiles toward **5**.

Introduction

Since the reports by Stork et al.,[1] a great development of enamine chemistry in many aspects has been achieved. As important intermediates, enamines have shown their potential in synthetic organic chemistry.[2] Heterocyclic ketene aminals or cyclic 1,1-enediamines belong to the family of enamines. Although earlier reports of such compounds may date back to 1950s,[3] there are only a few research results on them in the literature, especially compared with many papers concerned with enamines. Much attention has been given to them from the 1970s when Shell Oil Company patented a series of cyclic enediamines with nitro groups possessing biological activities that could be used as herbicides and pesticides.[4]

The general structure of cyclic 1,1-enediamines can be described by Figure 1. Due to the effects of the conjugation of the two strongly electron donating amino groups

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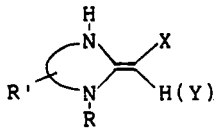
0022-3263/92/1957-0184$03.00/0



X, Y = electron-withdrawing group, such as NO_2, CO_2R'', COR'', CN, etc.

Figure 1. The structure of cyclic 1,1-enediamines.

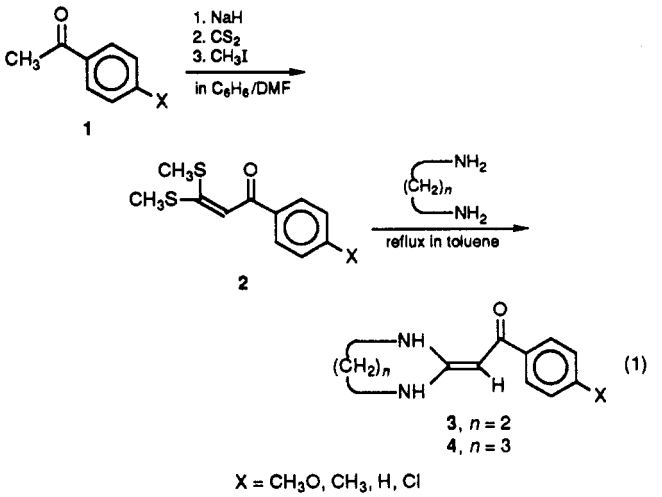
and electron-withdrawing group(s), the double bond is highly polarized. X-ray structure analyses of some compounds have shown that the length of the double bond is about 1.380–1.423 Å,[5] longer than that of normal olefins. Its β-carbon possesses much higher electron density. Its chemical shift is shifted upfield to the range of 50–90 ppm, some even to 30 ppm.[6] Thus, the nucleophilicity of the β-carbon is stronger than that of the nitrogen (NH), and usualy it attacks the electropositive point when treated with electrophiles.[7] In addition, the second amino group in the structure can also participate in the reaction. Therefore cyclic 1,1-enediamines may be used as bis-nucleophiles, and more attention has been given to their nucleophilic substitutions and additions with electron-deficient reagents, and a wide variety of fused heterocyclic compounds have been obtained through a sequence of these and cyclocondensation reaction.[8]

As we know, 1,3-dipolar cycloaddition is a powerful tool in heterocycle synthesis. Enamines as electron-rich olefins reacted easily with many 1,3-dipolar reagents, and some reaction mechanisms have been thoroughly studied.[9] However, to our knowledge, the reactions between 1,1-enediamines and 1,3-dipolar reagents have been reported only in a few cases.[10-13]

In our previous reports we investigated the synthesis, the tautomerism, and some reactions of a series of cyclic 1,1-enediamines.[14] To continue our studies, we intended to explore the possibility of the 1,3-dipolar reaction and the α-carbon's reaction of cyclic 1,1-enediamines and to extend the applications of them in the synthesis. Here we report the results of the reaction between the aroyl-substituted heterocyclic ketene aminals and aryl azides.

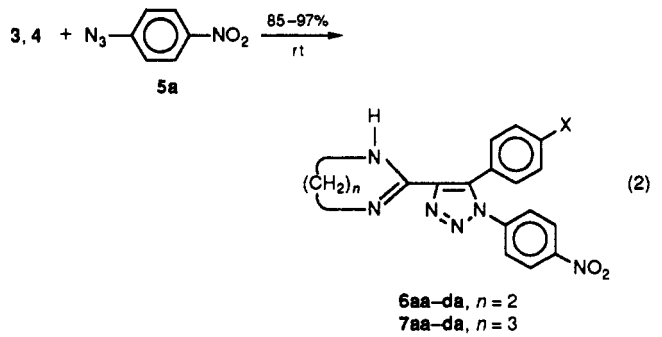
Results and Discussion

The cyclic 1,1-enediamines we chose were 2-[(*p*-substituted-benzoyl)methylene]imidazolidines **3** and 2-[(*p*-substituted-benzoyl)methylene]hexahydropyrimidines **4**. They were synthesized from the cyclocondensation of ethylenediamine or 1,3-diaminopropane and α-oxo ketene dithioacetals **2**[14] (eq 1).



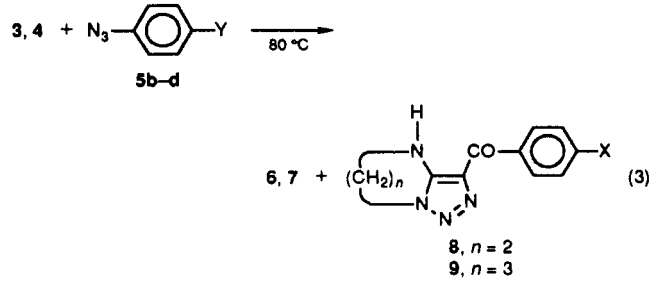
(1)

The reaction between **3** or **4** and *p*-nitrophenyl azide (**5a**) took place easily. The mixture of reactants in 1,4-dioxane give exclusively 1-(*p*-nitrophenyl)-4-(2-imidazolinyl)-5-aryl-1,2,3-triazoles **6aa–da** or 1-(*p*-nitrophenyl)-4-(2-tetrahydropyrimidinyl)-5-aryl-1,2,3-triazoles **7aa–da** in excellent yields, respectively (eq 2). When phenyl azide



(2)

5c and other substituted phenyl azides **5b,d** were used, the reaction proceeded much more slowly. In addition to the corresponding triazoles **6** or **7**, we also isolated 3-aroyl-5,6-dihydro-4*H*-imidazo[1,2-*c*][1,2,3]triazoles **8a–d** or 3-aroyl-4,5,6,7-tetrahydrotriazolo[1,5-*a*]pyrimidines **9a,d**, respectively (eq 3). The reaction conditions and yields are listed Table I.



(3)

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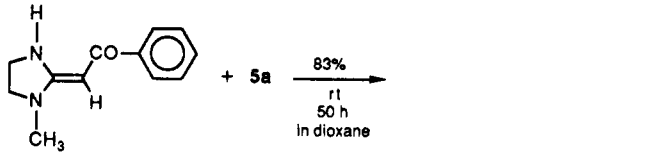
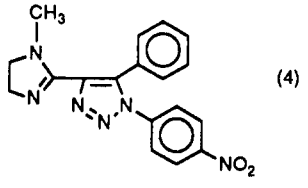
Table I. Reaction Conditions and Product Yield

X	Y	n	molar ratio (3 or 4:5)	time (h)	temp (°C)	yield of 6 or 7 (%)	yield of 8 or 9 (%)
CH_3O	NO_2	2	1:1	50	rt	**6aa**, 90	
CH_3	NO_2	2	1:1	50	rt	**6ba**, 85	
H	NO_2	2	1:1	50	rt	**6ca**, 89	
Cl	NO_2	2	1:1	50	rt	**6da**, 87	
CH_3O	Cl	2	1:1	31	80	**6ab**, 61	**8a**, 21
CH_3	Cl	2	1:1	31	80	**6bb**, 59	**8b**, 14
H	Cl	2	1:1	24	80	**6cb**, 49	**8c**, 13
Cl	Cl	2	1:1	72	80	**6db**, 48	**8d**, 6
CH_3O	H	2	1:1.1	24	80	**6ac**, 54	**8a**, 16
CH_3	H	2	1:1.1	24	80	**6bc**, 42	**8b**, 14
H	H	2	1:1.1	40	80	**6cc**, 39	**8c**, 13
Cl	H	2	1:1.1	48	80	**6dc**, 31	**8d**, 8
CH_3O	CH_3O	2	1:1.1	60	80	**6ad**, 18	**8a**, 23
CH_3	CH_3O	2	1:1.1	48	80	**6bd**, 14	**8b**, 21
H	CH_3O	2	1:1.1	60	80	**6cd**, 13	**8c**, 18
Cl	CH_3O	2	1:1.1	5 days	80	**6dd**, 8	**8d**, 10
CH_3O	NO_2	3	1:1	50	rt	**7aa**, 97	
CH_3	NO_2	3	1:1	50	rt	**7ba**, 91	
H	NO_2	3	1:1	50	rt	**7ca**, 97	
Cl	NO_2	3	1:1	50	rt	**7da**, 94	
CH_3O	Cl	3	1:1	6	80	**7ab**, 76	**9a**, 16
CH_3	Cl	3	1:1	6	80	**7bb**, 74	**9b**, 8
H	Cl	3	1:1	6	80	**7cb**, 73	**9c**, 7
Cl	Cl	3	1:1	7	80	**7db**, 73	**9d**, 6
CH_3O	H	3	1:1.1	5	80	**7ac**, 70	**9a**, 14
CH_3	H	3	1:1.1	5	80	**7bc**, 68	**9b**, 12
H	H	3	1:1.1	8	80	**7cc**, 61	**9c**, 11
Cl	H	3	1:1.1	10	80	**7dc**, 66	**9d**, 8
CH_3O	CH_3O	3	1:1.1	8	80	**7ad**, 45	**9a**, 31
CH_3	CH_3O	3	1:1.1	12	80	**7bd**, 30	**9b**, 23
H	CH_3O	3	1:1.1	12	80	**7cd**, 31	**9c**, 21
Cl	CH_3O	3	1:1.1	19	80	**7dd**, 35	**9d**, 15

1-Methyl-2-(benzoylmethylene)imidazolidine (**10**) also reacted facilely with **5a** at room temperature to afford 1-(*p*-nitrophenyl)-4-(1-methyl-2-imidazolinyl)-5-phenyl-1,2,3-triazole (**11**) in good yield (eq 4).



10



(4)

11

The constitution of triazoles **6** and **7** corresponded to an addition reaction between **3** or **4** and **5** in 1:1 molar ratio accompanied by the loss of 1 mol of water. From these results the structure of product may be **6** and **7** or their isomers, 1,4-diaryl-5-(2-imidazolinyl)-, or -5-(2-tetrahydropyrimidinyl)triazoles **12**, and fused heterocycles, triazolo[5,4-*e*][1,4]diazepines or triazolo[5,4-*b*][1,5]diazocines, **13** or **14**, which could result from 1,3-dipolar cycloaddition, cleavage of heterocyclic ring, and cyclocondensation reaction sequence. In the ^1H NMR spectra of the products, except for aromatic proton signals and deuterium exchangeable proton signals (NH), only a singlet at 3.43–3.57 ppm was detected for products **6**, even when using a 400-MHz instrument. For the products **7** a triplet signal at 3.20–3.25 ppm corresponding to 4 protons and quintet signal at 1.62–1.66 ppm corresponding to 2 protons were observed. These indicate that an 2-imidazolinyl or a 2-tetrahydropyrimidinyl moiety exist in the structures of **6** or **7**, respectively. Therefore the possibility of structure **13** or **14** was excluded. However it is difficult to distinguish the structure **6** or **7** from **12** by the spectral data. The structure of products **6** or **7** was established unambiguously as triazoles by X-ray structure analysis of 1-(*p*-nitrophenyl)-4-(2-imidazolinyl)-5-(*p*-chlorophenyl)-1,2,3-triazole, **6da**.[15] The IR and UV spectral data of the products are also completely consistent with the structures **6** or **7**.

The constitution of **8** or **9**, confirmed by microanalytical data and mass spectra, shows that an addition reaction in a 1:1 molar ratio of **3** or **4** and **5b–d** had taken place accompanied with the loss of 1 mol of Y-substituted anilines. Therefore the constitution of **8** or **9** is only varied with **3** or **4** with different substituents X, but unchanged with different substituted aryl azides **5b–d**. The other spectroscopic data of the products are also consistent with the structures **8** or **9**. The spectroscopic data of **8** and **9** shows that the bathochromic shift of the carbonyl absorption (1615–1633 cm^{-1}) in IR spectra and the upshield shift of the carbonyl carbon (181.5–184.9 ppm) in the ^{13}C NMR spectra are due to both the conjugation of the carbonyl group with the double bond and two nitrogen atoms and the intramolecular hydrogen bond formation as well. The intramolecular hydrogen bond formation is further confirmed by the downshield shift of nitrogen proton in the ^1H NMR spectra (6.65–7.57 ppm).

From the results (Table I) we know that the reaction between **3** or **4** and **5** was strongly depended upon the substituents X, Y both on the enediamines and azides, especially Y on the azides. First, the reaction rate decreased with the decrease of the electron-attracting ability of the Y, following the order $NO_2 > Cl > H > CH_3O$. Secondly, the electron-donating effect of X on the aroyl group was favorable to the reaction with the order CH_3O

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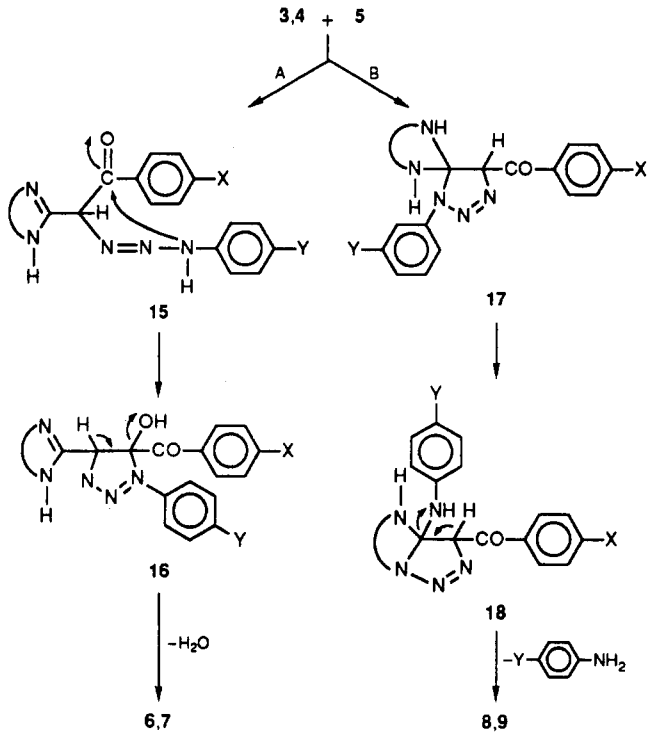
Scheme I



> CH_3 > H > Cl. In addition, and most importantly, the substituents Y affected the fashion of formation of products, i.e. the course of the reaction. The ratio of triazole to fused heterocycle 6/8 or 7/9 increased with the increase of the electron-withdrawing ability of Y. This trend went to the extreme with the case of *p*-nitrophenyl azide **5a** in which the reaction afforded the exclusive triazole products **6** or **7**. Finally, the nature of substituents X also played a role in determining the reaction pattern but to a lower degree.

According to the facts observed above, we suggest the reaction mechanisms depicted in Scheme I. There would be two competitive reaction pathways coexisting in the reaction. In route A, cyclic 1,1-enediamines **3** or **4** act as nucleophiles to react with the azide **5**. From the X-ray structural data of the products, this reaction was regiospecific, the β-carbon of **3** or **4** only attacked the terminal nitrogen atom of the azide to form the intermediate **15**. Through the cyclocondensation and aromatizing elimination sequence the triazoles **6** or **7** were formed. In route B, **3** or **4** reacted with **5** as 1,3-dipolarophiles. 1,3-Dipolar cycloaddition took place at first to form the intermediate **17**, the fused heterocycles **8** or **9** were obtained through the Dimroth rearrangement and deamination. The latter mechanism has been reported for the reaction of nitro-substituted heterocyclic ketene aminals with *p*-chlorobenzenesulfonyl azide.[13]

The results listed in Table I are best explained by the mechanisms proposed above. With the increase of the electron-donating ability of substituents X and the electron-withdrawing ability of substituents Y, the reaction rate increased due to the increased nucleophilicity of enediamines **3** and **4** and increased electrophilicity of azides **5**. The total yields of **6** and **8** or **7** and **9** increased correspondingly. For the same reason, the ratio of **6** to **8** and **7** to **9** increased, with the extreme example of **3** or **4** reacting with the good electrophile **5a** to yield only products **6aa–da** or **7aa–da**. Therefore we conclude that the reaction rate in route A was faster than that of route B. The slower reaction by route B may take place only in the case of unfavorable electronic factors to give **8** or **9** in low yields. The reason for cyclic 1,1-enediamines not behaving like 1,3-dipolarophiles can be rationalized as a leveling effect[16] arising from the amino and benzoyl groups in the molecule. Based on the frontier electron theory of Fukui, MO perturbation treatment of the reaction between phenyl azide and olefins shows that attaching of either an electron-releasing or an electron-withdrawing group to the olefin accelerates 1,3-dipolar addition but decreased the reactivity when both kinds of substituents were incorporated in one molecule. The influence of the amino groups in **3** or **4** may be compensated by that of aroyl group, meaning that the effects of the amino groups were at least partially cancelled by the electron-accepting aroyl group. In addition, ambident conjugation system in **3** or **4** may weaken the double-bond character.

Conclusion

In conclusion, heterocyclic ketene aminals, or cyclic 1,1-enediamines **3** or **4**, are better nucleophiles rather than 1,3-dipolarophiles toward aryl azides **5**. By the reaction of benzoyl-substituted heterocyclic ketene aminals with aryl azides, we provide a facile approach to synthesize 1,5-diaryl-4-(2-imidazolinyl)- or -4-(2-tetrahydropyrimidinyl)-1,2,3-triazoles, **6** or **7**.

Experimental Section

Melting points are not corrected. ^1H NMR spectra were determined with Varian EM-360L, JEOL FX-100, and Varian 400 spectrometers. ^{13}C NMR spectra were determined with a JEOL FX-100 spectrometer. IR spectra were recorded with a Perkin-Elmer 782 spectrometer. UV spectra were recorded with a Hitachi 340 spectrometer. Mass spectra were determined with a AEI MS-50 spectrometer. Elemental analyses were done by the Analytical Laboratory of the Institute.

General Procedure for 1-(*p*-Nitrophenyl)-5-(*p*-substituted-phenyl)-4-(2-imidazolinyl)-1,2,3-triazoles (6aa–da) and 1-(*p*-Nitrophenyl)-5-(*p*-substituted-phenyl)-4-(2-tetrahydropyrimidinyl)-1,2,3-triazoles (7aa–da). A mixture of cyclic 1,1-enediamines **3a–d** or **4a–d** (1.25 mmol) and *p*-nitrophenyl azide **5a** (1.25 mmol, 205 mg) in dried 1,4-dioxane (10 mL) was stirred at ambient temperature for 50 h. After removal of solvent the residue was recrystallized from ethyl acetate in yields of 85–97%.

1-(*p*-Nitrophenyl)-4-(2-imidazolinyl)-5-(*p*-methoxyphenyl)-1,2,3-triazole (6aa). The product (90%) formed pale yellow crystals, mp 181.5–182 °C: IR (KBr) 3312 (NH), 1520, 1340 cm^{-1} (NO_2); UV (EtOH) λ_{max} (lg ϵ) 218 (4.34), 258 nm (4.37); ^1H NMR (DMSO-d_6) δ 3.15 (s, 1, NH), 3.50 (s, 4, CH_2CH_2), 3.73 (s, 3, OCH_3), 8.26 (d, 2, J = 9.0 Hz), 7.29 (d, 2, J = 9.0 Hz), 7.58 (d, 2, J = 9.0 Hz), 8.26 (d, 2, J = 9.0 Hz); MS (EI, direct probe) m/z (rel intensity, ion) 364 (25, M^+), 363 (100, $M^+ - 1$), 335 (26, $M^+ - 1 - N_2$), 289 (30). Anal. Calcd for $C_{18}H_{16}N_6O_3$: C, 59.33; H, 4.43; N, 23.07. Found: C, 59.38; H, 4.40; N, 23.07.

1-(*p*-Nitrophenyl)-4-(2-imidazolinyl)-5-(*p*-methylphenyl)-1,2,3-triazole (6ba). The product (85%) formed pale yellow crystals, mp 191.5–192.5 °C: IR (KBr) 3330 (NH), 1525, 1347 cm^{-1} (NO_2); UV (EtOH) λ_{max} (lg ϵ) 217 (4.33), 249 nm (4.27); ^1H NMR (DMSO-d_6) δ 2.30 (s, 3, CH_3), 3.20 (s, 1, NH), 3.48 (s, 4, CH_2CH_2), 7.17 (s, 4), 7.54 (d, 2, J = 9.0), 8.21 (d, 2, J = 9.0); MS 348 (30, M^+), 347 (100, $M^+ - 1$), 319 (24, $M^+ - 1 - N_2$), 273 (43). Anal. Calcd for $C_{18}H_{16}N_6O_2$: C, 62.06; H, 4.63; N, 24.13. Found: C, 62.15; H, 4.62; N, 24.04.

1-(*p*-Nitrophenyl)-4-(2-imidazolinyl)-5-phenyl-1,2,3-triazole (6ca). The product (89%) formed pale yellow crystals, mp 227.5–228 °C: IR (KBr) 3320 (NH), 1525, 1350 cm^{-1} (NO_2); UV (EtOH) λ_{max} (lg ϵ) 223 (4.19), 264 nm (4.21); ^1H NMR (DMSO-d_6) δ 3.22 (s, 1, NH), 3.48 (s, 4, CH_2CH_2), 7.29 (s, 5), 7.52 (d, 2, J = 9.0), 8.19 (d, 2, J = 9.0); MS 334 (100, M^+), 305 (29, $M^+ - 1 - N_2$),

(16) Sustmann, R. *Pure Appl. Chem.* **1974**, *40*, 569 and references therein.

259 (44). Anal. Calcd for $C_{17}H_{14}N_6O_2$: C, 61.07; H, 4.22; N, 25.14. Found: C, 60.78; H, 4.22; N, 25.17.

1-(*p*-Nitrophenyl)-4-(2-imidazolinyl)-5-(*p*-chlorophenyl)-1,2,3-triazole (6da). The product (87%) formed yellow crystals, mp 215.5–216 °C: IR (KBr) 3325 (NH), 1515, 1340 cm^{-1} (NO_2); UV (EtOH) λ_{max} (lg ϵ) 220 (4.29), 248 nm (4.30); ^1H NMR (DMSO-d_6) δ 3.17 (s, 1, NH), 3.50 (s, 4, CH_2CH_2), 7.34 (s, 4), 7.57 (d, 2, J = 9.0), 8.22 (d, 2, J = 9.0); MS 368 (30, M^+), 367 (100, $M^+ - 1$), 339 (29, $M^+ - 1 - N_2$), 293 (30). Anal. Calcd for $C_{17}H_{13}ClN_6O_2$: C, 55.36; H, 3.55; N, 22.79. Found: C, 55.46; H, 3.62; N, 22.78.

1-(*p*-Nitrophenyl)-4-(2-tetrahydropyrimidinyl)-5-(*p*-methoxyphenyl)-1,2,3-triazole (7aa). The product (87%) formed pale yellow crystals, mp 180.5–181 °C: IR (KBr) 3380 (NH), 1524, 1344 cm^{-1} (NO_2); UV (EtOH) λ_{max} (lg ϵ) 260 (4.20), 276 nm (sh); ^1H NMR (DMSO-d_6) δ 1.65 (quin, 2), 3.24 (t, 4), 3.71 (s, 3, OCH_3), 6.90 (s, 1, NH), 6.82 (d, 2, J = 9.0), 7.23 (d, 2, J = 9.0), 7.54 (d, 2, J = 9.0), 8.24 (d, 2, J = 9.0); MS 378 (100, M^+), 350 (100, $M^+ - N_2$). Anal. Calcd for $C_{19}H_{18}N_6O_3$: C, 60.31; H, 4.79; N, 22.21. Found: C, 60.12; H, 4.91; N, 22.05.

1-(*p*-Nitrophenyl)-4-(2-tetrahydropyrimidinyl)-5-(*p*-methylphenyl)-1,2,3-triazole (7ba). The product (91%) was pale yellow crystals, mp 193–194 °C: IR (KBr) 3370 (NH), 1520, 1339 cm^{-1} (NO_2); UV (EtOH) λ_{max} (lg ϵ) 240 (4.20), 264 nm (sh); ^1H NMR (DMSO-d_6) δ 1.65 (quin, 2), 3.24 (t, 4), 2.28 (s, 3, CH_3), 6.97 (s, 1, NH), 7.11 (s, 4), 7.54 (d, 2, J = 9.0), 8.19 (d, 2, J = 9.0); MS 362 (33, M^+), 361 (100, $M^+ - 1$), 334 (25, $M^+ - N_2$), 333 (64, $M^+ - 1 - N_2$). Anal. Calcd for $C_{19}H_{18}N_6O_2$: C, 62.97; H, 5.01; N, 23.19. Found: C, 63.00; H, 5.18; N, 23.29.

1-(*p*-Nitrophenyl)-4-(2-tetrahydropyrimidinyl)-5-phenyl-1,2,3-triazole (7ca). The product (97%) formed pale yellow crystals, mp 151–152 °C: IR (KBr) 3385 (NH), 1522, 1345 cm^{-1} (NO_2); UV (EtOH) λ_{max} (lg ϵ) 232 (4.15), 267 nm (4.14); ^1H NMR (DMSO-d_6) δ 1.66 (quin, 2), 3.20 (t, 4), 6.97 (s, 1, NH), 7.21 (s, 5), 7.43 (d, 2, J = 9.0), 8.14 (d, 2, J = 9.0); MS 348 (20, M^+), 347 (100, $M^+ - 1$), 320 (13, $M^+ - N_2$), 319 (21, $M^+ - 1 - N_2$). Anal. Calcd for $C_{18}H_{16}N_6O_2$: C, 62.06; H, 4.63; N, 24.13. Found: C, 61.62; H, 4.51; N, 23.74.

1-(*p*-Nitrophenyl)-4-(2-tetrahydropyrimidinyl)-5-(*p*-chlorophenyl)-1,2,3-triazole (7da). The product (94%) formed yellow crystals, mp 191–192 °C: IR (KBr) 3400 (NH), 1519, 1345 cm^{-1} (NO_2); UV (EtOH) λ_{max} (lg ϵ) 244 (4.21), 262 nm (sh); ^1H NMR (DMSO-d_6) δ 1.63 (quin, 2), 3.22 (t, 4), 6.83 (s, 1, NH), 7.23 (s, 4), 7.45 (d, 2, J = 9.0), 8.14 (d, 2, J = 9.0); MS 382 (45, M^+), 354 (37, $M^+ - N_2$). Anal. Calcd for $C_{18}H_{15}ClN_6O_2$: C, 56.47; H, 3.95; N, 21.96. Found: C, 56.04; H, 4.28; N, 21.97.

General Procedure for 1,5-Diaryl-4-(2-imidazolinyl)-1,2,3-triazoles (6ab–dd) or 1,5-Diaryl-4-(2-tetrahydropyrimidinyl)-1,2,3-triazoles (7ab–dd) and Fused Heterocycles 8a–d or 9a–d. A mixture of **3** or **4** (1.25 mmol) and *p*-chlorophenyl azide **5b** (1.25 mmol), or excess amount of phenyl azide **5c**, *p*-methoxyphenyl azide **5d** (1.375 mmol) (see Table I), was held at 80 °C with stirring for a period of time (see Table I). When the starting material had vanished (monitored by TLC) the reaction was terminated. After removal of the solvent, the residue was chromatographed on an activated basic aluminum oxide column and eluted with petroleum ether (30–60 °C) containing a gradually increasing amount of ethyl acetate to pure ethyl acetate at the end. **6ab–dd** or **7ab–dd** and **8a–d** or **9a–d** were thus separated and recrystallized from ethyl acetate and petroleum ether (30–60 °C)–ethyl acetate, respectively.

1-(*p*-Chlorophenyl)-4-(2-imidazolinyl)-5-(*p*-methoxyphenyl)-1,2,3-triazole (6ab) and 3-(*p*-Methoxyphenyl)-5,6-dihydro-4*H*-imidazo[1,2-*c*][1,2,3]triazole (8a). 6ab was obtained (61%) as white crystals, mp 192.5–194 °C: IR (KBr) 3330 cm^{-1} (NH); UV (EtOH) λ_{max} (lg ϵ) 228 (4.38), 246 nm (sh); ^1H NMR (DMSO-d_6) δ 3.24 (s, 1, NH), 3.43 (s, 4, CH_2CH_2), 3.66 (s, 3, OCH_3), 6.73 (d, 2, J = 9.0), 7.15 (d, 2, J = 9.0), 7.19 (d, 2, J = 9.0), 7.36 (d, 2, J = 9.0); MS 355 (40), 354 (35), 353 (100, M^+), 324 (50, $M - 1 - N_2$). Anal. Calcd for $C_{18}H_{16}ClN_5O$: C, 61.10; H, 4.56; N, 19.80. Found: C, 61.03; H, 4.58; N, 19.90. **8a** was obtained (21%) as a white solid, mp 215–216 °C: IR (KBr) 3310 (NH), 1615 cm^{-1} (C=O); UV (EtOH) λ_{max} (lg ϵ) 220 (4.38), 286 (sh), 311 nm (4.34); ^1H NMR (DMSO-d_6) δ 3.83 (s, 3, OCH_3), 4.25, 4.44 (A_2B_2, 2 H each, J = 7.0 Hz), 7.06 (d, 2, J = 9.0 Hz), 7.31 (s, 1, NH), 8.39 (d, 2, J = 9.0 Hz); ^{13}C NMR (DMSO-d_6) δ 44.8 ($HNCH_2$), 53.1 (NCH_2), 56.0 (OCH_3), 126.2 (C=*C*CO), 114.0, 130.2, 132.4, 163.2 (carbon of phenyl ring), 155.9 (*C*=CCO), 182.3 (C=O); MS 244 (39, M^+), 215 (100, $M^+ - 1 - N_2$), 190 (25). Anal. Calcd for $C_{12}H_{12}N_4O_2$: C, 59.01; H, 4.95; N, 22.94. Found: C, 59.02; H, 4.94; N, 22.97.

1-(*p*-Chlorophenyl)-4-(2-imidazolinyl)-5-(*p*-methylphenyl)-1,2,3-triazole (6bb) and 3-(*p*-Methylbenzoyl)-5,6-dihydro-4*H*-imidazo[1,2-*c*][1,2,3]triazole (8b). 6bb was obtained (59%) as white crystals, mp 198–199 °C: IR (KBr) 3320 cm^{-1}; UV (EtOH) λ_{max} (lg ϵ) 226 (4.38), 246 nm (sh); ^1H NMR (DMSO-d_6) δ 2.27 (s, 3, CH_3), 3.21 (s, 1, NH), 3.46 (s, 4, CH_2CH_2), 7.15 (s, 4), 7.26 (d, 2, J = 9.0), 7.43 (d, 2, J = 9.0); MS 337 (26, M^+), 336 (100, $M^+ - 1$), 308 (52, $M^+ - 1 - N_2$). Anal. Calcd for $C_{18}H_{16}ClN_5$: C, 64.00; H, 4.77; N, 20.73. Found: C, 64.27; H, 4.76; N, 20.60. **8b** was obtained (14%) as a white solid, mp 229–231 °C: IR (KBr) 3318 (NH), 1622 cm^{-1} (C=O); UV (EtOH) λ_{max} (lg ϵ) 215 (4.27), 258 (4.12), 308 nm (4.08); ^1H NMR (DMSO-d_6) δ 2.38 (s, 3, CH_3), 4.25, 4.44 (A_2B_2, 2 H each, CH_2CH_2, J = 7.0 Hz), 7.32 (d, 2, J = 9.0), 7.36 (s, 1, NH), 8.25 (d, 2, J = 9.0); ^{13}C NMR (DMSO-d_6) δ 21.1 (CH_3), 44.2 ($HNCH_2$), 52.5 (NCH_2), 125.5 (C=*C*CO), 128.8, 129.7, 134.3, 142.5 (carbon of phenyl ring), 155.3 (*C*=CCO), 182.7 (C=O); MS 228 (71, M^+), 200 (100, $M^+ - N_2$), 170 (50). Anal. Calcd for $C_{12}H_{12}N_4O$: C, 63.14; H, 5.30; N, 24.55. Found: C, 63.14; H, 5.30; N, 24.56.

1-(*p*-Chlorophenyl)-4-(2-imidazolinyl)-5-phenyl-1,2,3-triazole (6cb) and 3-Benzoyl-5,6-dihydro-4*H*-imidazo[1,2-*c*][1,2,3]triazole (8c). 6cb was obtained (49%) as white crystals, mp 221–221.5 °C: IR (KBr) 3368 cm^{-1} (NH); UV (EtOH) λ_{max} (lg ϵ) 222 (4.34), 242 nm (sh); ^1H NMR (DMSO-d_6) δ 3.22 (s, 1, NH), 3.48 (s, 4, CH_2CH_2), 7.28 (s, 5), 7.30 (d, 2, J = 9.0), 7.43 (d, 2, J = 9.0); MS 323 (25, M^+), 322 (100, $M^+ - 1$), 294 (52, $M^+ - 1 - N_2$). Anal. Calcd for $C_{17}H_{14}ClN_5$: C, 63.06; H, 4.36; N, 21.63. Found: C, 63.15; H, 4.34; N, 21.38. **8c** was obtained (13%) as a white solid, mp 199.5–201 °C: IR (KBr) 3320 (NH), 1620 cm^{-1} (C=O); UV (EtOH) λ_{max} (lg ϵ) 208 (4.07), 249 (4.05), 311 nm (3.96); ^1H NMR (DMSO-d_6) δ 4.26, 4.46 (A_2B_2, 2 H each, CH_2CH_2, J = 7.0), 7.57 (s, 1, NH), 7.43–8.35 (m, 5); ^{13}C NMR (DMSO-d_6) δ 44.2 ($HNCH_2$), 52.5 (NCH_2), 125.4 (C=*C*CO), 128.1, 129.5, 132.2, 137.0 (carbon of phenyl ring), 155.3 (*C*=CCO), 183.1 (C=O); MS 214 (75, M^+), 186 (100, $M^+ - N_2$), 158 (50). Anal. Calcd for $C_{11}H_{10}N_4O$: C, 61.67; H, 4.71; N, 26.16. Found: C, 61.60; H, 4.69; N, 26.20.

1,5-Bis(*p*-chlorophenyl)-4-(2-imidazolinyl)-1,2,3-triazole (6db) and 3-(*p*-Chlorobenzoyl)-5,6-dihydro-4*H*-imidazo[1,2-*c*][1,2,3]triazole (8d). 6db was obtained (48%) as white crystals, mp 224.5–225.5 °C: IR (KBr) 3330 cm^{-1} (NH); UV (EtOH) λ_{max} (lg ϵ) 224 (4.40), 244 nm (sh); ^1H NMR (DMSO-d_6) δ 3.15 (s, 1, NH), 3.44 (s, 4, CH_2CH_2), 7.21 (s, 4), 7.24 (d, 2, J = 9.0), 7.34 (d, 2, J = 9.0); MS 357 (25, M^+), 356 (100, $M^+ - 1$), 328 (50, $M^+ - 1 - N_2$). Anal. Calcd for $C_{17}H_{13}Cl_2N_5$: C, 57.00; H, 3.66; N, 19.55. Found: C, 56.77; H, 3.65; N, 19.61. **8d** was obtained (6%) as a white solid, mp 222–223 °C: IR (KBr) 3320 (NH), 1624 cm^{-1} (C=O); UV (EtOH) λ_{max} (lg ϵ) 214 (4.32), 257 (4.19), 315 nm (4.06); ^1H NMR (DMSO-d_6) δ 4.26, 4.44 (A_2B_2, 2 H each, CH_2CH_2, J = 7.0), 7.50 (s, 1, NH), 7.58 (d, 2, J = 9.0), 8.34 (d, 2, J = 9.0); ^{13}C NMR (DMSO-d_6) δ 44.3 ($HNCH_2$), 52.5 (NCH_2), 125.3 (C=*C*CO), 128.3, 131.3, 135.4, 137.3 (carbon of phenyl ring), 155.5 (*C*=CCO), 181.5 (C=O); MS 248 (42, M^+), 220 (100, $M^+ - N_2$), 192 (40). Anal. Calcd for $C_{11}H_9ClN_4O$: C, 53.13; H, 3.65; N, 22.53. Found: C, 53.14; H, 3.67; N, 22.42.

1-(*p*-Chlorophenyl)-4-(2-tetrahydropyrimidinyl)-5-(*p*-methoxyphenyl)-1,2,3-triazole (7ab) and 3-(*p*-Methoxybenzoyl)-4,5,6,7-tetrahydro[1,2,3]triazolo[1,5-*a*]pyrimidine (9a). 7ab was obtained (76%) as white crystals, mp 172.5–173.5 °C: IR (KBr) 3405 cm^{-1} (NH); UV (EtOH) λ_{max} (lg ϵ) 228 nm (4.33); ^1H NMR (DMSO-d_6) δ 1.63 (quin, 2), 3.23 (t, 4), 3.69 (s, 3, OCH_3), 6.90 (s, 1, NH), 6.75 (d, 2, J = 9.0), 7.14 (d, 2, J = 9.0), 7.20 (d, 2, J = 9.0), 7.38 (d, 2, J = 9.0); MS 367 (24, M^+), 366 (75, $M^+ - 1$), 339 (49, $M^+ - N_2$), 338 (100, $M^+ - 1 - N_2$). Anal. Calcd for $C_{19}H_{18}ClN_5O$: C, 62.04; H, 4.93; N, 19.04. Found: C, 62.15; H, 5.08; N, 19.46. **9a** was obtained (16%) as a white solid, mp 171–172 °C: IR (KBr) 3350 (NH), 1633 cm^{-1} (C=O); UV (EtOH) λ_{max} (lg ϵ) 220 (3.94), 250 (3.86), 320 nm (4.07); ^1H NMR ($CDCl_3$) δ 2.13 (quin, 2), 3.45 (t, 2), 4.31 (t, 2), 3.84 (s, 3, OCH_3), 6.65 (s, 1, NH), 6.98 (d, 2, J = 9.0), 8.57 (d, 2, J = 9.0); ^{13}C NMR ($CDCl_3$) δ 20.4 (CH_2), 38.4 (CH_2NH), 43.0 (CH_2N), 55.2 (OCH_3), 128.4 [C=*C*(C=O)N], 145.7 [C=*C*(N)N], 113.2, 129.9, 132.1, 162.8

(carbon of phenyl ring), 183.9 (C=O); MS 258 (100, M^+), 230 (15, $M^+ - N_2$), 229 (55, $M^+ - 1 - N_2$). Anal. Calcd for $C_{13}H_{14}N_4O_2$: C, 60.45; H, 5.46; N, 21.69. Found: C, 60.68; H, 5.58; N, 21.59.

1-(*p*-Chlorophenyl)-4-(2-tetrahydropyrimidinyl)-5-(*p*-methylphenyl)-1,2,3-triazole (7bb) and 3-(*p*-Methylbenzoyl)-4,5,6,7-tetrahydro[1,2,3]triazolo[1,5-*a*]pyrimidine (9b). **7bb** was obtained (74%) as white crystals, mp 178–178.5 °C: IR (KBr) 3330 cm^{-1} (NH); UV (EtOH) λ_{max} (lg ϵ) 236 nm (4.15); ^1H NMR (DMSO-d_6) δ 1.65 (quin, 2), 3.24 (t, 4), 2.28 (s, 3, CH_3), 6.93 (s, 1, NH), 7.10 (s, 4), 7.25 (d, 2, J = 9.0), 7.44 (d, 2, J = 9.0); MS 351 (28, M^+), 350 (97, $M^+ - 1$), 323 (38, $M^+ - N_2$), 322 (100, $M^+ - 1 - N_2$). Anal. Calcd for $C_{19}H_{18}ClN_5$: C, 64.86; H, 5.16; N, 19.91. Found: C, 64.49; H, 5.29; N, 19.77. **9b** was obtained (8%) as a white solid, mp 155–156 °C: IR (KBr) 3340 (NH), 1620 cm^{-1} (C=O); UV (EtOH) λ_{max} (lg ϵ) 215 (4.04), 253 (4.11), 318 nm (4.13); ^1H NMR ($CDCl_3$) δ 2.13 (quin, 2), 3.46 (t, 2), 4.30 (t, 2), 2.39 (s, 3, CH_3), 6.72 (s, 1, NH), 7.24 (d, 2, J = 9.0), 8.39 (d, 2, J = 9.0); ^{13}C NMR ($CDCl_3$) δ 20.1 (CH_2), 21.0 (CH_3), 38.1 (CH_2NH), 42.7 (CH_2N), 128.0 [C=*C*(C=O)N], 145.5 [C=*C*(N)N], 128.3, 129.5, 134.2, 142.2 (carbon of phenyl ring), 184.5 (C=O); MS 242 (100, M^+), 214 (10, $M^+ - N_2$), 213 (52, $M^+ - 1 - N_2$). Anal. Calcd for $C_{13}H_{14}N_4O$: C, 64.44; H, 5.82; N, 23.13. Found: C, 64.77; H, 5.88; N, 23.42.

1-(*p*-Chlorophenyl)-4-(2-tetrahydropyrimidinyl)-5-phenyl-1,2,3-triazole (7cb) and 3-Benzoyl-4,5,6,7-tetrahydro[1,2,3]triazolo[1,5-*a*]pyrimidine (9c). **7cb** was obtained (73%) as white crystals, mp 195.5–196 °C: IR (KBr) 3405 cm^{-1} (NH); UV (EtOH) λ_{max} (lg ϵ) 240 nm (4.16); ^1H NMR (DMSO-d_6) δ 1.65 (quin, 2), 3.25 (t, 4), 6.93 (s, 1, NH), 7.20 (d, 2, J = 9.0), 7.25 (s, 5), 7.40 (d, 2, J = 9.0), MS (337 (26, M^+), 336 (92, $M^+ - 1$), 309 (37, $M^+ - N_2$), 308 (100, $M^+ - 1 - N_2$). Anal. Calcd for $C_{18}H_{16}ClN_5$: C, 64.00; H, 4.77; N, 20.73. Found: C, 64.20; H, 4.76; N, 21.10. **9c** was obtained (7%) as a white solid, mp 157.5–158.5 °C: IR (KBr) 3375 (NH), 1624 cm^{-1} (C=O); UV (EtOH) λ_{max} (lg ϵ) 226 (4.01), 246 (4.08), 319 nm (4.06); ^1H NMR ($CDCl_3$) δ 2.10 (quin, 2), 3.42 (t, 2), 4.26 (t, 2), 6.72 (s, 1, NH), 7.39–8.49 (m, 5); ^{13}C NMR ($CDCl_3$) δ 20.0 (CH_2), 38.2 (CH_2NH), 42.7 (CH_2N), 128.0 [C=*C*(C=O)N], 145.6 [C=*C*(N)N], 127.7, 129.4, 131.8, 136.7 (carbon of phenyl ring), 184.9 (C=O); MS 228 (100, M^+), 200 (11, $M^+ - N_2$), 199 (66, $M^+ - 1 - N_2$). Anal. Calcd for $C_{12}H_{12}N_4O$: C, 63.14; H, 5.30; N, 24.55. Found: C, 63.24; H, 5.31; N, 24.38.

1,5-Bis(*p*-chlorophenyl)-4-(2-tetrahydropyrimidinyl)-1,2,3-triazole (7db) and 3-(*p*-Chlorobenzoyl)-4,5,6,7-tetrahydro[1,2,3]triazolo[1,5-*a*]pyrimidine (9d). **7db** was obtained (73%) as white crystals, mp 176.5–177 °C: IR (KBr) 3410 cm^{-1} (NH); UV (EtOH) λ_{max} (lg ϵ) 243 nm (4.17); ^1H NMR (DMSO-d_6) δ 1.66 (quin, 2), 3.25 (t, 4), 6.92 (s, 1, NH), 7.18 (d, 2, J = 9.0), 7.23 (s, 4), 7.39 (d, 2, J = 9.0); MS 372 (6, M^+), 371 (20, $M^+ - 1$), 344 (10, $M^+ - N_2$), 343 (25, $M^+ - 1 - N_2$). Anal. Calcd for $C_{18}H_{15}Cl_2N_5$: C, 58.07; H, 4.06; N, 18.82. Found: C, 58.13; H, 4.08; N, 18.77. **9d** was obtained (6%) as white solid, mp 185.5–186 °C: IR (KBr) 3280 (NH), 1630 cm^{-1} (C=O); UV (EtOH) λ_{max} (lg ϵ) 215 (3.96), 252 (4.10), 323 nm (4.03); ^1H NMR ($CDCl_3$) δ 2.13 (quin, 2), 3.45 (t, 2), 4.31 (t, 2), 6.74 (s, 1, NH), 7.43 (d, 2, J = 9.0), 8.48 (d, 2, J = 9.0); ^{13}C NMR ($CDCl_3$) δ 20.3 (CH_2), 38.3 (CH_2NH), 42.8 (CH_2N), 128.0 [C=*C*(C=O)N], 145.8 [C=*C*(N)N], 127.9, 131.1, 135.3, 138.1 (carbon of phenyl ring), 183.2 (C=O); MS 262 (100, M^+), 234 (16, $M^+ - N_2$), 233 (69, $M^+ - 1 - N_2$). Anal. Calcd for $C_{12}H_{11}ClN_4O$: C, 54.86; H, 4.22; N, 21.33. Found: C, 54.96; H, 4.24; N, 21.41.

1-Phenyl-4-(2-imidazolinyl)-5-(*p*-methoxyphenyl)-1,2,3-triazole (6ac) and 8a. **6ac** was obtained (54%) as white needles, mp 162–162.5 °C: IR (KBr) 3308 cm^{-1} (NH); UV (EtOH) λ_{max} (lg ϵ) 228 (4.13), 250 nm (4.01); ^1H NMR (DMSO-d_6) δ 3.27 (s, 1, NH), 3.51 (s, 4, CH_2CH_2), 3.78 (s, 3, OCH_3), 6.99 (d, 2, J = 9.0 Hz), 7.29 (d, 2, J = 9.0 Hz), 7.39 (s, 5); MS 319 (50, M^+), 318 (100, $M^+ - 1$), 290 (51, $M^+ - 1 - N_2$). Anal. Calcd for $C_{18}H_{17}N_5O$: C, 67.69; H, 5.37; N, 21.93. Found: C, 68.12; H, 5.38; N, 21.92. **8a** was also obtained (16%).

1-Phenyl-4-(2-imidazolinyl)-5-(*p*-methylphenyl)-1,2,3-triazole (6bc) and 8b. **6bc** was obtained (42%) as white needles, mp 167.5–169 °C: IR (KBr) 3320 cm^{-1} (NH); UV (EtOH) λ_{max} (lg ϵ) 225 (4.18), 250 nm (4.13); ^1H NMR (DMSO-d_6) δ 2.26 (s, 3, CH_3), 3.18 (s, 1, NH), 3.46 (s, 4, CH_2CH_2), 7.07 (s, 4), 7.29 (s, 5); MS 303 (25, M^+), 302 (100, $M^+ - 1$), 274 (49, $M^+ - 1 - N_2$). Anal. Calcd for $C_{18}H_{17}N_5$: C, 71.26; H, 5.65; N, 23.09. Found: C, 71.24; H, 5.61; N, 23.00. **8b** was also obtained (14%).

1,5-Diphenyl-4-(2-imidazolinyl)-1,2,3-triazole (6cc) and 8c. **6cc** was obtained (39%) as white needles, mp 186–187 °C: IR (KBr) 3328 cm^{-1} (NH); UV (EtOH) λ_{max} (lg ϵ) 220 (4.05), 244 nm (4.04); ^1H NMR (DMSO-d_6) δ 3.17 (s, 1, NH), 3.48 (s, 4, CH_2CH_2), 7.24 (s, 5), 7.20–7.37 (m, 5); MS 289 (100, M^+), 260 (51, $M^+ - 1 - N_2$). Anal. Calcd for $C_{17}H_{15}N_5$: C, 70.57; H, 5.23; N, 24.21. Found: C, 70.39; H, 5.22; N, 24.16. **8c** was also obtained (13%).

1-Phenyl-4-(2-imidazolinyl)-5-(*p*-chlorophenyl)-1,2,3-triazole (6dc) and 8d. **6dc** was obtained (31%) as white needles, mp 180.5–181.5 °C: IR (KBr) 3320 cm^{-1} (NH); UV (EtOH) λ_{max} (lg ϵ) 230 (4.16), 246 nm (4.17); ^1H NMR (DMSO-d_6) δ 3.21 (s, 1, NH), 3.50 (s, 4, CH_2CH_2), 7.31 (s, 5), 7.35 (s, 4); MS 323 (26, M^+), 322 (100, $M^+ - 1$), 294 (54, $M^+ - 1 - N_2$). Anal. Calcd for $C_{17}H_{14}ClN_5$ C, 63.06; H, 4.36; N, 21.63. Found: C, 62.91; H, 4.34; N, 21.52. **8d** was also obtained (8%).

1-Phenyl-4-(2-tetrahydropyrimidinyl)-5-(*p*-methoxyphenyl)-1,2,3-triazole (7ac) and 9a. **7ac** was obtained (70%) as white needles, mp 165.5–166.5 °C; IR (KBr) 3400 cm^{-1} (NH); UV (EtOH) λ_{max} (lg ϵ) 229 (4.20), 256 nm (sh); ^1H NMR (DMSO-d_6) δ 1.65 (quin, 2), 3.23 (t, 4), 3.70 (s, 3, OCH_3), 6.90 (s, 1, NH), 6.77 (d, 2, J = 9.0 Hz), 7.16 (d, 2, J = 9.0 Hz), 7.20–7.46 (m, 5); MS 333 (33, M^+), 332 (90, $M^+ - 1$) 305 (68, $M^+ - N_2$), 304 (100, $M^+ - 1 - N_2$). Anal. Calcd for $C_{19}H_{19}N_5O$: C, 68.45; H, 5.74; N, 21.01. Found: C, 68.26; H, 5.78; N, 21.03. **9a** was also obtained (14%).

1-Phenyl-4-(2-tetrahydropyrimidinyl)-5-(*p*-methylphenyl)-1,2,3-triazole (7bc) and 9b. **7bc** was obtained (68%) as white needles, mp 156.5–157.5 °C: IR (KBr) 3410 cm^{-1} (NH); UV (EtOH) λ_{max} (lg ϵ) 228 (4.18), 242 nm (sh); ^1H NMR (DMSO-d_6) δ 1.66 (quin, 2), 3.24 (t, 4), 2.27 (s, 3, CH_3), 6.80 (s, 1, NH), 7.07 (s, 4), 7.23–7.46 (m, 5); MS 317 (20, M^+), 316 (100, $M^+ - 1$), 289 (45, $M^+ - N_2$), 288 (80, $M^+ - 1 - N_2$). Anal. Calcd for $C_{19}H_{19}N_5$: C, 71.90; H, 6.03; N, 22.07. Found: C, 71.47; H, 6.01; N, 21.98. **9b** was also obtained (12%).

1,5-Diphenyl-4-(2-tetrahydropyrimidinyl)-1,2,3-triazole (7cc) and 9c. **7cc** was obtained (61%) as white needles, mp 166–167 °C: IR (KBr) 3350 cm^{-1} (NH); UV (EtOH) λ_{max} (lg ϵ) 236 nm (4.06); ^1H NMR (DMSO-d_6) δ 1.65 (quin, 2), 3.23 (t, 4), 6.95 (s, 1, NH), 7.25 (s, 5), 7.23–7.46 (m, 5); MS 303 (31, M^+), 302 (100, $M^+ - 1$), 275 (44, $M^+ - N_2$), 274 (83, $M^+ - 1 - N_2$). Anal. Calcd for $C_{18}H_{17}N_5$: C, 71.26; H, 5.65; N, 23.09. Found: C, 71.33; H, 5.71; N, 23.27. **9c** was also obtained (11%).

1-Phenyl-4-(2-tetrahydropyrimidinyl)-5-(*p*-chlorophenyl)-1,2,3-triazole (7dc) and 9d. **7dc** was obtained (66%) as white needles, mp 162–163 °C: IR (KBr) 3350 cm^{-1} (NH); UV (EtOH) λ_{max} (lg ϵ) 236 nm (4.07); ^1H NMR (DMSO-d_6) δ 1.66 (quin, 2), 3.25 (t, 4), 6.93 (s, 1, NH), 7.29 (s, 4), 7.29–7.49 (m, 5); MS 337 (33, M^+), 336 (90, $M^+ - 1$), 309 (62, $M^+ - N_2$), 308 (100, $M^+ - 1 - N_2$). Anal. Calcd for $C_{18}H_{16}ClN_5$: C, 64.00; H, 4.77; N, 20.73. Found: C, 63.97; H, 4.78; N, 20.74. **9d** was also obtained (7%).

1,5-Bis(*p*-methoxyphenyl)-4-(2-imidazolinyl)-1,2,3-triazole (6ad) and 8a. **6ad** was obtained (18%) as a white solid, mp 212.5–214 °C: IR (KBr) 3320 cm^{-1} (NH); UV (EtOH) λ_{max} (lg ϵ) 228 (4.31), 251 nm (4.28); ^1H NMR (DMSO-d_6) δ 3.37 (s, 1, NH), 3.50 (s, 4, CH_2CH_2), 3.73 (s, 3, OCH_3), 3.76 (s, 3, OCH_3), 6.86 (d, 2, J = 9.0 Hz), 6.96 (d, 2, J = 9.0 Hz), 7.24 (d, 2, J = 9.0), 7.27 (d, 2, J = 9.0); MS 349 (28, M^+), 348 (100, $M^+ - 1$), 320 (90, $M^+ - 1 - N_2$). Anal. Calcd for $C_{19}H_{19}N_5O_2$: C, 65.31; H, 5.48; N, 20.05. Found: C, 65.09; H, 5.57; N, 20.06. **8a** was also obtained (23%).

1-(*p*-Methoxyphenyl)-4-(2-imidazolinyl)-5-(*p*-methylphenyl)-1,2,3-triazole (6bd) and 8b. **6bd** was obtained (14%) as a white solid, mp 171–172 °C: IR (KBr) 3390 cm^{-1} (NH); UV (EtOH) λ_{max} (lg ϵ) 228 (4.26), 244 nm (4.23); ^1H NMR (DMSO-d_6) δ 2.29 (s, 3, CH_3), 3.25 (s, 1, NH), 3.51 (s, 4, CH_2CH_2), 3.78 (s, 3, OCH_3), 6.97 (d, 2, J = 9.0), 7.19 (d, 2, J = 9.0), 7.20 (s, 4); MS 333 (30, M^+), 332 (100, $M^+ - 1$), 304 (56, $M^+ - 1 - N_2$). Anal. Calcd for $C_{19}H_{19}N_5O$: C, 68.45; H, 5.74; N, 21.01. Found: C, 68.16; H, 5.76; N, 20.80. **8b** was also obtained (21%).

1-(*p*-Methoxyphenyl)-4-(2-imidazolinyl)-5-phenyl-1,2,3-triazole (6cd) and 8c. **6cd** was obtained (13%) as a white solid, mp 164–166 °C: IR (KBr) 3330 cm^{-1} (NH); UV (EtOH) λ_{max} (lg ϵ) 229 (4.21), 244 nm (4.16); ^1H NMR (DMSO-d_6) δ 3.30 (s, 1, NH), 3.50 (s, 4, CH_2CH_2), 3.75 (s, 3, OCH_3), 6.95 (d, 2, J = 9.0), 7.24 (d, 2, J = 9.0), 7.31 (s, 5); MS 319 (25, M^+), 318 (100, $M^+ - 1$), 288 (90, $M^+ - 1 - N_2$). Anal. Calcd for $C_{18}H_{17}N_5O$: C, 67.69; H,

5.37; N, 21.93. Found: C, 67.30; H, 5.38; N, 21.74. **8c** was also obtained (18%).

1-(*p*-Methoxyphenyl)-4-(2-imidazolinyl)-5-(*p*-chlorophenyl)-1,2,3-triazole (6dd) and 8d. **6dd** was obtained (8%) as a white solid, mp 183–184.5 °C: IR (KBr) 3320 cm^{-1} (NH); UV (EtOH) λ_{max} (lg ϵ) 230 (4.28), 246 nm (4.25); ^1H NMR (DMSO-d_6) δ 3.18 (s, 1, NH), 3.50 (s, 4, CH_2CH_2), 3.74 (s, 3, OCH_3), 6.96 (d, 2, J = 9.0), 7.25 (d, 2, J = 9.0), 7.35 (s, 4); MS 353 (26, M^+), 352 (82, $M^+ - 1$), 324 (100, $M^+ - 1 - N_2$). Anal. Calcd for $C_{15}H_{16}ClN_5O$: C, 61.10; H, 4.56; N, 19.80. Found: C, 60.69; H, 4.62; N, 19.60. **8d** was also obtained (10%).

1,5-Bis(*p*-methoxyphenyl)-4-(2-tetrahydropyrimidinyl)-1,2,3-triazole (7ad) and 9a. **7ad** was obtained (45%) as white crystals, mp 199.5–200.5 °C: IR (KBr) 3350 cm^{-1}; UV (EtOH) λ_{max} (lg ϵ) 248 nm (4.14); ^1H NMR (DMSO-d_6) δ 1.65 (quin, 2), 3.25 (t, 4), 3.71 (s, 3, OCH_3), 3.74 (s, 3, OCH_3), 6.83 (s, 1, NH), 6.78 (d, 2, J = 9.0), 7.06 (d, 2, J = 9.0), 6.90 (d, 2, J = 9.0), 7.16 (d, 2, J = 9.0); MS 363 (24, M^+), 363 (72, $M^+ - 1$), 335 (42, $M^+ - N_2$), 334 (100, $M^+ - 1 - N_2$). Anal. Calcd for $C_{20}H_{21}N_5O_2$: C, 66.10; H, 5.83; N, 19.27. Found: C, 66.12; H, 5.83; N, 19.39. **9a** was also obtained (31%).

1-(*p*-Methoxyphenyl)-4-(2-tetrahydropyrimidinyl)-5-(*p*-methylphenyl)-1,2,3-triazole (7bd) and 9b. **7bd** was obtained (30%) as white crystals, mp 193–194 °C: IR (KBr) 3350 cm^{-1} (NH); UV (EtOH) λ_{max} (lg ϵ) 235 nm (4.17); ^1H NMR (DMSO-d_6) δ 1.62 (quin, 2), 3.21 (t, 4), 2.24 (s, 3, CH_3), 3.71 (s, 3, OCH_3), 6.67 (s, 1, NH), 7.05 (s, 4), 6.88 (d, 2, J = 9.0), 7.11 (d, 2, J = 9.0); MS 347 (29, M^+), 346 (80, $M^+ - 1$), 319 (35, $M^+ - N_2$), 318 ($M^+ - 1 - N_2$). Anal. Calcd for $C_{20}H_{21}N_5O$: C, 69.14; H, 6.09; N, 20.16. Found: C, 69.44; H, 6.09; N, 20.12. **9b** was also obtained (23%).

1-(*p*-Methoxyphenyl)-4-(2-tetrahydropyrimidinyl)-5-phenyl-1,2,3-triazole (7cd) and 9c. **7cd** was obtained (31%) as white crystals, mp 178.5–179.5 °C: IR (KBr) 3370 cm^{-1} (NH); UV (EtOH) λ_{max} (lg ϵ) 228 (4.27), 242 nm (sh); ^1H NMR (DMSO-d_6) δ 1.65 (quin, 2), 3.23 (t, 4), 3.73 (s, 3, OCH_3), 6.63 (s, 1, NH), 6.88 (d, 2, J = 9.0), 7.13 (d, 2, J = 9.0), 7.21 (s, 5); MS 333 (32, M^+), 332 (93, $M^+ - 1$), 305 (32, $M^+ - N_2$), 304 (100, $M^+ - 1 - N_2$). Anal. Calcd for $C_{19}H_{19}N_5O$: C, 68.45; H, 5.74; N, 21.01. Found: C, 68.65; H, 5.84; N, 20.72. **9c** was also obtained (21%).

1-(*p*-Methoxyphenyl)-4-(2-tetrahydropyrimidinyl)-5-(*p*-chlorophenyl)-1,2,3-triazole (7dd) and 9d. **7dd** was obtained (35%) as white crystals, mp 205–206 °C: IR (KBr) 3348 cm^{-1} (NH); UV (EtOH) λ_{max} (lg ϵ) 228 (4.35), 248 nm (sh); ^1H NMR (DMSO-d_6) δ 1.65 (quin, 2), 3.23 (t, 4), 3.75 (s, 3, OCH_3), 6.75 (s, 1, NH), 6.92 (d, 2, J = 9.0 Hz), 7.17 (d, 2, J = 9.0 Hz), 7.26 (s, 4); MS 367 (27, M^+), 366 (69, $M^+ - 1$), 339 (34, $M^+ - N_2$), 338 (100, $M^+ - 1 - N_2$). Anal. Calcd for $C_{19}H_{18}ClN_5O$: C, 62.04; H, 4.93; N, 19.04. Found: C, 62.45; H, 5.16; N, 19.27. **9d** was also obtained (15%).

Preparation of 1-(*p*-Nitrophenyl)-4-(1-methyl-2-imidazolinyl)-5-phenyl-1,2,3-triazole (11). A mixture of 1-methyl-2-(benzoylmethylene)imidazoline (**10**) (253 mg, 1.25 mol) and **5a** (205 mg, 1.25 mol) in dried 1,4-dioxine (10 mL) was stirred at ambient temperature for 50 h. After partial removal of solvent, **11** (390 mg, 83%) was crystallized out as yellow crystals, mp 209.5–210.5 °C: IR (KBr) 1520, 1340 (NO_2), 1588, 1560, 1495 cm^{-1}; UV (EtOH) λ_{max} (lg ϵ) 223 (4.23), 264 nm (4.22); ^1H NMR (DMSO-d_6) δ 2.76 (s, 3, CH_3), 3.15–3.75 (m, 4, CH_2CH_2), 7.31 (s, 5), 7.60 (d, 2, J = 9.0), 8.25 (d, 2, J = 9.0); MS 348 (40, M^+), 347 (100, $M^+ - 1$), 319 (30, $M^+ - 1 - N_2$). Anal. Calcd for $C_{18}H_{16}N_6O_2$: C, 62.06; H, 4.63; N, 24.13. Found: C, 62.62; H, 4.63; N, 24.00.

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Novel Dimroth Rearrangements of the Benzotriazole System: 4-Amino-1-(arylsulfonyl)benzotriazoles to 4-[(Arylsulfonyl)amino]benzotriazoles

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A variety of mono- and diarylsulfonyl-substituted 4-aminobenzotriazoles were prepared. Thermal rearrangements of 4-amino-1-(arylsulfonyl)benzotriazoles to 4-[(arylsulfonyl)amino]benzotriazoles were observed and confirmed by separation of the rearrangement products. Their structures were characterized by spectral methods and by X-ray crystallography. The rearrangement rates were studied by variable-temperature NMR experiments. Crossover experiments support an intramolecular mechanism involving a heterolytic benzotriazole ring cleavage to form a diazo intermediate followed by recyclization to the 4-amino group.

Molecular rearrangements constitute an important aspect of ring-transformation reactions of heterocyclic compounds.[1] It has been known for a long time that 1*H*-1,2,3-triazoles **1** can exist in thermal equilibria with diazo imines **2** which may recyclize to **3**. This constitutes a subsection of the general class of heterocyclic reactions now known as Dimroth rearrangements.[2-4] Several molecular rearrangements of 4- or 5-substituted 1,2,3-triazoles **1** involving intermediates of type **2** have previously been reported,[5] in which the substituent was amino (**1** ⇌ **3**, R^5 = NH_2),[6] hydrazino (**1** ⇌ **5**, R^5 = $NHNH_2$),[7] diazomethyl (**1** ⇌ **6**, R = CHN_2),[8] and iminomethyl (**1** ⇌ **4**, R^4 = CH=NR).[9] Solvent and substituent effects on these rear-

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